Chemical Equilibrium

Edited by: **Simon Boman**

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PREFACE

Chemical equilibrium refers to the state of a system in which the concentration of the reactant and the concentration of the products do not change with time and the system does not display any further change in properties. The definition of chemical equilibrium is the point at which the concentrations of reactants and products do not change with time. It appears as though the reaction has stopped but in fact the rates of the forward and reverse reactions are equal so reactants and products are being created at the same rate. When equilibrium reactions are disrupted, such as the binding of oxygen by hemoglobin, as in carbon monoxide poisoning, it can be life threatening. Conversely, controlling an equilibrium reaction is important in chemical manufacturing, like in the synthesis of ammonia.

This book is designed for learners with background in material and energy balances, chemical reactions, calculus, numerical methods, and basic thermodynamics. You will understand the principles of chemical equilibrium thermodynamics to solve multiphase equilibria and chemical reaction equilibria. This book contains seven chapters. Chapter 1: First and Second Law of Thermodynamics; chapter 2: Introduction to Equilibrium; chapter 3: Equilibria of Reactions Involving Gases; chapter 4: Phase Rule; chapter 5: Phase Equilibria in Single Component Systems; chapter 6: Ideal Solutions; chapter 7: Reaction Equilibrium in Solutions: Electrolyte. The equilibrium properties of electrolyte solutions can be studied experimentally by electrochemical measurements, freezing-

point depressions, solubility determinations, osmotic pressures, or measurements of vapor pressure. Most electrolytes, such as salts, are nonvolatile at ordinary temperature, and, in that event, the vapor pressure exerted by the solution is the same as the partial pressure of the solvent. The activity coefficient of the solvent can, therefore, be found from total-pressure measurements, and, using the Gibbs-Duhem equation, it is then possible to calculate the activity coefficient of the electrolyte solute.

FIRST AND SECOND LAW OF THERMODYNAMICS

INTRODUCTION

The First Law of Thermodynamics states that heat is a form of energy, and thermodynamic processes are therefore subject to the principle of conservation of energy. This means that heat energy cannot be created or destroyed. It can, however, be transferred from one location to another and converted to and from other forms of energy.

The second law of thermodynamics states that any spontaneously occurring process will always lead to an escalation in the entropy (S) of the universe. In simple words, the law explains that an isolated system's entropy will never decrease over time.

Nonetheless, in some cases where the system is in thermodynamic equilibrium or going through a reversible process, the total

entropy of a system and its surroundings remains constant. The second law is also known as the Law of Increased Entropy.

1.1. THE FIRST LAW OF THERMODYNAMICS

The first law of thermodynamics is also known as the Law of Conservation of Energy. It states that energy cannot be destroyed or created; it is conserved in the universe and must end up somewhere, even if it changes forms. It involves the study of system work, heat, and energy. Heat engines often prompt a discussion of the first law of thermodynamics; however, it is considered one of the most fundamental laws of nature.

Once people delve into the study of the first law of thermodynamics, they immediately begin to analyze and compute the equation associated with the law: $\Delta U = Q - W$. This equation means that the change in internal energy of the system is equal to the heat added to the system less the work done by the system. In the alternative, sometimes the equation $\Delta U = Q + W$ is used. The only difference is that is computes the work done on the system, instead of the work done by the system. In other words, work is positive when the system does work on its surrounding system and negative when the surroundings do work on the system.

When studying physics, there is a common example that involves adding heat to a gas in a closed system. The example continues by expanding that gas so that it does work. It can be visualized as a piston pushing down or applying pressure on gases in an internal combustion engine. Thus, work is done by the system. In the alternative, when studying chemical processes and reactions, it is typical to study conditions where work is done on the system.

The standard unit for computing the first law of thermodynamics is Joules (J); however, many people studying the law also make their computations in terms of the calorie or the British Thermal Unit (BTU). It is sometimes helpful to calculate conservation with actual numbers, doing so allows people to see how the law works. If a motor does 4,000 J of work on its surrounding, the internal

energy decreases by 4,000 J. If it also releases 5,000 J of heat while it is working, then the internal energy decreases by an additional 5,000 J. As a result, the internal energy of the system decreases by a total of -9,000 J.

In an alternative computation, if a system does 4,000 J of work on its surroundings and then absorbs 5,000 J of heat from its surroundings, the result is different. In that case, there is 5,000 J of energy going in and 4,000 J of energy going out. Thus, the system's total internal energy is 1,000 J.

Lastly, negative work or work done on the system by the surroundings can be exemplified through calculations regarding the first law of thermodynamics, as well. For example, if the system absorbs 4,000 J as the surroundings simultaneously perform 5,000 J or work on the system, another result will be seen. Since all the energies are flowing into the system, the total internal energy jumps up to 9,000 J

So far, we have considered various forms of energy such as heat Q, work W, and total energy E individually, and no attempt has been made to relate them to each other during a process. The first law of thermodynamics, also known as the conservation of energy principle, provides a sound basis for studying the relationships among the various forms of energy and energy interactions. Based on experimental observations, the first law of thermodynamics states that energy can be neither created nor destroyed during a process; it can only change forms.

Therefore, every bit of energy should be accounted for during a process. We all know that a rock at some elevation possesses some potential energy, and part of this potential energy is converted to kinetic energy as the rock falls. Experimental data show that the decrease in potential energy (mgz) exactly equals the increase in kinetic energy when the air resistance is negligible, thus confirming the conservation of energy principle for mechanical energy. The first law of thermodynamics can be expressed for a general system inasmuch as the net change in the total energy of a system during a process is equal to the difference between the

total energy entering and the total energy leaving the system:

$$E_{in} - E_{out} = \Delta E_{system}$$

In rate form,

$$\dot{E}_{in} - \dot{E}_{out} = \frac{dE}{dt}$$

For a closed system undergoing a process between initial and final states (states 1 and 2) with heat and work interactions with the surroundings:

$$E_{in} - E_{out} = \Delta E_{system}$$
$$(Q_{in} + W_{in}) - (Q_{out} + W_{out}) = \Delta U + \Delta KE + \Delta PE$$
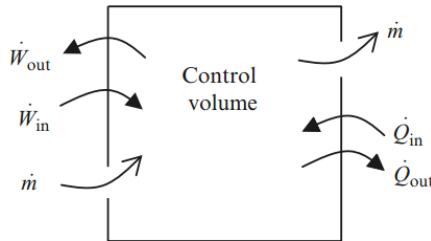
Figure 1. A general · steady-flow control volume with mass, heat, and work interactions.
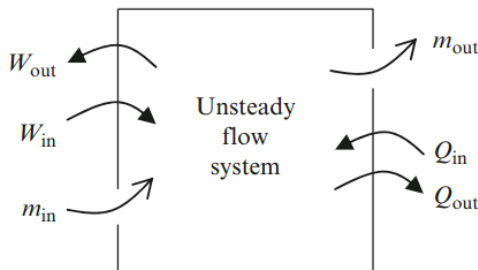
Figure 2. A general unsteady-flow process with mass, heat, and work interactions.

If there is no change in kinetic and potential energies:

$$(Q_{in} + W_{in}) - (Q_{out} + W_{out}) = \Delta U = m(u_2 - u_1)$$

Let us consider a control volume involving a steady-flow process. Mass is entering and leaving the system and there are heat and work interactions with the surroundings (Figure 1). During a steady-flow process, the total mass and energy content of the control volume remains constant, and thus the total energy change of the system is zero. Then the first law of thermodynamics can be expressed through the balance equation as

$$\dot{E}_{in} - \dot{E}_{out} = \frac{dE}{dt} = 0$$

$$\dot{E}_{in} = \dot{E}_{out}$$

$$\dot{Q}_{in} + \dot{W}_{in} + \dot{m}\left(h_{in} + \frac{V_{in}^2}{2} + gz_{in}\right) = \dot{Q}_{out} + \dot{W}_{out} + \dot{m}\left(h_{out} + \frac{V_{out}^2}{2} + gz_{out}\right)$$

If the changes in kinetic and potential energies are negligible, it results in

$$\dot{Q}_{in} + \dot{W}_{in} + \dot{m}h_{in} = \dot{Q}_{out} + \dot{W}_{out} + \dot{m}h_{out}$$

Charging and discharging processes may be modeled as unsteady-flow processes. Consider an unsteady-flow process as shown in Figure 2. Assuming uniform flow conditions, the mass and energy balance relations may be expressed as

$$m_{in} - m_{out} = m_2 - m_1$$

$$E_{in} - E_{out} = \Delta E_{system}$$

$$Q_{in} + W_{in} + m_{in}\left(h_{in} + \frac{V_{in}^2}{2} + gz_{in}\right) - Q_{out} - W_{out}$$

$$- m_{out}\left(h_{out} + \frac{V_{out}^2}{2} + gz_{out}\right) = m_2 u_2 - m_1 u_1$$

Heat engines

The classic example of a heat engine is a steam engine, although all modern engines follow the same principles. Steam engines operate in a cyclic fashion, with the piston moving up and down once for each cycle. Hot high-pressure steam is admitted to the cylinder in the first half of each cycle, and then it is allowed to escape again in the second half. The overall effect is to take heat Q_1 generated by burning a fuel to make steam, convert part of it to do work, and exhaust the remaining heat Q_2 to the environment at a lower temperature. The net heat energy absorbed is then $Q = Q_1 - Q_2$. Since the engine returns to its initial state, its internal energy U does not change ($\Delta U = 0$). Thus, by the first law of thermodynamics, the work done for each complete cycle must be $W = Q_1 - Q_2$. In other words, the work done for each complete cycle is just the difference between the heat Q_1 absorbed by the engine at a high temperature and the heat Q_2 exhausted at a lower temperature. The power of thermodynamics is that this conclusion is completely independent of the detailed working mechanism of the engine. It relies only on the overall conservation of energy, with heat regarded as a form of energy.

In order to save money on fuel and avoid contaminating the environment with waste heat, engines are designed to maximize the conversion of absorbed heat Q_1 into useful work and to minimize the waste heat Q_2. The Carnot efficiency (η) of an engine is defined as the ratio W/Q_1—i.e., the fraction of Q_1 that is converted into work. Since $W = Q_1 - Q_2$, the efficiency also can be expressed in the form

$$\eta = \frac{Q_1 - Q_2}{Q_1} = 1 - \frac{Q_2}{Q_1} \qquad (2)$$

If there were no waste heat at all, then $Q_2 = 0$ and $\eta = 1$, corresponding to 100 percent efficiency. While reducing friction in an engine decreases waste heat, it can never be eliminated; therefore, there is a limit on how small Q_2 can be and thus on how large the efficiency can be. This limitation is a fundamental law of nature—in fact, the second law of thermodynamics.

Isothermal and adiabatic processes

Because heat engines may go through a complex sequence of steps, a simplified model is often used to illustrate the principles of thermodynamics. In particular, consider a gas that expands and contracts within a cylinder with a movable piston under a prescribed set of conditions. There are two particularly important sets of conditions. One condition, known as an isothermal expansion, involves keeping the gas at a constant temperature. As the gas does work against the restraining force of the piston, it must absorb heat in order to conserve energy. Otherwise, it would cool as it expands (or conversely heat as it is compressed). This is an example of a process in which the heat absorbed is converted entirely into work with 100 percent efficiency. The process does not violate fundamental limitations on efficiency, however, because a single expansion by itself is not a cyclic process.

The second condition, known as an adiabatic expansion is one in which the cylinder is assumed to be perfectly insulated so that no heat can flow into or out of the cylinder. In this case the gas cools as it expands, because, by the first law, the work done against the restraining force on the piston can only come from the internal energy of the gas. Thus, the change in the internal energy of the gas must be $\Delta U = -W$, as manifested by a decrease in its temperature. The gas cools, even though there is no heat flow, because it is doing work at the expense of its own internal energy. The exact amount of cooling can be calculated from the heat capacity of the gas.

Many natural phenomena are effectively adiabatic because there is insufficient time for significant heat flow to occur. For example, when warm air rises in the atmosphere, it expands and cools as the pressure drops with altitude, but air is a good thermal insulator, and so there is no significant heat flow from the surrounding air. In this case the surrounding air plays the roles of both the insulated cylinder walls and the movable piston. The warm air does work against the pressure provided by the surrounding air as it expands, and so its temperature must drop. A more-detailed analysis of this adiabatic expansion explains most of the decrease

of temperature with altitude, accounting for the familiar fact that it is colder at the top of a mountain than at its base.

1.1.1. The First Law of Thermodynamics for Closed Systems

The first law of thermodynamics for closed systems was originally induced from empirically observed evidence, including calorimetric evidence. It is nowadays, however, taken to provide the definition of heat via the law of conservation of energy and the definition of work in terms of changes in the external parameters of a system. The original discovery of the law was gradual over a period of perhaps half a century or more, and some early studies were in terms of cyclic processes.

The following is an account in terms of changes of state of a closed system through compound processes that are not necessarily cyclic. This account first considers processes for which the first law is easily verified because of their simplicity, namely adiabatic processes (in which there is no transfer as heat) and a dynamic processes (in which there is no transfer as work).

System boundary

CLOSED
SYSTEM

(m = constant)
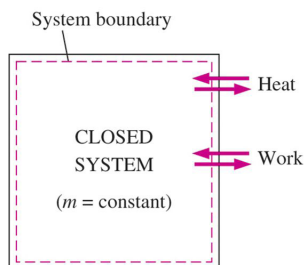
Heat

Work

Energy can cross the boundaries of a closed system in the form of heat and work

Adiabatic processes

In an adiabatic process, there is transfer of energy as work but not as heat. For all adiabatic process that takes a system from a given

initial state to a given final state, irrespective of how the work is done, the respective eventual total quantities of energy transferred as work are one and the same, determined just by the given initial and final states. The work done on the system is defined and measured by changes in mechanical or quasi-mechanical variables external to the system. Physically, adiabatic transfer of energy as work requires the existence of adiabatic enclosures.

For instance, in Joule's experiment, the initial system is a tank of water with a paddle wheel inside. If we isolate the tank thermally, and move the paddle wheel with a pulley and a weight, we can relate the increase in temperature with the distance descended by the mass. Next, the system is returned to its initial state, isolated again, and the same amount of work is done on the tank using different devices (an electric motor, a chemical battery, a spring). In every case, the amount of work can be measured independently. The return to the initial state is not conducted by doing adiabatic work on the system. The evidence shows that the final state of the water (in particular, its temperature and volume) is the same in every case. It is irrelevant if the work is electrical, mechanical, chemical,... or if done suddenly or slowly, as long as it is performed in an adiabatic way, that is to say, without heat transfer into or out of the system.
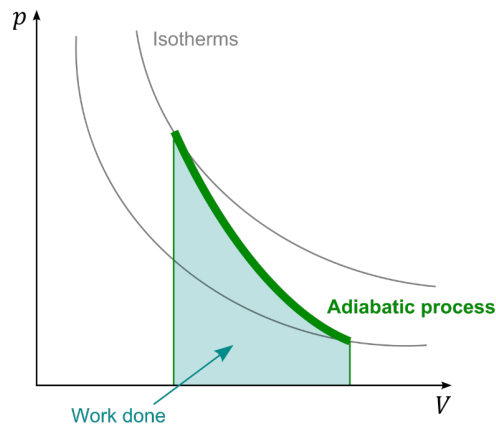
Evidence of this kind shows that to increase the temperature of the water in the tank, the qualitative kind of adiabatically performed work does not matter. No qualitative kind of adiabatic work has

ever been observed to decrease the temperature of the water in the tank.

A change from one state to another, for example an increase of both temperature and volume, may be conducted in several stages, for example by externally supplied electrical work on a resistor in the body, and adiabatic expansion allowing the body to do work on the surroundings. It needs to be shown that the time order of the stages, and their relative magnitudes, does not affect the amount of adiabatic work that needs to be done for the change of state. According to one respected scholar: "Unfortunately, it does not seem that experiments of this kind have ever been carried out carefully. ... We must therefore admit that the statement which we have enunciated here, and which is equivalent to the first law of thermodynamics, is not well founded on direct experimental evidence." Another expression of this view is "... no systematic precise experiments to verify this generalization directly have ever been attempted."

This kind of evidence, of independence of sequence of stages, combined with the above-mentioned evidence, of independence of qualitative kind of work, would show the existence of an important state variable that corresponds with adiabatic work, but not that such a state variable represented a conserved quantity. For the latter, another step of evidence is needed, which may be related to the concept of reversibility, as mentioned below.

In an adiabatic process, adiabatic work takes the system either from a reference state O with internal energy $U(O)$ to an arbitrary one A with internal energy $U(A)$, or from the state A to the state O:

$$U(A) = U(O) - W_{O \to A}^{adiabatic} \text{ or } U(O) = U(A) - W_{A \to O}^{adiabatic}$$

Except under the special, and strictly speaking, fictional, condition of reversibility, only one of the processes adiabatic, $O \to A$ or adiabatic, $A \to O$ is empirically feasible by a simple application of externally supplied work. The reason for this is given as the second law of thermodynamics and is not considered in the present article.

The fact of such irreversibility may be dealt with in two main ways, according to different points of view:

The most accepted way to deal with it nowadays, followed by Carathéodory, is to rely on the previously established concept of quasi-static processes as follows. Actual physical processes of transfer of energy as work are always at least to some degree irreversible. The irreversibility is often due to mechanisms known as dissipative, that transform bulk kinetic energy into internal energy. Examples are friction and viscosity. If the process is performed more slowly, the frictional or viscous dissipation is less. In the limit of infinitely slow performance, the dissipation tends to zero and then the limiting process, though fictional rather than actual, is notionally reversible, and is called quasi-static. Throughout the course of the fictional limiting quasi-static process, the internal intensive variables of the system are equal to the external intensive variables, those that describe the reactive forces exerted by the surroundings. This can be taken to justify the formula

$$W_{A \to O}^{\text{adiabatic, quasi-static}} = -W_{O \to A}^{\text{adiabatic, quasi-static}} \qquad (1)$$

Another way to deal with it is to allow that experiments with processes of heat transfer to or from the system may be used to justify the formula (1) above. Moreover, it deals to some extent with the problem of lack of direct experimental evidence that the time order of stages of a process does not matter in the determination of internal energy. This way does not provide theoretical purity in terms of adiabatic work processes, but is empirically feasible, and is in accord with experiments actually done, such as the Joule experiments mentioned just above, and with older traditions.

The formula (1) above allows that to go by processes of quasi-static adiabatic work from the state A to the state B we can take a path that goes through the reference state O, since the quasi-static adiabatic work is independent of the path

$$-W_{A \to B}^{adiabatic, quasi-static} = -W_{A \to O}^{adiabatic, quasi-static} - W_{O \to B}^{adiabatic, quasi-static}$$
$$= W_{O \to A}^{adiabatic, quasi-static} - W_{O \to B}^{adiabatic, quasi-static}$$
$$= -U(A) + U(B) = \Delta U$$

This kind of empirical evidence, coupled with theory of this kind, largely justifies the following statement:

For all adiabatic processes between two specified states of a closed system of any nature, the net work done is the same regardless the details of the process, and determines a state function called internal energy, U."

Adynamic Processes

A complementary observable aspect of the first law is about heat transfer. Adynamic transfer of energy as heat can be measured empirically by changes in the surroundings of the system of interest by calorimetry. This again requires the existence of adiabatic enclosure of the entire process, system and surroundings, though the separating wall between the surroundings and the system is thermally conductive or radiatively permeable, not adiabatic. A calorimeter can rely on measurement of sensible heat, which requires the existence of thermometers and measurement of temperature change in bodies of known sensible heat capacity under specified conditions; or it can rely on the measurement of latent heat, through measurement of masses of material that change phase, at temperatures fixed by the occurrence of phase changes under specified conditions in bodies of known latent heat of phase change. The calorimeter can be calibrated by adiabatically doing externally determined work on it. The most accurate method is by passing an electric current from outside through a resistance inside the calorimeter. The calibration allows comparison of calorimetric measurement of quantity of heat transferred with quantity of energy transferred as work.

When the system evolves with transfer of energy as heat, without energy being transferred as work, in an adynamic process, the

heat transferred to the system is equal to the increase in its internal energy:

$$Q_{A \to B}^{\text{adynamic}} = \Delta U$$

General case for Reversible Processes

Heat transfer is practically reversible when it is driven by practically negligibly small temperature gradients. Work transfer is practically reversible when it occurs so slowly that there are no frictional effects within the system; frictional effects outside the system should also be zero if the process is to be globally reversible. For a particular reversible process in general, the work done reversibly on the system, $W_{A \to B}^{\text{path} P_0, \text{reversible}}$ and the heat transferred reversibly to the system, $Q_{A \to B}^{\text{path} P_0, \text{reversible}}$ are not required to occur respectively adiabatically or adynamically, but they must belong to the same particular process defined by its particular reversible path, P_0, through the space of thermodynamic states. Then the work and heat transfers can occur and be calculated simultaneously.

Putting the two complementary aspects together, the first law for a particular reversible process can be written

$$-W_{A \to B}^{\text{path} P_0, \text{reversible}} + Q_{A \to B}^{\text{path} P_0, \text{reversible}} = \Delta U$$

This combined statement is the expression the first law of thermodynamics for reversible processes for closed systems.

In particular, if no work is done on a thermally isolated closed system we have

$\Delta U = 0$

This is one aspect of the law of conservation of energy and can be stated:

The internal energy of an isolated system remains constant.

General Case for Irreversible Processes

If, in a process of change of state of a closed system, the energy transfer is not under a practically zero temperature gradient and practically frictionless, then the process is irreversible.

Then the heat and work transfers may be difficult to calculate, and irreversible thermodynamics is called for. Nevertheless, the first law still holds and provides a check on the measurements and calculations of the work done irreversibly on the system, $W_{A \to B}^{\text{path } P_1, \text{ irreversible}}$, and the heat transferred irreversibly to the system, $Q_{A \to B}^{\text{path } P_1, \text{ irreversible}}$, which belong to the same particular process defined by its particular irreversible path, P_1, through the space of thermodynamic states.

$$-W_{A \to B}^{\text{path } P_1, \text{ irreversible}} + Q_{A \to B}^{\text{path } P_1, \text{ irreversible}} = \Delta U$$

This means that the internal energy ΔU is a function of state and that the internal energy change ΔU between two states is a function only of the two states.

Overview of the Weight of Evidence for the Law

The first law of thermodynamics is so general that its predictions cannot all be directly tested. In many properly conducted experiments it has been precisely supported, and never violated. Indeed, within its scope of applicability, the law is so reliably established, that, nowadays, rather than experiment being considered as testing the accuracy of the law, it is more practical and realistic to think of the law as testing the accuracy of experiment.

An experimental result that seems to violate the law may be assumed to be inaccurate or wrongly conceived, for example due to failure to account for an important physical factor. Thus, some may regard it as a principle more abstract than a law.

1.1.2. First Law of Thermodynamics for Open Systems

For the first law of thermodynamics, there is no trivial passage of physical conception from the closed system view to an open system view. For closed systems, the concepts of an adiabatic enclosure and of an adiabatic wall are fundamental. Matter and internal energy cannot permeate or penetrate such a wall. For an open system, there is a wall that allows penetration by matter. In general, matter in diffusive motion carries with it some internal energy, and some microscopic potential energy changes accompany the motion. An open system is not adiabatically enclosed.

There are some cases in which a process for an open system can, for particular purposes, be considered as if it were for a closed system. In an open system, by definition hypothetically or potentially, matter can pass between the system and its surroundings. But when, in a particular case, the process of interest involves only hypothetical or potential but no actual passage of matter, the process can be considered as if it were for a closed system.

Energy Balance for Opened System

$$E_{in} - E_{out} = \Delta E$$

$$Q - W + (E_{mass,in} - E_{mass,out}) = \Delta U + \Delta KE + \Delta PE$$

Where $E_{mass} = m(W_{flow} + e)$

$W_{flow}(flow\ energy) = Pv$ and $e = u + ke + pe$

$$E_{mass} = m(h + \frac{V^2}{2} + gz) \quad (kJ)$$

Internal Energy for an Open System

Since the revised and more rigorous definition of the internal energy of a closed system rests upon the possibility of processes by which adiabatic work takes the system from one state to another, this leaves a problem for the definition of internal energy for an

open system, for which adiabatic work is not in general possible. According to Max Born, the transfer of matter and energy across an open connection "cannot be reduced to mechanics". In contrast to the case of closed systems, for open systems, in the presence of diffusion, there is no unconstrained and unconditional physical distinction between convective transfer of internal energy by bulk flow of matter, the transfer of internal energy without transfer of matter (usually called heat conduction and work transfer), and change of various potential energies. The older traditional way and the conceptually revised (Carathéodory) way agree that there is no physically unique definition of heat and work transfer processes between open systems.

In particular, between two otherwise isolated open systems an adiabatic wall is by definition impossible. This problem is solved by recourse to the principle of conservation of energy. This principle allows a composite isolated system to be derived from two other component non-interacting isolated systems, in such a way that the total energy of the composite isolated system is equal to the sum of the total energies of the two component isolated systems. Two previously isolated systems can be subjected to the thermodynamic operation of placement between them of a wall permeable to matter and energy, followed by a time for establishment of a new thermodynamic state of internal equilibrium in the new single un-partitioned system. The internal energies of the initial two systems and of the final new system, considered respectively as closed systems as above, can be measured. Then the law of conservation of energy requires that

$$\Delta U_S + \Delta U_O = 0$$

where ΔU_S and ΔU_O denote the changes in internal energy of the system and of its surroundings respectively. This is a statement of the first law of thermodynamics for a transfer between two otherwise isolated open systems, that fits well with the conceptually revised and rigorous statement of the law stated above.

For the thermodynamic operation of adding two systems with internal energies U_1 and U_2, to produce a new system with internal energy U, one may write $U = U_1 + U_2$;the reference states for U, U_1 and U_2 should be specified accordingly, maintaining also that the internal energy of a system be proportional to its mass, so that the internal energies are extensive variables.

There is a sense in which this kind of additivity expresses a fundamental postulate that goes beyond the simplest ideas of classical closed system thermodynamics; The extensivity of some variables is not obvious, and needs explicit expression; indeed one author goes so far as to say that it could be recognized as a fourth law of thermodynamics.

$$\Delta N_S + \Delta N_O = 0$$
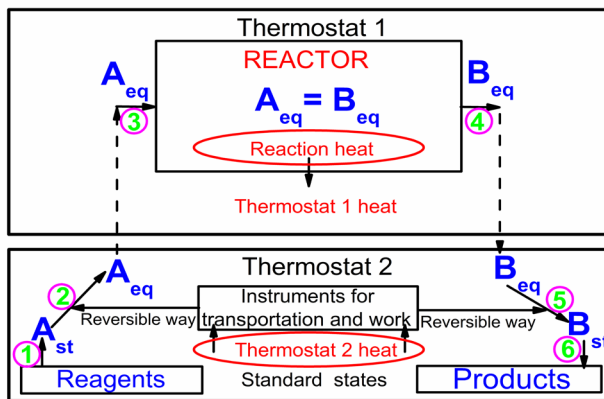
Process of Transfer of Matter between an Open System and Its Surroundings

A system connected to its surroundings only through contact by a single permeable wall, but otherwise isolated, is an open system. If it is initially in a state of contact equilibrium with a surrounding subsystem, a thermodynamic process of transfer of matter can be made to occur between them if the surrounding subsystem is subjected to some thermodynamic operation, for example, removal of a partition between it and some further surrounding subsystem.

The removal of the partition in the surroundings initiates a process of exchange between the system and its contiguous surrounding subsystem. An example is evaporation. One may consider an open system consisting of a collection of liquid, enclosed except where it is allowed to evaporate into or to receive condensate from its vapor above it, which may be considered as its contiguous surrounding subsystem, and subject to control of its volume and temperature. A thermodynamic process might be initiated by a thermodynamic operation in the surroundings that mechanically increases in the controlled volume of the vapor.

Some mechanical work will be done within the surroundings by the vapor, but also some of the parent liquid will evaporate and enter the vapor collection which is the contiguous surrounding subsystem. Some internal energy will accompany the vapor that leaves the system, but it will not make sense to try to uniquely identify part of that internal energy as heat and part of it as work. Consequently, the energy transfer that accompanies the transfer of matter between the system and its surrounding subsystem cannot be uniquely split into heat and work transfers to or from the open system. The component of total energy transfer that accompanies the transfer of vapor into the surrounding subsystem is customarily called 'latent heat of evaporation', but this use of the word heat is a quirk of customary historical language, not in strict compliance with the thermodynamic definition of transfer of energy as heat. In this example, kinetic energy of bulk flow and potential energy with respect to long-range external forces such as gravity are both considered to be zero. The first law of thermodynamics refers to the change of internal energy of the open system, between its initial and final states of internal equilibrium.

Open System with Multiple Contacts

An open system can be in contact equilibrium with several other systems at once. This includes cases in which there is contact equilibrium between the system, and several subsystems in its surroundings, including separate connections with subsystems through walls that are permeable to the transfer of matter and

internal energy as heat and allowing friction of passage of the transferred matter, but immovable, and separate connections through adiabatic walls with others, and separate connections through diathermic walls impermeable to matter with yet others. Because there are physically separate connections that are permeable to energy but impermeable to matter, between the system and its surroundings, energy transfers between them can occur with definite heat and work characters. Conceptually essential here is that the internal energy transferred with the transfer of matter is measured by a variable that is mathematically independent of the variables that measure heat and work. With such independence of variables, the total increase of internal energy in the process is then determined as the sum of the internal energy transferred from the surroundings with the transfer of matter through the walls that are permeable to it, and of the internal energy transferred to the system as heat through the diathermic walls, and of the energy transferred to the system as work through the adiabatic walls, including the energy transferred to the system by long range forces. These simultaneously transferred quantities of energy are defined by events in the surroundings of the system. Because the internal energy transferred with matter is not in general uniquely resolvable into heat and work components, the total energy transfer cannot in general be uniquely resolved into heat and work components. Under these conditions, the following formula can describe the process in terms of externally defined thermodynamic variables, as a statement of the first law of thermodynamics:

$$\Delta U_0 = Q - W - \sum_{i=1}^{m} \Delta U_i$$

(2)

where ΔU_0 denotes the change of internal energy of the system, and ΔU_i denotes the change of internal energy of the ith of the m surrounding subsystems that are in open contact with the system, due to transfer between the system and that ith surrounding subsystem, and Q denotes the internal energy transferred as heat from the heat reservoir of the surroundings to the system, and W denotes the energy transferred from the system to the surrounding

subsystems that are in adiabatic connection with it. The case of a wall that is permeable to matter and can move so as to allow transfer of energy as work is not considered here.

1.2. THE SECOND LAW OF THERMODYNAMICS

Energy is a conserved property, and no process is known to have taken place in violation of the first law of thermodynamics. Therefore, it is reasonable to conclude that a process must satisfy the first law to occur. However, satisfying the first law alone does not ensure that the process will actually take place. It is common experience that a cup of hot coffee left in a cooler room eventually loses heat. This process satisfies the first law of thermodynamics because the amount of energy lost by the coffee is equal to the amount gained by the surrounding air. Now let us consider the reverse process: the hot coffee getting even hotter in a cooler room as a result of heat transfer from the room air. We all know that this process never takes place. Yet, doing so would not violate the first law as long as the amount of energy lost by the air is equal to the amount gained by the coffee. As another familiar example, consider the heating of a room by the passage of electric current through a resistor. Again, the first law dictates that the amount of electric energy supplied to the resistance wires be equal to the amount of energy transferred to the room air as heat.
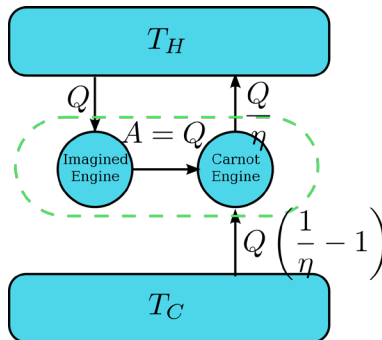
Now let us attempt to reverse this process. It will come as no surprise that transferring some heat to the wires does not cause an equivalent amount of electric energy to be generated in the wires.

Finally, consider a paddle-wheel mechanism that is operated by the fall of a mass. The paddle wheel rotates as the mass falls and stirs a fluid within an insulated container. As a result, the potential energy of the mass decreases, and the internal energy of the fluid increases in accordance with the conservation of energy principle. However, the reverse process, raising the mass by transferring heat from the fluid to the paddle wheel, does not occur in nature, although doing so would not violate the first law of thermodynamics. It is clear from these arguments that processes advance in a certain direction and not in the reverse direction. The first law places no restriction on the direction of a process, but satisfying the first law does not ensure that the process can actually occur.

This inadequacy of the first law to identify whether a process can take place is remedied by introducing another general principle, the second law of thermodynamics. This violation is easily detected with the help of a property called entropy. A process cannot occur unless it satisfies both the first and the second laws of thermodynamics. The use of the second law of thermodynamics is not limited to identifying the direction of processes. The second law also asserts that energy has quality as well as quantity. The first law is concerned with the quantity of energy and the transformations of energy from one form to another with no regard to its quality. Preserving the quality of energy is of major concern to engineers, and the second law provides the necessary means to determine the quality as well as the degree of degradation of energy during a process.

The second law of thermodynamics is also used in determining the theoretical limits for the performance of commonly used engineering systems such as heat engines and refrigerators, as well as predicting the degree of completion of chemical reactions. The second law is also closely associated with the concept of perfection. In fact, the second law defines perfection for thermodynamic processes. It can be used to quantify the level of perfection of a process, and point out the direction to eliminate imperfections effectively. Energy has quality as well as quantity.

More of the high-temperature thermal energy can be converted to work. Therefore, it results in "the higher the temperature is, the higher the quality of the energy." Large quantities of solar energy, for example, can be stored in large bodies of water called solar ponds at about 350 K. This stored energy can then be supplied to a heat engine to produce work (electricity).

However, the efficiency of solar pond power plants is very low (under 5%) because of the low quality of the energy stored in the source, and the construction and maintenance costs are relatively high. Therefore, they are not competitive even though the energy supply of such plants is free. The temperature (and thus the quality) of the solar energy stored could be raised by utilizing concentrating collectors, but the equipment cost in that case becomes very high. Work is a more valuable form of energy than heat inasmuch as 100% of work can be converted to heat, but only a fraction of heat can be converted to work. When heat is transferred from a high-temperature body to a lower temperature one, it is degraded because less of it can now be converted to work. For example, if 100 kJ of heat are transferred from a body at 1,000 K to a body at 300 K, at the end we will have 100 kJ of thermal energy stored at 300 K, which has no practical value. But if this conversion were made through a heat engine, up to $1300/1000 = 0.70 = 70\%$ of it could be converted to work, which is a more valuable form of energy. Thus 70 kJ of work potential is wasted as a result of this heat transfer, and energy is degraded. There are numerous forms of second law statements. Two classical statements are as follows.

- *The Kelvin–Plank statement*: It is impossible to construct a device, operating in a cycle (e.g., heat engine), that accomplishes only the extraction of heat energy from some source and its complete conversion to work. This simply shows the impossibility of having a heat engine with a thermal efficiency of 100%.

- *The Clausius statement*: It is impossible to construct a device, operating in a cycle (e.g., refrigerator and heat pump), that transfers heat from the low-temperature side (cooler) to the high-temperature side (hotter), and producing no other effect.

The second law of thermodynamics asserts that processes occur in a certain direction and that the energy has quality as well as quantity. The first law places no restriction on the direction of a process, and satisfying the first law does not guarantee that the process will occur. Thus, we need another general principle (second law) to identify whether a process can occur or not

Figure 3. Heat transfer from a hot container to the cold surroundings is possible; however, the reveres process (although satisfying the first law) is impossible.

A process can occur when and only when it satisfies both the first and the second laws of thermodynamics. The second law also asserts that energy has a quality. Preserving the quality of energy is a major concern of engineers. In the above example, the energy stored in a hot container (higher temperature) has higher quality (ability to work) in comparison with the energy contained (at lower temperature) in the surroundings.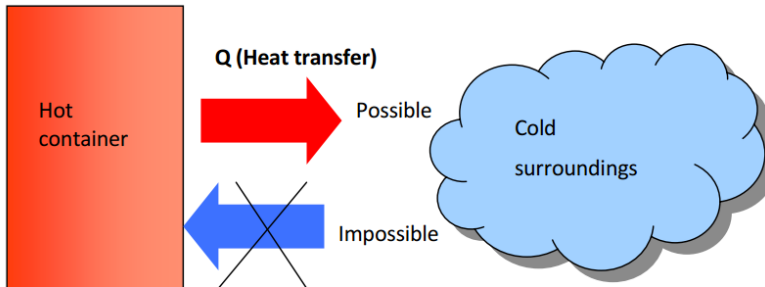 The second law is also used in determining the theoretical limits for the performance of commonly used engineering systems, such as heat engines and refrigerators etc.

1.2.1. Entropy

Entropy and efficiency limits

The concept of entropy was first introduced in 1850 by Clausius as a precise mathematical way of testing whether the second law of

thermodynamics is violated by a particular process. The test begins with the definition that if an amount of heat Q flows into a heat reservoir at constant temperature T, then its entropy S increases by $\Delta S = Q/T$. (This equation in effect provides a thermodynamic definition of temperature that can be shown to be identical to the conventional thermometric one.) Assume now that there are two heat reservoirs R_1 and R_2 at temperatures T_1 and T_2. If an amount of heat Q flows from R_1 to R_2, then the net entropy change for the two reservoirs is

$$\Delta S = \frac{Q}{T_2} - \frac{Q}{T_1}$$

ΔS is positive, provided that $T_1 > T_2$. Thus, the observation that heat never flows spontaneously from a colder region to a hotter region (the Clausius form of the second law of thermodynamics) is equivalent to requiring the net entropy change to be positive for a spontaneous flow of heat. If $T_1 = T_2$, then the reservoirs are in equilibrium and $\Delta S = 0$.

The condition $\Delta S \geq 0$ determines the maximum possible efficiency of heat engines. Suppose that some system capable of doing work in a cyclic fashion (a heat engine) absorbs heat Q_1 from R_1 and exhausts heat Q_2 to R_2 for each complete cycle. Because the system returns to its original state at the end of a cycle, its energy does not change. Then, by conservation of energy, the work done per cycle is $W = Q_1 - Q_2$, and the net entropy change for the two reservoirs is

$$\Delta S = \frac{Q_2}{T_2} - \frac{Q_1}{T_1}$$

To make W as large as possible, Q_2 should be kept as small as possible relative to Q_1. However, Q_2 cannot be zero, because this would make ΔS negative and so violate the second law of thermodynamics. The smallest possible value of Q_2 corresponds to the condition $\Delta S = 0$, yielding

$$\left(\frac{Q_2}{Q_1}\right)_{min} = \frac{T_2}{T_1}$$

This is the fundamental equation limiting the efficiency of all heat engines whose function is to convert heat into work (such as electric power generators). The actual efficiency is defined to be the fraction of Q_1 that is converted to work (W/Q_1), which is equivalent to equation (2).

The maximum efficiency for a given T_1 and T_2 is thus

$$\eta_{max} = 1 - \left(\frac{Q_2}{Q_1}\right)_{min} = 1 - \frac{T_2}{T_1}$$

(3)

A process for which $\Delta S = 0$ is said to be reversible because an infinitesimal change would be sufficient to make the heat engine run backward as a refrigerator.

As an example, the properties of materials limit the practical upper temperature for thermal power plants to $T_1 \cong 1,200$ K. Taking T_2 to be the temperature of the environment (300 K), the maximum efficiency is 1 − 300/1,200 = 0.75. Thus, at least 25 percent of the heat energy produced must be exhausted into the environment as waste heat to avoid violating the second law of thermodynamics. Because of various imperfections, such as friction and imperfect thermal insulation, the actual efficiency of power plants seldom exceeds about 60 percent. However, because of the second law of thermodynamics, no amount of ingenuity or improvements in design can increase the efficiency beyond about 75 percent.

Entropy and heat death

The example of a heat engine illustrates one of the many ways in which the second law of thermodynamics can be applied. One way to generalize the example is to consider the heat engine and its heat reservoir as parts of an isolated (or closed) system—i.e., one that does not exchange heat or work with its surroundings. For example, the heat engine and reservoir could be encased in a rigid container with insulating walls. In this case the second law of thermodynamics (in the simplified form presented here) says that no matter what process takes place inside the container,

its entropy must increase or remain the same in the limit of a reversible process. Similarly, if the universe is an isolated system, then its entropy too must increase with time. Indeed, the implication is that the universe must ultimately suffer a "heat death" as its entropy progressively increases toward a maximum value and all parts come into thermal equilibrium at a uniform temperature. After that point, no further changes involving the conversion of heat into useful work would be possible. In general, the equilibrium state for an isolated system is precisely that state of maximum entropy. (This is equivalent to an alternate definition for the term *entropy* as a measure of the disorder of a system, such that a completely random dispersion of elements corresponds to maximum entropy, or minimum information.

Entropy and the arrow of time

The inevitable increase of entropy with time for isolated systems provides an "arrow of time" for those systems. Everyday life presents no difficulty in distinguishing the forward flow of time from its reverse. For example, if a film showed a glass of warm water spontaneously changing into hot water with ice floating on top, it would immediately be apparent that the film was running backward because the process of heat flowing from warm water to hot water would violate the second law of thermodynamics. However, this obvious asymmetry between the forward and reverse directions for the flow of time does not persist at the level of fundamental interactions. An observer watching a film showing two water molecules colliding would not be able to tell whether the film was running forward or backward.

So what exactly is the connection between entropy and the second law? Recall that heat at the molecular level is the random kinetic energy of motion of molecules, and collisions between molecules provide the microscopic mechanism for transporting heat energy from one place to another. Because individual collisions are unchanged by reversing the direction of time, heat can flow just as well in one direction as the other. Thus, from the point of

view of fundamental interactions, there is nothing to prevent a chance event in which a number of slow-moving (cold) molecules happen to collect together in one place and form ice, while the surrounding water becomes hotter. Such chance events could be expected to occur from time to time in a vessel containing only a few water molecules. However, the same chance events are never observed in a full glass of water, not because they are impossible but because they are exceedingly improbable. This is because even a small glass of water contains an enormous number of interacting molecules (about 10^{24}), making it highly unlikely that, in the course of their random thermal motion, a significant fraction of cold molecules will collect together in one place. Although such a spontaneous violation of the second law of thermodynamics is not impossible, an extremely patient physicist would have to wait many times the age of the universe to see it happen.

The foregoing demonstrates an important point: the second law of thermodynamics is statistical in nature. It has no meaning at the level of individual molecules, whereas the law becomes essentially exact for the description of large numbers of interacting molecules. In contrast, the first law of thermodynamics, which expresses conservation of energy, remains exactly true even at the molecular level.

The example of ice melting in a glass of hot water also demonstrates the other sense of the term *entropy*, as an increase in randomness and a parallel loss of information. Initially, the total thermal energy is partitioned in such a way that all of the slow-moving (cold) molecules are located in the ice and all of the fast-moving (hot) molecules are located in the water (or water vapour). After the ice has melted and the system has come to thermal equilibrium, the thermal energy is uniformly distributed throughout the system. The statistical approach provides a great deal of valuable insight into the meaning of the second law of thermodynamics, but, from the point of view of applications, the microscopic structure of matter becomes irrelevant. The great beauty and strength of classical thermodynamics are that its predictions are completely independent of the microscopic structure of matter.

1.2.2. Open Systems

Thermodynamic Potentials

Most real thermodynamic systems are open systems that exchange heat and work with their environment, rather than the closed systems described thus far. For example, living systems are clearly able to achieve a local reduction in their entropy as they grow and develop; they create structures of greater internal energy (i.e., they lower entropy) out of the nutrients they absorb. This does not represent a violation of the second law of thermodynamics, because a living organism does not constitute a closed system.

In order to simplify the application of the laws of thermodynamics to open systems, parameters with the dimensions of energy, known as thermodynamic potentials, are introduced to describe the system. The resulting formulas are expressed in terms of the Helmholtz free energy F and the Gibbs free energy G, named after the 19th-century German physiologist and physicist Hermann von Helmholtz and the contemporaneous American physicist Josiah Willard Gibbs. The key conceptual step is to separate a system from its heat reservoir. A system is thought of as being held at a constant temperature T by a heat reservoir (i.e., the environment), but the heat reservoir is no longer considered to be part of the system. Recall that the internal energy change (ΔU) of a system is given by

$$\Delta U = Q - W$$

where Q is the heat absorbed and W is the work done. In general, Q and W separately are not state functions, because they are path-dependent. However, if the path is specified to be any reversible isothermal process, then the heat associated with the maximum work (W_{max}) is $Q_{max} = T\Delta S$. With this substitution the above equation can be rearranged as

$$-W_{max} = \Delta U - T\Delta S$$

Note that here ΔS is the entropy change just of the system being held at constant temperature, such as a battery. Unlike the case of an isolated system as considered previously, it does not include the entropy change of the heat reservoir (i.e., the surroundings) required to keep the temperature constant. If this additional entropy change of the reservoir were included, the total entropy change would be zero, as in the case of an isolated system. Because the quantities U, T, and S on the right-hand side are all state functions, it follows that $-W_{max}$ must also be a state function. This leads to the definition of the Helmholtz free energy

$$F = U - TS$$

such that, for any isothermal change of the system,

$$\Delta F = \Delta U - T\Delta S$$

is the negative of the maximum work that can be extracted from the system. The actual work extracted could be smaller than the ideal maximum, or even zero, which implies that $W \leq -\Delta F$, with equality applying in the ideal limiting case of a reversible process. When the Helmholtz free energy reaches its minimum value, the system has reached its equilibrium state, and no further work can be extracted from it. Thus, the equilibrium condition of maximum entropy for isolated systems becomes the condition of minimum Helmholtz free energy for open systems held at constant temperature. The one additional precaution required is that work done against the atmosphere be included if the system expands or contracts in the course of the process being considered. Typically, processes are specified as taking place at constant volume and temperature in order that no correction is needed.

Although the Helmholtz free energy is useful in describing processes that take place inside a container with rigid walls, most processes in the real world take place under constant pressure rather than constant volume. For example, chemical reactions in an open test tube—or in the growth of a tomato in a garden—take place under conditions of (nearly) constant atmospheric pressure. It is for the description of these cases that the Gibbs free energy was introduced. As previously established, the quantity

$$-W_{max} = \Delta U - T\Delta S$$

is a state function equal to the change in the Helmholtz free energy. Suppose that the process being considered involves a large change in volume (ΔV), such as happens when water boils to form steam. The work done by the expanding water vapour as it pushes back the surrounding air at pressure P is $P\Delta V$. This is the amount of work that is now split out from W_{max} by writing it in the form

$$W_{max} = W'_{max} + P\Delta V$$

where W'_{max} is the maximum work that can be extracted from the process taking place at constant temperature T and pressure P, other than the atmospheric work ($P\Delta V$). Substituting this partition into the above equation for $-W_{max}$ and moving the $P\Delta V$ term to the right-hand side then yields $-W'_{max} = \Delta U + P\Delta V - T\Delta S$

This leads to the definition of the Gibbs free energy

$$G = U + PV - TS$$

such that, for any isothermal change of the system at constant pressure,

$$\Delta G = \Delta U + P\Delta V - T\Delta S$$

is the negative of the maximum work W'_{max} that can be extracted from the system, other than atmospheric work. As before, the actual work extracted could be smaller than the ideal maximum, or even zero, which implies that $W' \leq -\Delta G$, with equality applying in the ideal limiting case of a reversible process. As with the Helmholtz case, when the Gibbs free energy reaches its minimum value, the system has reached its equilibrium state, and no further work can be extracted from it. Thus, the equilibrium condition becomes the condition of minimum Gibbs free energy for open systems held at constant temperature and pressure, and the direction of spontaneous change is always toward a state of lower free energy for the system (like a ball rolling downhill into a valley). Notice in particular that the entropy can now spontaneously decrease (i.e., $T\Delta S$ can be negative), provided that this decrease is more than offset by the $\Delta U + P\Delta V$ terms in the definition of ΔG. As

further discussed below, a simple example is the spontaneous condensation of steam into water. Although the entropy of water is much less than the entropy of steam, the process occurs spontaneously provided that enough heat energy is taken away from the system to keep the temperature from rising as the steam condenses.

A familiar example of free energy changes is provided by an automobile battery. When the battery is fully charged, its Gibbs free energy is at a maximum, and when it is fully discharged (i.e., dead), its Gibbs free energy is at a minimum. The change between these two states is the maximum amount of electrical work that can be extracted from the battery at constant temperature and pressure. The amount of heat absorbed from the environment in order to keep the temperature of the battery constant (represented by the $T\Delta S$ term) and any work done against the atmosphere (represented by the $P\Delta V$ term) are automatically taken into account in the energy balance.

Gibbs free energy and chemical reactions

All batteries depend on some chemical reaction of the form reactants → products for the generation of electricity or on the reverse reaction as the battery is recharged. The change in free energy ($-\Delta G$) for a reaction could be determined by measuring directly the amount of electrical work that the battery could do and then using the equation $W_{max} = -\Delta G$. However, the power of thermodynamics is that $-\Delta G$ can be calculated without having to build every possible battery and measure its performance. If the Gibbs free energies of the individual substances making up a battery are known, then the total free energies of the reactants can be subtracted from the total free energies of the products in order to find the change in Gibbs free energy for the reaction,

$$\Delta G = G_{products} - G_{reactants}$$

Once the free energies are known for a wide variety of substances, the best candidates for actual batteries can be quickly discerned. In fact, a good part of the practice of thermodynamics

is concerned with determining the free energies and other thermodynamic properties of individual substances in order that ΔG for reactions can be calculated under different conditions of temperature and pressure.

In the above discussion, the term *reaction* can be interpreted in the broadest possible sense as any transformation of matter from one form to another. In addition to chemical reactions, a reaction could be something as simple as ice (reactants) turning to liquid water (products), the nuclear reactions taking place in the interior of stars, or elementary particle reactions in the early universe. No matter what the process, the direction of spontaneous change (at constant temperature and pressure) is always in the direction of decreasing free energy.

Enthalpy and the *heat of reaction*

As discussed above, the free energy change $W_{max} = -\Delta G$ corresponds to the maximum possible useful work that can be extracted from a reaction, such as in an electrochemical battery. This represents one extreme limit of a continuous range of possibilities. At the other extreme, for example, battery terminals can be connected directly by a wire and the reaction allowed to proceed freely without doing any useful work. In this case $W' = 0$, and the first law of thermodynamics for the reaction becomes

$$\Delta U = Q_0 - P\Delta V$$

where Q_0 is the heat absorbed when the reaction does no useful work and, as before, $P\Delta V$ is the atmospheric work term. The key point is that the quantities ΔU and $P\Delta V$ are exactly the same as in the other limiting case, in which the reaction does maximum work. This follows because these quantities are state functions, which depend only on the initial and final states of a system and not on any path connecting the states. The amount of useful work done just represents different paths connecting the same initial and final states. This leads to the definition of enthalpy (H), or heat content, as

$H = U + PV$

Its significance is that, for a reaction occurring freely (i.e., doing no useful work) at constant temperature and pressure, the heat absorbed is

$Q_0 = \Delta U + P\Delta V = \Delta H$

)where ΔH is called the heat of reaction. The heat of reaction is easy to measure because it simply represents the amount of heat that is given off if the reactants are mixed together in a beaker and allowed to react freely without doing any useful work.

The above definition for enthalpy and its physical significance allow the equation for ΔG to be written in the particularly illuminating and instructive form

$\Delta G = \Delta H - T\Delta S$

Both terms on the right-hand side represent heats of reaction but under different sets of circumstances. ΔH is the heat of reaction (i.e., the amount of heat absorbed from the surroundings in order to hold the temperature constant) when the reaction does no useful work, and $T\Delta S$ is the heat of reaction when the reaction does maximum useful work in an electrochemical cell. The (negative) difference between these two heats is exactly the maximum useful work − ΔG that can be extracted from the reaction. Thus, useful work can be obtained by contriving for a system to extract additional heat from the environment and convert it into work. The difference $\Delta H - T\Delta S$ represents the fundamental limitation imposed by the second law of thermodynamics on how much additional heat can be extracted from the environment and converted into useful work for a given reaction mechanism. An electrochemical cell (such as a car battery) is a contrivance by means of which a reaction can be made to do the maximum possible work against an opposing electromotive force, and hence the reaction literally becomes reversible in the sense that a slight increase in the opposing voltage will cause the direction of the reaction to reverse and the cell to start charging up instead of discharging.

As a simple example, consider a reaction in which water turns reversibly into steam by boiling. To make the reaction reversible, suppose that the mixture of water and steam is contained in a cylinder with a movable piston and held at the boiling point of 373 K (100 °C) at 1 atmosphere pressure by a heat reservoir. The enthalpy change is ΔH = 40.65 kilojoules per mole, which is the latent heat of vaporization. The entropy change is

$$\Delta S = \frac{40.65}{373} = 0.109 \text{ kilojoules per mole} \cdot \text{K}$$

representing the higher degree of disorder when water evaporates and turns to steam. The Gibbs free energy change is $\Delta G = \Delta H - T\Delta S$. In this case the Gibbs free energy change is zero because the water and steam are in equilibrium, and no useful work can be extracted from the system (other than work done against the atmosphere). In other words, the Gibbs free energy per molecule of water (also called the chemical potential) is the same for both liquid water and steam, and so water molecules can pass freely from one phase to the other with no change in the total free energy of the system.

1.2.3. Thermal Energy Reservoirs

Thermal energy reservoirs are hypothetical bodies with a relatively large thermal energy capacity (mass x specific heat) that can supply or absorb finite amounts of heat without undergoing any change in temperature. Lakes, rivers, atmosphere, oceans are example of thermal reservoirs. A two-phase system can be modeled as a reservoir since it can absorb and release large quantities of heat while remaining at constant temperature. A reservoir that supplies energy in the form of heat is called a source and one that absorbs energy in the form of heat is called a sink.

Heat Engines

Heat engines convert heat to work. There are several types of heat engines, but they are characterized by the following:

- They all receive heat from a high-temperature source (oil furnace, nuclear reactor, etc.)
- They convert part of this heat to work
- They reject the remaining waste heat to a low-temperature sink
- They operate in a cycle.
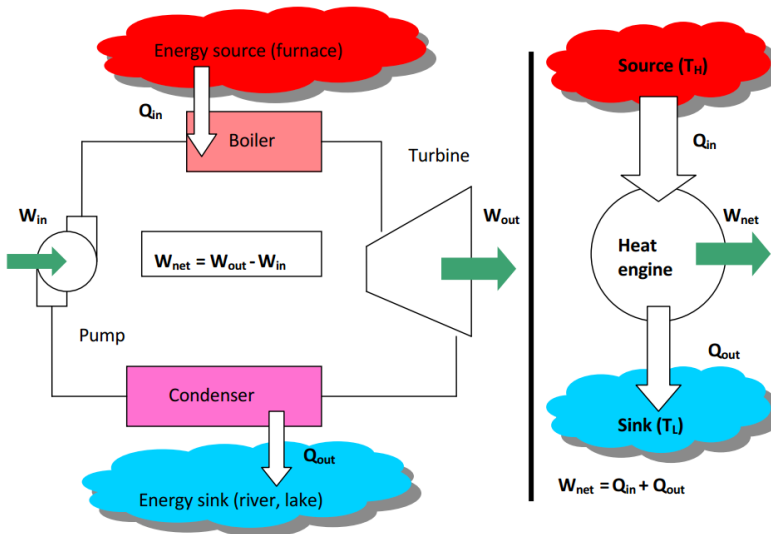
Figure 4. Steam power plant is a heat engine.

Thermal efficiency: is the fraction of the heat input that is converted to the network output (efficiency = benefit / cost).

$$\eta_{th} = \frac{W_{net,out}}{Q_{in}} \quad and \quad W_{net,out} = Q_{in} - Q_{out}$$

$$\eta_{th} = 1 - \frac{Q_{out}}{Q_{in}}$$

The thermal efficiencies of work-producing devices are low. Ordinary spark-ignition automobile engines have a thermal efficiency of about 20%, diesel engines about 30%, and power plants in the order of 40%.

Is it possible to save the rejected heat Q_{out} in a power cycle? The answer is NO, because without the cooling in condenser the cycle cannot be completed.

The Second Law: Kelvin-Planck Statement

It is impossible for any device that operates on a cycle to receive heat from a single reservoir and produce a net amount of work. In other words, no heat engine can have a thermal efficiency of 100%.
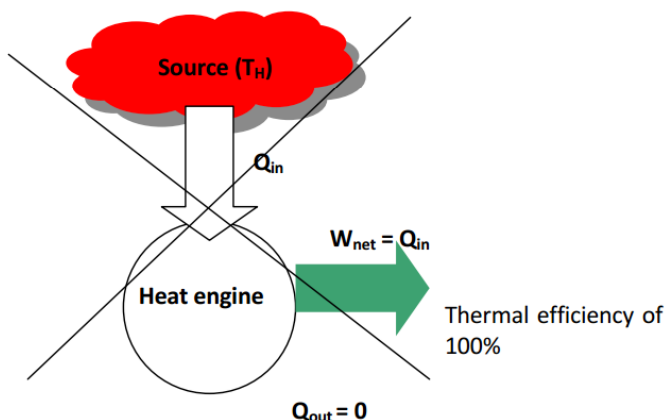
Figure 5. A heat engine that violates the Kelvin-Planck statement of the second law cannot be built.

Refrigerators and Heat Pumps

In nature, heat flows from high-temperature regions to low-temperature ones. The reverse process, however, cannot occur by itself. The transfer of heat from a low- temperature region to a high-temperature one requires special devices called refrigerators. Refrigerators are cyclic devices, and the working fluids used in the cycles are called refrigerant. Heat pumps transfer heat from a low-temperature medium to a high-temperature one. Refrigerators and heat pumps are essentially the same devices; they differ in their

objectives only. Refrigerator is to maintain the refrigerated space at a low temperature. On the other hand, a heat pump absorbs heat from a low-temperature source and supplies the heat to a warmer medium.
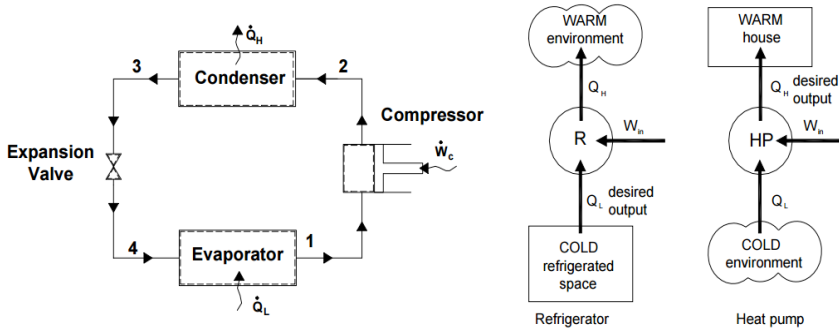
Figure 6. Objectives of refrigerator and heat pump.

1.2.4. The Second Law of Thermodynamics for Clausius Statement

It is impossible to construct a device that operates in a cycle and produces no effect other than the transfer of heat from a lower-temperature body to higher-temperature body. In other words, a refrigerator will not operate unless its compressor is driven by an external power source. Kelvin-Planck and Clausius statements of the second law are negative statements, and a negative statement cannot be proved. So, the second law, like the first law, is based on experimental observations.

The two statements of the second law are equivalent. In other words, any device violates the Kelvin-Planck statement also violates the Clausius statement and vice versa.
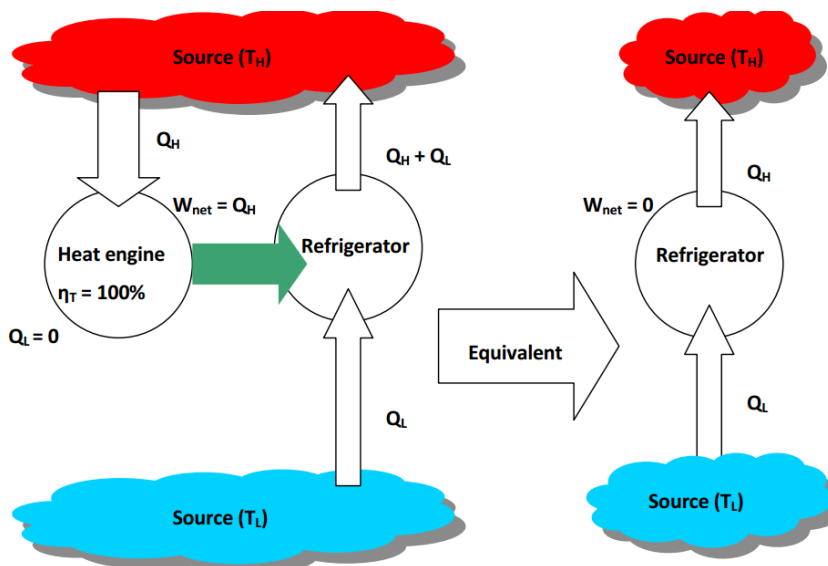
Figure 7. The violation of the Kelvin-Planck statement leads to violation of Clausius.

Any device that violates the first law of thermodynamics (by creating energy) is called a perpetual-motion machine of the first kind (PMM1), and the device that violates the second law is called a perpetual-motion machine of the second kind (PMM2).

1.2.5. Reversible and Irreversible Process

A reversible process is defined as a process that can be reversed without leaving any trace on the surroundings. It means both system and surroundings are returned to their initial states at the end of the reverse process. Processes that are not reversible are called irreversible. Reversible processes do not occur and they are only idealizations of actual processes. We use reversible process concept because, a) they are easy to analyze (since system passes through a series of equilibrium states); b) they serve as limits (idealized models) to which the actual processes can be compared.

Some factors that cause a process to become irreversible:

- Friction

- Unrestrained expansion and compression
- mixing
- Heat transfer (finite ΔT)
- Inelastic deformation
- Chemical reactions

In a reversible process things happen very slowly, without any resisting force, without any space limitation → everything happens in a highly organized way (it is not physically possible - it is an idealization).

Internally reversible process: if no irreversibilities occur within the boundaries of the system. In these processes a system undergoes through a series of equilibrium states, and when the process is reversed, the system passes through exactly the same equilibrium states while returning to its initial state.

Externally reversible process: if no irreversibilities occur outside the system boundaries during the process. Heat transfer between a reservoir and a system is an externally reversible process if the surface of contact between the system and reservoir is at the same temperature.

Totally reversible (reversible): both externally and internally reversible processes.
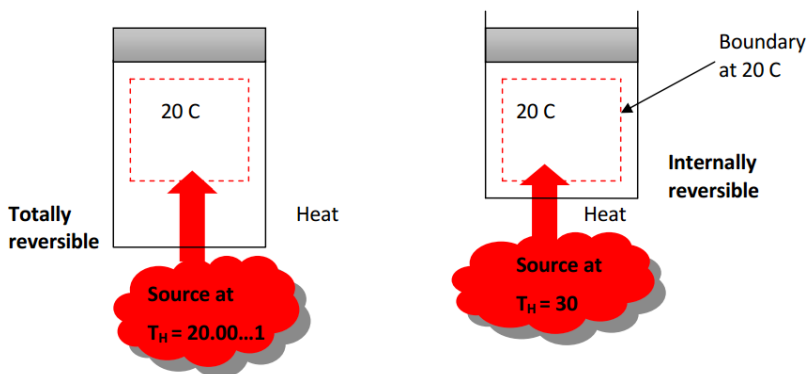
Figure 8. Reversible and irreversible process.

1.2.6. The Carnot Cycle

The efficiency of a heat-engine cycle greatly depends on how the individual processes that make up the cycle are executed. The network (or efficiency) can be maximized by using reversible processes. The best known reversible cycle is the Carnot cycle. Note that the reversible cycles cannot be achieved in practice because of irreversibilities associated with real processes. But, the reversible cycles provide upper limits on the performance of real cycles. Consider a gas in a cylinder-piston (closed system). The Carnot cycle has four processes:

- 1-2 Reversible isothermal expansion: The gas expands slowly, doing work on the surroundings. Reversible heat transfer from the heat source at TH to the gas which is also at TH.

- 2-3 Reversible adiabatic expansion: The cylinder-piston is now insulated (adiabatic) and gas continues to expand reversibly (slowly). So, the gas is doing work on the surroundings, and as a result of expansion the gas temperature reduces from TH to TL.

- 3-4: Reversible isothermal compression: The gas is allowed to exchange heat with a sink at temperature TL as the gas is being slowly compressed. So, the surroundings is doing work (reversibly) on the system and heat is transferred from the system to the surroundings (reversibly) such that the gas temperature remains constant at TL.

- 4-1: Reversible adiabatic compression: The gas temperature is increasing from TL to TH as a result of compression.

Carnot cycle is the most efficient cycle operating between two specified temperature limits. The efficiency of all reversible heat engines operating between the two same reservoirs are the same. The thermal efficiency of a heat engine (reversible or irreversible) is:

$$\eta_{th} = 1 - \frac{Q_L}{Q_H}$$

For the Carnot cycle, it can be shown:

$$\eta_{th,Carnot} = 1 - \frac{T_L}{T_H}$$
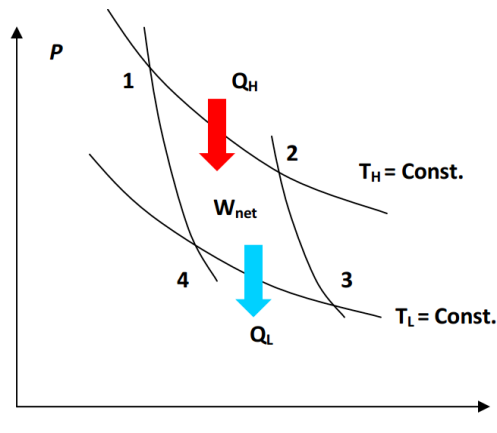
Figure 9. P-v diagram for the Carnot cycle.

The efficiency of an irreversible (real) cycle is always less than the efficiency of the Carnot cycle operating between the same two reservoirs.

$$\eta_{th} = \begin{cases} < \eta_{th,rev} & \text{irreversible heat engine} \\ = \eta_{th,rev} & \text{reversible heat engine} \\ > \eta_{th,rev} & \text{impossible heat engine!} \end{cases}$$

Consider a Carnot heat engine working between two thermal reservoirs TL = 300 K and TH. The thermal efficiency of the heat engine increases as the heat source temperature TH is increased.

T_H K	η_{th} %
1000	70
900	66.6
500	40
350	14.3

The thermal efficiency of actual heat engine can be maximized by supplying heat to the engine at the highest possible temperature (limited by material strength) and rejecting heat to lowest possible temperature (limited by the cooling medium temperature such as atmosphere, lake, river temperature). From the above table, it can also be seen that the energy has a quality. More of the high-temperature thermal energy can be converted to work. Therefore, the higher the temperature, the higher the quality of the energy will be.

The Carnot Refrigeration and Heat Pump Cycle

A refrigerator or heat pump that operates on the reverse Carnot cycle is called a Carnot Refrigerator, or a Carnot heat pump. The Coefficient of performance of any refrigerator or heat pump (reversible or irreversible) is given by:

$$COP_R = \frac{1}{Q_H/Q_L - 1} \quad \text{and} \quad COP_{HP} = \frac{1}{1 - Q_L/Q_H}$$

COP of all reversible refrigerators or heat pumps can be determined from:

$$COP_{R,rev} = \frac{1}{T_H/T_L - 1} \quad \text{and} \quad COP_{HP,rev} = \frac{1}{1 - T_L/T_H}$$

Also, similar to heat engine, one can conclude:

$$COP_R = \begin{cases} < COP_{R,rev} & \text{irreversible refrigerator} \\ = COP_{th,rev} & \text{reversible refrigerator} \\ > COP_{th,rev} & \text{impossible refrigerator!} \end{cases}$$

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2

INTRODUCTION TO EQUILIBRIUM

INTRODUCTION

Equilibrium is a state of balance between opposing forces or actions that is either static (as in a body acted on by forces whose resultant is zero) or dynamic (as in a reversible chemical reaction when the rates of reaction in both directions are equal)

Sometimes, when a chemical reaction takes place, it proceeds for a period of time and then seems to stop before all the reactants are consumed. But the reaction does not actually stop. Instead, the reaction reaches a point of chemical equilibrium in which the reverse reaction is converting products into reactants as fast as products are formed in the forward reaction. At equilibrium, with both the forward and reverse reactions taking place at the same rate, the concentration of every species no longer changes.

Every reaction has a point in which equilibrium is established. For many reactions, it occurs at the point when essentially all reactants are converted to products; for practical purposes, scientists say that the reaction has gone to completion. But for other reactions, equilibrium occurs when only part of the reactants are converted into products. In these cases and with enough information, it is possible to calculate the concentration of one or more species at equilibrium. In addition, it is possible to predict how the equilibrium will be affected by a change in temperature or an increase or decrease in concentration of a reactant or product. The state of equilibrium is especially important in solutions, and there are many vital equilibria in the chemistry of the body.

2.1 BASIC CONCEPT OF EQUILIBRIUM

Equilibrium is a state in which no net change is occurring. Something in this state could be considered to be stable, balanced, or unchanging, and this is extremely rare, usually only existing for brief periods of time before something disturbs the balance. This concept is very important in the sciences, influencing everything from mathematics to the study of the universe, and there are a number of different types of equilibrium. In all cases, the term describes a stable state.

At equilibrium, the rate of the forward reaction is equal to the rate of the reverse.

Forward reaction: A→B rate $= k_f [A]$

Reverse reaction: B→A rate $= k_r [B]$

Where k_f and k_r are the rate constants for the forward and reverse reactions.

Suppose we start with pure compound A in a closed container. As A reacts to form compound B, the concentration of A decreases while the concentration of B increases.   As A decreases, the rate of the forward reaction decreases. Likewise, as B increases, the rate of the reverse reaction increases. Eventually, the reaction reaches

a point where the forward and reverse reactions are the same. At equilibrium:

k_f [A] $= k_r$ [B]

Rearranging

[B]/[A] $= k_f / k_r$ = a constant

This does not mean A and B stop reacting. On the contrary, the equilibrium is *dynamic*. (Compound A→B and B → A, signified by A ⇔ B

A famous equilibrium reaction is the Haber process for synthesizing ammonia.

N_2 (g) + $3H_2$ (g) ⇔ 2 NH_3 (g)

The Haber process consists of putting together N_2 and H_2 in a high pressure tank in the presence of a catalyst and a temperature of several hundred degrees Celsius. Eventually, an equilibrium will be reached where there is a mixture of

N_2, H_2, and NH_3. If only ammonia is placed in the tank, again, a mixture of the three will occur. Therefore, equilibrium can be reached from either direction.

2.1.1 The Equilibrium Constant

A relationship between the concentrations of reactants and products at equilibrium can be determined. This is referred to as the Law of mass action.

$aA + bB$ ⇔ $pP + qQ$

where A,B,P,Q are the chemicals involved and *a, b, p, q* are the coefficients in the balanced equation.

According to this law, the equilibrium condition is expressed by the equation:

$$K_c = \frac{[P]^p \, [Q]^q}{[A]^a \, [B]^b}$$

the square brackets signify molar concentrations. The constant K_c is called the equilibrium constant. The c indicates that concentrations expressed in molarity are used.

The value of the equilibrium constant will vary with tempera-ture.

Equilibrium constants can also be expressed in terms of pressure.

When the reactants and products in a chemical equation are gases, we can formulate the equilibrium expression in terms of partial pressures (usually in atms) instead of molar concentrations

When using partial pressures, the equilibrium constant is K_p

$$K_p = \frac{(P_P)^p (P_Q)^q}{(P_A)^a (P_B)^b}$$

where P_A is the partial pressure of a and so forth. The numerical values for K_c and K_p will obviously be different so be careful.

For gases, we can use the ideal gas law to convert between K_s and K_p.

$PV = nRT$ rearranging $P = (n/V) RT$ and since n/V is expressed as moles per liter, this is molarity.

$P = MRT$

For substance A, $P_A = [A] \, (RT)$; for substance B, $P_B = [B] \, (RT)$ and so on.

Substitute each equation into the K_p equation, you will end up with

$K_p = K_c \, (RT)^{\Delta n}$ where Δn is the change in number of moles going from reactants to products. It is equal to the number of moles of gaseous products minus number of moles of gaseous reactants.

For example

N_2 (g) + $3H_2$ (g) $\Leftrightarrow$ $2NH_3$
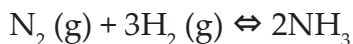
Δn = 2- (3+1) = -2

Example: A mixture of nitrogen and hydrogen in a reaction vessel is allowed to attain equilibrium at 472°C the equilibrium mixture of gases was analyzed and found to contain 0.127 M H_2, 0.0402 M N_2, and 0.00272 M NH_3. From this data calculate K_c. Then, using the value for K_c calculate K_p.

2.1.2 Magnitude and direction of the Chemical Equation and K.

If the equilibrium constant is very large, the products are favored and it is said equilibrium lies to the right.

If the equilibrium constant is much less than one, we say the reactants are favored and the equilibrium lies to the left.

Because an equilibrium can be approached from either direction, the direction in which we write the equilibrium is arbitrary.

N_2O_4(g) $\Leftrightarrow$ $2NO_2$ (g)
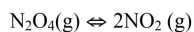
$$K_c = \frac{[NO_2]^2}{[N_2O_4]} = 0.212 \text{ (at 100°C)}$$

OR

$2NO_2$ (g) $\Leftrightarrow$ N_2O_4(g)
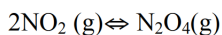
$$K_c = \frac{[N_2O_4]}{[NO_2]^2} = \frac{1}{0.212} = 4.72 \text{ (at 100°C)}$$

Notice: The equilibrium constant for the reaction written in one direct is the reciprocal of the reaction written in the reverse direction.

It is very important then to specify not only temperature, but how the equilibrium expression is written.

2.1.3 Heterogeneous Equilibrium

Equilibrium in which all reactants and products are of the same phase are called Homogeneous equilibrium. If different phases are involved, it is referred to as heterogeneous equilibrium.

$$CaCO_3(s) \Leftrightarrow CaO(s) + CO_2(g)$$
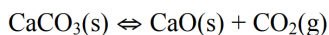
$$K_c = \frac{[CaO][CO_2]}{[CaCO_3]}$$

When we are looking at concentrations of liquids and solids, we are really looking at density divided by molar mass.

$$Density/MM = \frac{g/cm^3}{g/mol} = \frac{mol}{cm^3}$$

since the density of any given liquid or solid is constant and changes very little with temperature, we can effectively say it is a constant.

$$K_c = \frac{(constant\ 1)\ [CO_2]}{(constant\ 2)}$$

$$K_c{}' = K_c\ constant\ 2/constant\ 1\ = [CO_2]$$

We can therefore exclude liquids and solids from the expression. However, even though they do not appear in the expression, they must be present for an equilibrium to be established.

2.1.4 Applications of Equilibrium Constants

A. To determine Concentrations of other species in a chemical reaction if one species is known. Use the following procedure:

1. Tabulate the known initial and equilibrium concentrations of all species involved.

2. For those species for which both the initial equilibrium concentrations are known, calculate the change in concentration that occurs as the system reaches equilibrium.

3. Use the stoichiometry of the reaction to calculate the changes in concentration for all other species in the equilibrium.

4. From the initial concentrations and changes in concentration, calculate the equilibrium concentrations these are used to evaluate the equilibrium constant.

Example: A mixture of 5.000×10^{-3} mol of H_2 and 1.000×10^{-2} mol of I_2 is placed in a 5.000 L container at 448°C and allowed to come to equilibrium. Analysis of the equilibrium mixture shows that the concentration of HI is 1.87×10^{-3} M. Calculate K_c at 448°C for the reaction: H_2 (g) + I_2 (g) ⇔ 2HI (g).

First, tabulate the initial and equilibrium concentrations of all species as well as the change in concentrations. It is convenient to use the equation as a heading for the table.

In this example, the initial concentrations of H_2 and I_2 must be calculated.

$[H_2]_{initial} = (5.000 \times 10^{-3} \text{ mol}) / (5.000 \text{ L}) = 1.000 \times 10^{-3} M$

$[I_2]_{initial} = (1.000 \times 10^{-2} \text{ mol}) / (5.000 \text{ L}) = 2.000 \times 10^{-3} M$

	$H_2(g)$	+	$I_2(g)$	⇔	2HI (g)
Initial	$1.000 \times 10^{-3} M$		$2.000 \times 10^{-3} M$		0 M
Change					
Equilibrium					$1.87 \times 10^{-3} M$

Second, calculate the change in concentration of HI using initial and equilibrium values. The change is $1.87 \times 10^{-3} M$.

third, use the stoichiometry of the reaction to calculate the other species. The balanced chemical equation shows for 2 mol of HI formed, 1 mol of H_2 must be consumed. Thus the amount of H_2 consumed is:

(1.87 x 10^{-3} mol HI/liter) (1 mol H_2/ 2 mol HI) = 9.35 x 10^{-4} mol H_2/liter

The same line of reasoning gives the same value for I_2

Fourth, calculate the equilibrium concentrations using initial and change values the equilibrium concentration is the initial minus that consumed. The table now looks like:

	$H_2(g)$	+	$I_2(g)$	⇔	2HI (g)
Initial	1.000 x 10^{-3}M		2.000 x 10^{-3}M		0 M
Change	-0.935 x 10^{-3} M		-0.935 x 10^{-3} M		+1.87 x 10^{-3}M
Equilibrium	0.065 x 10^{-3} M		1.065 x 10^{-3}M		1.87 x 10^{-3}M

Finally, calculate the equilibrium constant.

$$K_c = \frac{[HI]}{[H_2][I_2]} = \frac{(1.87 \times 10^{-3})^2}{(0.065 \times 10^{-3})(1.065 \times 10^{-3})} = 51$$

B. Predicting the direction of a reaction

When we substitute reactant and product information into the equilibrium expression, the result is known as the reaction quotient and is represented by the letter Q. The reaction quotient will equal the equilibrium constant K only if the concentrations are such that the system is at equilibrium. When Q> K substances on the right side of the equation will react to form those on the left. If Q<K, the reaction will achieve equilibrium by forming more products.

Example: At 448°C the K_c for the reaction $H_2(g) + I_2(g) ⇔ 2HI (g)$ is 51. Predict how the reaction will proceed to reach equilibrium if we start with 1.0 x 10^{-2}M HI, 5.0 x 10^{-3}M H_2, and 1.5 x 10^{-2}M I_2.

Solution: the reaction quotient is

$Q = [HI]^2/[H_2][I_2] = (1.0 \times 10^{-2})^2/ (5.0 \times 10^{-3})(1.5 \times 10^{-2}) = 1.3$

Q<K therefore, [HI] will need to increase and [H_2] and [I_2] decrease to reach equilibrium. the reaction will proceed to the left.

C. Calculation of Equilibrium Concentrations

Example: For the Haber process, N_2 (g) + $3H_2$ (g) $\Leftrightarrow$ $2NH_3$, K_p=1.45 x 10^{-5} at 500° C. In an equilibrium mixture of the three gases, the partial pressure of H_2 is 0.928 atm and that of N_2 is 0.432 atm. What is the partial pressure of NH_3?
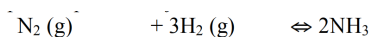
	N_2 (g)	+ $3H_2$ (g)	$\Leftrightarrow$ $2NH_3$
Equilibrium pressure (atm):	*0.432*	*0.928*	*x*

At equilibrium, the pressures must satisfy the equilibrium expression:

$$K_p = \frac{P_{NH3}^2}{P_{N2}P_{H2}^3} = \frac{x^2}{(0.432)(0.928)^3} = 1.45 \times 10^{-5}$$

Solving for x gives 2.24 x 10^{-3} atm

Example: A 1.000 l flask is filled with 1.000 mol H_2 and 2.000 mol I_2 at 448°C. The value of the equilibrium constant, K_c, for the reaction
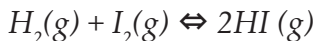
$$H_2(g) + I_2(g) \Leftrightarrow 2HI (g)$$

at 448°C is 50.5. What are the concentrations of H_2, I_2 and HI at equilibrium?

Solution: In this case we are not given any of the equilibrium concentrations. We proceed by first constructing a table with initial concentrations as follows.

	H_2(g)	+	I_2(g)	$\Leftrightarrow$	2HI (g)
Initial	1.000 M		2.000 M		0 M
Change					
Equilibrium					

At equilibrium, the concentration of HI must be greater than 0 and the concentrations of H_2 and I_2 must decrease. Let's represent the change in concentration of H_2 by the variable x. Since the moles of I_2 are in a 1:1 ratio with H_2 the change in concentration of I_2 can also be x. However, 2 moles of HI are formed so its concentration change is $2x$.

	H_2(g)	+	I_2(g)	$\Leftrightarrow$	2HI (g)
Initial	1.000 M		2.000 M		0 M
Change	-x M		-x M		+2x M
Equilibrium	(1.000-x)M		(2.000-x)M		2x M

Substitute the equilibrium concentrations into the equilibrium expression.

$$K_c = \frac{[HI]^2}{[H_2][I_2]} = \frac{(2x^2)}{(1.000\text{-}x)(2.000\text{-}x)} = 50.5$$

Through the use of the quadratic equation, x = 2.323 or 0.935.

Using the first value, we will end up with negative concentrations. Since a negative concentration is not meaningful, we reject that value and use 0.935.

The equilibrium concentrations are then found to be

$[H_2] = (1.000 - 0.935) = 0.065M$

$[I_2] = 1.065M$

$[HI] = 1.870M$

You can double check for correctness by plugging these values into the equilibrium expression and see if you end up with a K_c around 50.5.

2.1.5 Le Châtelier's Principle

If a system at equilibrium is disturbed by a change in temperature, pressure, or concentration of one of the components, the system will shift its equilibrium position so as to contract the disturbance.

Change in reactant or product concentrations.

If a chemical substance is at equilibrium and we add more of a reactant or product, the reaction will shift to consume whatever is added. Conversely, removal of some of the reactants or products will result in the reaction moving in the direction that forms more of what was removed.

Effect of volume and pressure changes.

Reducing the volume (hence increasing pressure), causes the reaction to shift to the direction that produces less moles.

Note: keep in mind this shifts of volume, pressure and concentrations do not change the value of K_c only the concentrations of reactants and products.

The effect of temperature changes

Changes in temperature will change the value of the equilibrium constant.

To notice the shifts in equilibrium, we need to be aware whether the reaction is endothermic or exothermic and place heat either as a reactant or product:

Endothermic: Reactants + heat ⇔ products Exothermic: Reactants ⇔ products + heat.

When the temperature is increased, the equilibrium shifts to the direction to use up the heat. For example, in an endothermic reaction, this would mean a shift to the right in the direction of the products. What would this do the value of K?

Endothermic: Increasing T results in _____ of K

Exothermic: Increasing T results in _____ of K

2.1.6 Quantitative Aspect of Equilibrium State

The chemical equilibrium state describes concentrations of reactants and products in a reaction taking place in a closed system, which no longer change with time. In other words, the rate of the forward reaction equals the rate of the reverse reaction, such that the concentrations of reactants and products remain fairly stable, in a chemical reaction. Equilibrium is denoted in a chemical equation by the ⇌ symbol.

Many chemical reactions involve an equilibrium process. During a dynamic equilibrium, the rate of the forward reaction equals the rate of the reverse reaction. This means that both reactants and products will be present at any given point in time. The equilibrium may favor either the reactants or products. The extent to which the reaction proceeds towards products is measured by an equilibrium constant. This constant is a specific ratio of the products to the reactants. This ratio is often referred to as a mass action expression.

Law of Equilibrium and Concentration Equilibrium Constant

Consider the following equilibrium

$$H_2(g) + I_2(g) \rightleftharpoons 2HI\ (g)$$
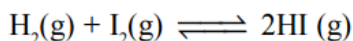
At equilibrium the concentrations of H_2, I_2 and HI become constant. Also, it has been found experimentally that irrespective of the starting concentrations of H_2 and I_2 the following ratio of concentration terms always remains constant.

$$K_c = \frac{[HI]^2}{[H_2][I_2]}$$

Here $[H_2]$, $[I_2]$ and $[HI]$ represent the equilibrium molar concentrations of H_2, I_2 and HI respectively and K_e is called the concentration equilibrium constant (sometimes it is written as simply K). In general, for reversible reaction

$$aA + bB \rightleftharpoons cC + dD$$

at equilibrium, the following ratio of concentration terms always remains constant at a given temperature.

$$K_c = \frac{[C]^c [D]^d}{[A]^a [B]^b}$$

The above relation is known as the law of equilibrium. It may be noted here that all the concentrations values in the law of equilibrium are the equilibrium concentrations of reactants and products. The numerator of the law of equilibrium is the product of equilibrium molar concentrations of products, each term being raised to the power equal to its stoichiometric coefficient in the chemical equation and the denominator contains products of similar concentration terms of reactants.

Pressure Equilibrium Constant K_p

In case of gases their partial pressures can also be used in place of molar concentrations (since the two are directly proportional to each other) in the law of equilibrium. The new equilibrium constant, K_p, is called the pressure equilibrium constant. For the reaction between H_2 and I_2, K_p is given by

$$K_p = \frac{p^2_{HI}}{p_{H_2} \times p_{I_2}}$$

Here p_{H_2}, p_{I_2} and p_{HI} are the equilibrium partial pressures of H_2, I_2 and HI respectively. For the general gas phase reaction:

$$a A\,(g) + b B\,(g) \rightleftharpoons c C\,(g) + d D\,(g)$$
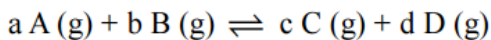
it is given by :

$$k_p = \frac{p^c_C \times p^d_D}{p^a_A \times p^b_B}$$

Relation between K_p and K_c

For a general gas phase reaction at equilibrium

$$a A\,(g) + b B\,(g) \rightleftharpoons c C\,(g) + d D\,(g)$$
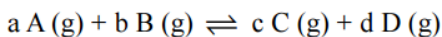
The pressure and concentration equilibrium constants K_p and K_c are

$$k_p = \frac{p_C^c \times p_D^d}{p_A^a \times p_B^b} \quad \text{and} \quad k_c = \frac{[C]^c [D]^d}{[A]^a [B]^b}$$

For a gaseous substance i, the ideal gas equation is

$$p_i V = n_i RT$$

where p_i and n_i are its partial pressure and amount in a gaseous mixture and V and T are its volume and temperature and R is the gas constant. The relation may be written as

$$p_i = \frac{n_i}{V} RT = c_i\, RT$$

Where c_i is the molar concentration or molarity of 'i' expressed in moles per litre. This relation can be used for replacing the partial pressure terms in the expression for K_p.

$$K_p = \frac{(c_C\, RT)^c\, (c_D RT)^d}{(c_A\, RT)^a\, (c_B\, RT)^b}$$

$$= \frac{c_C^c\, c_D^d}{c_A^a\, c_B^b} (RT)^{(c+d)-(a+b)}$$

Using the square bracket notation for molar concentration the relation can be written as

$$K_p = \frac{[C]^c [D]^d}{[A]^a [B]^b} (RT)^{(n_P - n_R)}$$

$$= K_c (RT)^{\Delta n_g}$$

where Δn_g is the change in the moles of gaseous substances in the reaction and is equal to the difference in the moles of gaseous products n_P and the moles of gaseous reactants, n_R. Δn_g may be zero positive or negative.

(i)   In the reaction

$$H_2\,(g) + I_2\,(g) \rightleftharpoons 2HI\,(g)$$
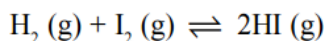
Here n_P = moles of the gaseous product is equal to 2

n_R = moles of gaseous reactant H_2 and I_2 is equal to 2 (as 1 + 1).

Hence $\Delta n_g = n_P - n_R = 2 - 2 = 0$

$\Delta n_g = 0$

    (ii)   In the reaction

        $N_2 (g) + 3H_2 (g) \rightleftharpoons 2NH_3 (g)$
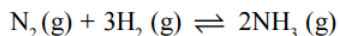
        $n_P = 2, n_R = 1 + 3 = 4$

        and $\Delta n_g = 2 - 4 = -2$

    (iii) In the reaction involving solids and gases

        $CaCO_3 (s) \rightleftharpoons CaO (s) + CO_2 (g)$
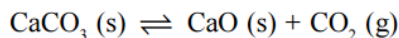
        $\Delta n_g = 1$

2.1.7 Factors Affecting Equilibrium State

Concentration, temperature and pressure effect chemical equilibrium. We explain them in detail one by one. However, we first give you Le Chatelier's principle of equilibrium; if one of the factors like temperature, pressure or concentration of system is changed then system react this change to conserve equilibrium.

Supposing a reaction has reached the equilibrium state and then some conditions like concentrations, temperature, pressure etc. are changed, would it be affecting the equilibrium state.

The state of equilibrium is in a dynamic balance between forward and backward reaction. This balance can be disturbed by changing concentration, temperature or pressure. If done so a certain net change occurs in the system. The direction of change can be predicted with the help of Le-Chatelier principle.

Le Chatelier Principles

It states that when a system in equilibrium is disturbed by a change in concentration, pressure or temperature, a 'net' change occurs in it in a direction that tends to decrease the disturbing factor. In 1884 the French chemist and engineer Henry-Louis Le Chatelier proposed one of the central concepts of chemical equilibria. Le

Chatelier's principle can be stated as follows: A change in one of the variables that describe a system at equilibrium produces a shift in the position of the equilibrium that counteracts the effect of this change.

Le Chatelier's principle describes what happens to a system when something momentarily takes it away from equilibrium. This section focuses on three ways in which we can change the conditions of a chemical reaction at equilibrium:

- Changing the concentration of one of the components of the reaction
- Changing the pressure on the system
- Changing the temperature at which the reaction is run.

Changes in Reactant or Product Concentrations

When a reactant or product is added to a system at equilibrium, the system will shift so as to remove some of the added material. If a reaction component is removed from an equilibrium mixture, the system will shift so as to replace some of it.

Why does this happen? Consider our generic equilibrium A $\rightleftharpoons$ B where the forward and reverse steps are elementary steps. Then

$k_f[A] = k_r[B]$

If some B is added, then

$k_f[A] > k_r[B]$

In the figures below, A is added 5 minutes into the reaction causing an upward spike in its concentration? As time goes by, [A] will decrease and [B] will increase (Figure 1) until the ratio of their rates returns to the original value (Figure 2). At that time, the equilibrium will be reestablished. In the new equilibrium, there will be more of both A and B than in the original equilibrium (Figure 1). But the real reason the equilibrium shifts is because the reaction rate increases. Adding more A means there are more reactant molecules and hence more collisions per unit time.

Since there are no more B molecules (at the instant the extra A is added) this rate cannot increase until the additional reactions of A molecules produce B products.
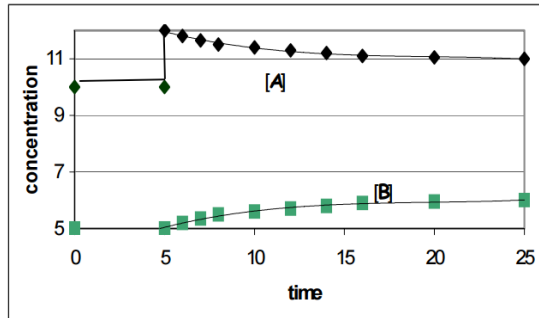
Figure 1
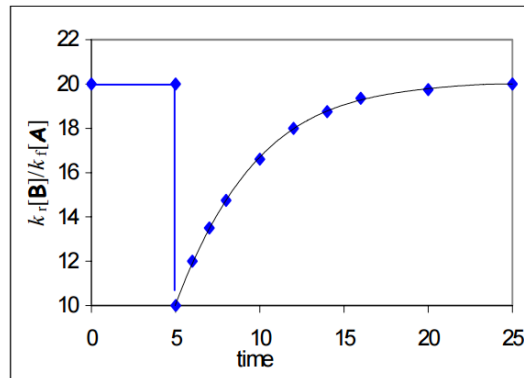
Figure 2

A somewhat more complicated example would be the equilibrium:

$$A_{(g)} + C_{(g)} \rightleftharpoons B_{(g)}$$
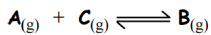
If some A is added, once again the forward rate increases for the same reasons described in the above paragraph. However, this time while there is more A and B in the new equilibrium, there is less C. This is because some of the existing C must be used to convert the added A to B. Since no extra C was added, the amount of it must decrease.

Change in Concentration

Consider the state of equilibrium for the formation of ammonia from nitrogen and hydrogen.

$$N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g), \quad \Delta H = -92.4 \text{ kJ/mol}$$
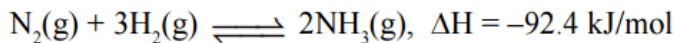
The concentration of nitrogen, hydrogen and ammonia become constant at the point of equilibrium. Now if any amount of reactants or ammonia is added or removed their concentration will change and the equilibrium will get disturbed.

(i)   Increase concentration of reactant: When the concentration of either nitrogen or hydrogen is increased; a net forward reaction will take place which consumes the added reactant.

(ii) Increase in the concentration of any product : If the concentration of product ammonia is increased, a net backward reaction would take place to utilize the added ammonia

Change in Pressure

Change in pressure affects equilibrium involving gaseous phase either in a homogeneous or heterogeneous system. Le Chatelier principle for systems involving gases can be studied as follows:

(i)   When the number of moles of products is more than the total number of moles of reactants as in the following system

$$N_2O_4(g) \rightleftharpoons 2NO_2(g)$$

Increase in total pressure keeping the temperature constant, will cause a decrease in volume. This means that the number of moles per unit volume will increase. A net change will take place in the equilibrium in the direction where the number of moles decrease i.e. backward direction.

(ii)   When the number of moles of products is less than reactants. As in the following case

$N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$
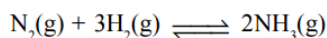
According to Le Chatelier's principle increase in total pressure will bring a net change to the equilibrium in the direction where the total number of moles is decreasing i.e. to the product side as $\Delta n_g = 2$. Decrease in total pressure will bring the net change to equilibrium in the direction where the total number of moles is increasing i.e. backward direction.

(iii)   When there is no change in the total number of moles of reactant and product as in the following state of equilibrium.

$H_2(g) + I_2(g) \rightleftharpoons 2HI$
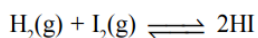
There is no net change in equilibrium state when pressure is changed.

Change of Temperature

According to Le Chatelier principle when the temperature is changed (increased or decreased) the equilibrium system reacts to nullify the change in heat content. However, the net change in equilibrium is directed by the exothermic or endothermic nature of reaction.

(i)   Exothermic equilibrium: For the following system of equilibrium of exothermic nature:

$N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g); \qquad \Delta H = -92.4 \text{ kJ/mol}$
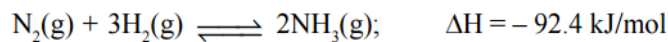
According to Le Chatelier principle increase in temperature brings a net change in the equilibrium state in that direction where this extra heat is consumed. The net change is in the backward direction and some ammonia will decompose producing nitrogen and hydrogen. Similarly if the temperature is decreased the equilibrium shifts to the forward direction.

(ii)   Endohermic equilibrium

$N_2(g) + O_2(g) \rightleftharpoons 2NO(g);$ $\Delta H = + 180.7 \text{ kJ/mol}^{-1}$
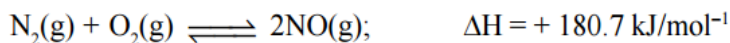
If the temperature is increased the added heat will be absorbed by the reactant and the net change takes place to the equilibrium in the forward direction. If the temperature in decreased it will bring a 'net' change to equilibrium in the backward direction i.e. direction in which it is exothermic.

2.2 EQUILIBRIUM IN PHYSICAL PROCESSES

Equilibrium represents the state of a process in which the properties like temperature, pressure, concentration of the system do not show any change with the passage of time.

If the opposing processes involve chemical changes i.e. the opposing processes are chemical reaction, the equilibrium is called chemical equilibrium. At equilibrium, the two opposing processes take place at equal rate. The mixture of reactants and products at equilibrium is called equilibrium mixture. A chemical reaction is represented as:

$aA + bB \rightleftharpoons xX + yY$

where A and B are the reactants and X and Y are the products. The double arrow between the reactants and products show that the reaction is taking place in both the directions simultaneously.

Chemical reactions may be classified into categories based on the extent of reaction before equilibrium is attained:

1)   Those reaction which proceed almost to completion i.e. concentration of the reactants left are negligible.

2)   Those reactions in which only a small amount of the reactants react and equilibrium is attained i.e. the amount of product formed is very small and the amount of the reactants left at equilibrium are quite large.

3) Those reactions which proceed to such an extent that the concentration of the reactants and products at equilibrium are compatible. The extent to which the reaction proceeds before equilibrium is attained depends upon the experimental conditions.

Just the way chemical reactions attain a state of equilibrium, there exists equilibrium in physical processes too. This refers to the equilibrium that develops between different states or phases of a substance such as solid, liquid and gas. Let's try and understand equilibrium in physical processes in more detail. Substances undergo different phase transformation processes such as –

solid $\rightleftharpoons$ liquid

liquid $\rightleftharpoons$ gas

solid $\rightleftharpoons$ gas

2.2.1 Solid-Liquid Equilibrium

What happens if you keep ice and water in a perfectly insulated manner, such as in a thermos flask at a temperature of 273K and atmospheric pressure? We see that the mass of ice and water do not change and that the temperature remains constant, indicating a state of equilibrium.

However, the equilibrium is not static because there is intense activity at the boundary between ice and water. Some ice molecules escape into liquid water and some molecules of water collide with ice and adhere to it. Despite this exchange, there is no change in mass of ice and water. This is because the rates of transfer of ice molecules to water and the reverse process are equal at 273K and atmospheric pressure.

It is evident that ice and water are in equilibrium only at a particular pressure and temperature. Therefore, for any pure substance at atmospheric pressure, the temperature at which the solid and liquid phases are at equilibrium is called the normal melting point or normal freezing point of the substance.

The system of ice and water is in dynamic equilibrium and we can conclude the following –

- Both opposing processes occur at the same time.
- The two processes occur at the same rate such that the amount of ice and water remain constant.

Liquid-vapour Equilibrium

Equilibrium Vapor Pressure

To understand this concept, let's perform the following experiment.

Experiment:

- Place a drying agent like anhydrous calcium chloride for a few hours in a transparent box with a U-tube containing mercury i.e. manometer. This will soak up all the moisture in the box.
- Remove the drying agent by tilting the box to one side and quickly place a petri dish containing water.

Observations:

- The mercury in the manometer rises slowly and then attains a constant value. This is because the pressure inside the manometer increases due to the addition of water molecules into the gaseous phase.
- Initially, there is no water vapour in the box. As the water in the petri dish evaporates, the volume of water in the petri dish decreases and the pressure in the box increases.
- The rate of increase in pressure decreases with time because of condensation of vapour into water.
- Finally, it reaches an equilibrium where there is no net evaporation or condensation.

Conclusion: Equilibrium is reached when –

rate of evaporation = rate of condensation

$H_2O(l) \rightleftharpoons H_2O \text{ (vap)}$

At equilibrium, the pressure that the water molecules exert at a given temperature remains constant and is called the equilibrium vapour pressure of water. The vapour pressure of water increases with temperature.

Boiling Point

At the same temperature, different liquids have different equilibrium vapour pressures. The liquid with a higher vapour pressure is more volatile and has a lower boiling point. Let's understand this concept with the following experiment.

Experiment:

- Expose three Petri dishes containing 1ml each of acetone, water and ethyl alcohol to the atmosphere.
- Repeat the experiment with different liquid volumes in a warmer room.

Observations:

- In all cases, the liquid eventually disappears.
- The time taken for complete evaporation of each liquid differs.

Conclusions:

- The time taken for complete evaporation of the liquid depends on – the nature of the liquid, the amount of liquid and the temperature.

- In an open system i.e. when the petri dish is kept open, the rate of evaporation remains constant but the molecules of the liquid are dispersed into a larger volume of the room. Consequently, the rate of evaporation is much higher than the rate of condensation from vapour to liquid. Therefore, open systems do not reach an equilibrium.

On the other hand, in a closed vessel or system, water and water vapour are in equilibrium at atmospheric pressure (1.013 bar) and 100°C.

For any pure liquid at one atmospheric pressure, the temperature at which the liquid and vapour are at equilibrium is called the normal boiling point of the liquid.

For water, the boiling point is 100°C at atmospheric pressure. The boiling point of liquids depends on atmospheric pressure i.e. the altitude of the place. Boiling point decreases at higher altitudes.

Solid-Vapor Equilibrium

Have you ever observed what happens to solid iodine placed in a closed jar? The jar gets filled up with violet coloured vapour and the colour intensity increases with time! The intensity of the colour becomes constant after a certain time i.e. equilibrium is reached. In this way, solid iodine sublimes to give iodine vapour while the vapour condenses to form solid iodine. The equilibrium in this process is given as –

$I_2(solid) \rightleftharpoons I_2(vapour)$
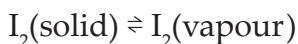
Other substances that show this kind of equilibrium are –

Camphor (solid) ⇌ Camphor (vapour)

NH_4Cl (solid) ⇌ NH_4Cl (vapour)

Equilibrium Involving Dissolution of Solid or Gases in Liquids

Solids in Liquids

What happens when you make a thick sugar solution by dissolving sugar at high temperature, then allow it to cool at room temperature. Yes, the sugar crystals separate out.

In this case, the thick sugar solution is a saturated solution because no more solute i.e. sugar can be dissolved in it at a given temperature. The concentration of solute in a saturated solution depends on the temperature. A dynamic equilibrium exists between the solute molecules in the solid state and in solution in a saturated solution.

Sugar (solution)⇌Sugar (solid)

Also, the rate of dissolution of sugar = rate of crystallization of sugar. Let's understand this further, using an example. What happens when you add radioactive sugar to a saturated solution of non-radioactive sugar? You will see radioactivity both in the solution and solid sugar after some time. Initially, there are no radioactive sugar molecules in the solution.

But, due to the dynamic nature of equilibrium, there is an exchange between the radioactive and non-radioactive sugar molecules from the two phases. Thus, the ratio of radioactive to non-radioactive sugar molecules in the solution increases till it reaches a constant value.

Gases in Liquids

Why do we see fizz and hear a sound when we open soda bottles? This happens because some of the CO_2 dissolved in it fizzes out

rapidly due to the difference in solubility of CO_2 at different pressures. The equilibrium between the CO_2 molecules in the gaseous state and those dissolved in liquid under pressure is given as –

$CO_2(gas) \rightleftharpoons CO_2(in\ solution)$

This equilibrium is governed by Henry's law. It states that the mass of a gas dissolved in a given mass of a solvent at any temperature is proportional to the pressure of the gas above the solvent. This amount decreases with increase in temperature.

The soda bottle is sealed under the pressure of the gas where its solubility in water is high. When the bottle is opened, some of the CO2 escapes trying to reach a new equilibrium or its partial pressure in the atmosphere. This is why soda water turns flat when the bottle is left open for too long.

Features of Equilibrium in Physical Processes:

Process	Conclusion
Solid $\rightleftharpoons$ Liquid $H_2O(s) \rightleftharpoons H_2O(l)$	Melting point is fixed at constant pressure.

Liquid $\rightleftharpoons$ Vapour $H_2O(l) \rightleftharpoons H_2O(g)$	pH_2O constant at given temperature.
Solute(s) $\rightleftharpoons$ Solute (solution) Sugar(s) $\rightleftharpoons$ Sugar (solution)	Concentration of solute in solution is constant at a given temperature.
Gas(g) $\rightleftharpoons$ Gas (aq) $CO_2(g) \rightleftharpoons CO_2(aq)$	[gas(aq)]/[gas(g)] is constant at a given temperature. $[CO_2(aq)]/[CO_2(g)]$ is constant at a given temperature.

General Characteristics of Equilibrium in Physical Processes

The following characteristics are common to the state of equilibrium in physical processes.

- At a given temperature, equilibrium in physical processes is achieved only in a closed system.
- The opposing processes occur at the same rate and there exists a dynamic but stable condition during equilibrium in physical processes.
- All properties of the system that are measurable remain constant.
- Equilibrium in physical processes is characterized by a constant value of one of its parameters at a given temperature.
- The extent to which a physical process has progressed before reaching equilibrium is indicated by the magnitude of the abovementioned parameter at any stage.

2.2.2 Types of Physical Equilibrium

Phase Equilibrium:

At 0°C, the number of water molecules becoming ice is equal to the water molecules as ice melting to form liquid water. Rate of freezing of water is equal to the rate of melting of ice. Thus, there is an equilibrium between solid ice and liquid water.

Ice (s) ⇌ Water (l)

The number of molecules of a liquid becoming vapour will be equal to the number of molecules condensing into liquid in a closed container. Rate of evaporation of liquid water is equal to the rate of condensation of water vapour. Liquid phase is in equilibrium with its own vapour phase.

Water (l) ⇌ Water (g)
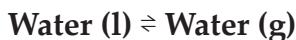
Solute-Solid Equilibrium:

When a solute in a saturated solution is in contact with undissolved solute, the number of molecules going (depositing) out of the solution is equal to the number of molecules entering (dissolving) from the solid into the liquid. So the solute in a solution is in equilibrium with the undissolved solid.

Solute (aq) ⇌ Solute (s)
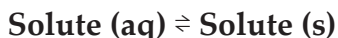
Gas-Liquid Equilibrium:

Gases that do not react with liquid may dissolve directly related to the pressure in the liquid. In a closed container, there is an equilibrium between the gas inside the liquid and the gas present above the liquid. In soft drinks, for example, carbon dioxide gas in the liquid is in equilibrium with the gas in the empty space of the container.

Gas (solution) ⇌ Gas (g)

Examples of Solid-Liquid Equilibria:

Consider ice and water in a perfectly insulated thermos flask at 0^0C in an open atmosphere. There will be no change in the level of water and quantity of ice, which implies that the rate of transfer of molecules from water to ice is equal to the rate of transfer of molecules from ice to water.

Hence, we can conclude that this system is in a steady state. This can be represented by the following equation:

H_2O (s)⇌ H_2O (l)
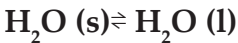
The rate of melting = Rate of freezing

2.3 EQUILIBRIUM MOLECULAR INTERACTIONS IN PURE GASES

The equilibrium molecular interactions in pure real gases are investigated based on the chemical thermodynamics principles. The parallels between clusters in real gases and chemical compounds in equilibrium media have been used to improve understanding of the real gas structure. A new approach to the equilibrium constants for the cluster fractions and new methods to compute them and their significant parameters from the experimental thermophysical data are developed. These methods have been applied to some real gases, such as Argon and Water vapors and gaseous Alkanes. It is shown that the four-particle clusters make a noticeable contribution in the thermophysical properties of the equilibrium Water vapor. It is shown also that the effective bond energy for dimers in Alkanes linearly grows with the number of carbon atoms in the molecule.

Modern technologies benefit from the utilization of extra pure and highly uniform materials and substances and precise knowledge of their thermophysical properties. For computer-aided design and control of technological processes, precise models of

thermophysical properties and equations of state for pure gases are very important because the real gases are widely used both as initial and intermediate materials in modern technologies. The models for pure gases can be used to build more complex models for mixtures of different gases. This work has a goal to show no obvious relations between equilibrium molecular interaction parameters in pure real gases and to find useful expressions to predict equilibrium properties of pure gases in changing external conditions. The work is based on a phenomenological approach that, nevertheless, provides a vision of the real gas structure on a microscopic level.

The following questions, arising in courses of molecular and chemical physics.(i)What are the equilibrium constants and bond energies for real gas clusters considered as the low bond energy analogues of chemical compounds?(ii)How to define the bond energies for clusters that in contrast to a wide separation of quantum levels of compounds have a dense spacing of multiple energetic levels?(iii)How to build the bridge between the virial equations of state based on variables that are sums of partial quantities for cluster fractions and the chemical equilibrium law, where arguments for concentrations of chemical compounds are the partial concentrations of reacting components?(iv)How to transform the Sackur-Tetrode equation for entropy of ideal atomic gases for real gases with account of the molecular interactions and internal movements?

One of ways to understand the properties of real gases is their comparison with chemical media, where dimerized compounds, such as Alkali metal or Nitrogen Dioxide dimers, may be formed in equilibrium conditions from their monomers. While the concentrations of chemical compounds and their equilibrium constants may be found from spectroscopic measurements, the thermal movement shadows and erodes the spectral lines of clusters. There are many works on molecular dynamics simulation of gaseous clusters, which do not build the bridge between the molecular interaction parameters and the thermophysical properties of real gases. This work develops the reverse methods

to estimate the bond parameters of clusters in pure real gases from thermophysical data.

There is a productive way to the clusters' equilibrium constants and molecular interaction parameters, based on the processing of known thermophysical data. But found so the cluster fractions' apparent equilibrium constants responsible for the Pressure-Density-Temperature relations (PDT equilibrium constants) are essentially different from the potential-energy (PE) based equilibrium constants in real gases, while this difference for chemical compounds may be negligible.

All conclusions of the developed here theory are verified with the utilization of precise experimental data from the NIST (the National Institute of Standards and Technology USA) databases. Now, to provide the computer-aided design and quality control for many technological processes, comprehensive databases of thermophysical properties for every used substance are accumulated and regularly updated. In modern science and technology, their creation goes on constantly with a steady growth of the data abundance and precision. Constant improvement of comprehensive and precise databases of the NIST is the best example of this kind of scientific activity. The systematization of experimental data, from one side, provides practical application, testing, and correction of the existing theoretical models and methods but, from the other side, opens possibilities for further development of the theoretical basis.

2.3.1 Clusters and Monomers in Real Gases

Real gas consists of basic particles (atoms or molecules), interacting through their interaction potential. The main part of gas consists of monomers that are the free moving basic particles performing elastic interactions with other particles without falling in bound states. Due to the attraction part of the interaction potential, some basic particles collect in temporary stable agglomerations with different numbers of particles, Figure 3. These agglomerations are named clusters that move in a gas-like free particles and sometimes

collide with other clusters or monomers. In spite of the plurality of clusters existing in a real gas, all equilibrium thermophysical properties of real gases are estimated for a fixed number of basic particles. Due to constantly changing interactions between basic particles in a real gas, it is difficult to define correctly the monomers and clusters from the microscopic point of view.
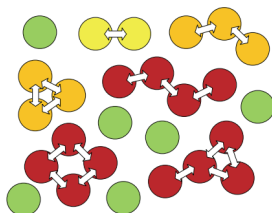
Figure 3. Schematic view of the real gas structure: the basic particles of the real gas (balls of all colors) in forms of monomers (green balls) and clusters (other colors). Yellow balls: dimer; orange balls: trimers with open chain and closed isomer configurations; red balls: tetramers (quatromers) with open chain, closed, and partly closed structures; white arrows: intermolecular bonds.

The thermophysical properties of the monomer and cluster fractions are found by processing the known thermophysical properties for all real gas. The results of this processing are not obvious; they reflect both elastic and no elastic interactions between basic particles. Figure 3 presents the schematic view of the real gas structure that is used here only for interpretation of the computer-aided analysis of experimental data, but not for microscopic computations of the real gas properties.

Figure 3 does not show all types of the 4-particle isomers and does not show larger clusters at all. Not to overload the picture, there is not shown the tetragonal configuration of the tetramer with 6 bonds between particles. But the figure clearly shows that different isomers at the same number of particles in a cluster can possess different numbers of bonds. The number of bonds characterizes the cluster's bond energy, and the isomer configuration determines the cluster's entropic factor, connected with the number of states in this configuration. Two of these factors are responsible

for prevailing of some types of isomer structures at a given temperature and for a change of the prevailing types with a change of temperature. It will be shown how interaction parameters found by phenomenological analysis of the experimental data point out on the prevailing types of isomers. The collisions in a gas can be divided on elastic and no elastic types. After an elastic collision, the numbers of basic particles in colliding clusters and their isomer configurations stay not changed. Figure 3 shows only the bonds between basic particles resulting from the no elastic collisions but does not show the elastic forces between particles that influence significantly the thermophysical properties of real gases. Clusters at any type of collisions, even at the no elastic, conserve their common momentum. Two colliding monomers perform only the elastic collision and after this collision fly apart again as monomers. To form the bound state of a dimer, the two monomers at their meeting should collide also with the third particle (monomer or cluster) to give off the excess of their common kinetic energy.

Generally speaking, the clusters are the products of the no elastic collisions, in which the cluster's bound state is formed by transferring the excess kinetic energy to some third particle. After the no elastic collision, the colliding particles fall into potential wells created by the attraction part of molecular interactions, Figure 4.
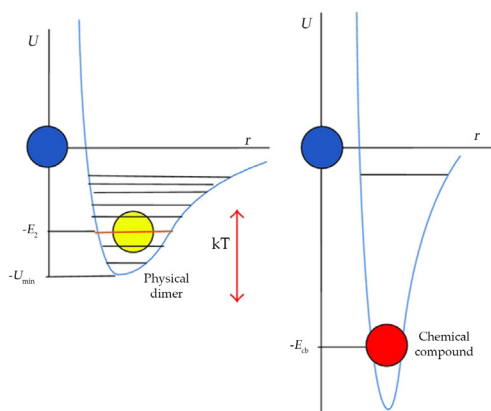
Figure 4. Comparison of a cluster with a chemical compound. Blue lines: molecular interaction potentials (r); narrow lines: energetic levels

densely spaced in the cluster and widely separated in the chemical compound. E_2: the cluster's effective bond energy, comparable with kT; E_{cb}: the chemical bond energy, greatly exceeding the kT value.

Figure 4 shows principal differences between molecular interactions in clusters and chemical compounds.(i)The potential well for particles in a cluster is not as deep as in a chemical compound that shortens the clusters' lifetimes by many orders of magnitude as compared to chemical compounds.(ii)The average width of the potential well in a cluster is much larger than in a chemical compound that lowers distances between energetic levels in clusters by many orders of magnitude as compared to chemical compounds.(iii)The average numbers of bound states in clusters are many orders of magnitude larger than the numbers of bound states in chemical compounds.(iv)The potential well around one gaseous particle may attract several particles, but the chemical potential well may disappear for the third particle after formation of the two-particle compound.

Particles in clusters and compounds do not occupy the position at the minimum of their potential. In gases, the thermal movement lifts the particles to higher levels, but, in compounds, their ground level stays over the potential minimum due to quantum laws. We should develop the method of finding the average energy of clusters in their bound states as an equivalent to the Schrodinger equation for the ground level of chemical compounds.

2.3.2 The Equilibrium Structure of Real Gases

The real gas consists of cluster fractions with a fixed number n of basic particles and with a definite isomer structure of bonds. The equilibrium structure of a real gas can be expressed through the cluster fractions' populations. The cluster fractions keep dynamic equilibrium of their populations through basic particles exchange. Unlike crystals, where structure means the configuration of the elementary cell, regularly repeated in space, the equilibrium structure of gases is disordered but statistically stable and determining properties of real gases. Due to differences

between the isomers' energy and entropy factors, some isomer configurations are prevailing at a given temperature. The change of prevailing types of isomers is responsible for the temperature dependences of the clusters' molecular interaction parameters that may be found from the equilibrium thermophysical properties of gases.

The bonds between basic particles in real gases are much weaker than the chemical bonds, how it is reflected by the Figure 4. Their values in most cases are comparable with the energy of thermal movement; therefore, the relaxation time to establish the cluster fractions populations is much lower than the typical times for experimental determination of thermophysical properties of gases. But this rule may be not valid for overcooled gases and for the sound speed or the complex dielectric permeability measurements.

In this work, the main variable for the computer-aided analysis of thermophysical properties is the molar density of the monomer fraction, D_m. The values of the monomer fraction density can be found from the isothermal pressure dependence of the total density D.

2.3.3 Monomer Fraction Density and the Chemical Potential

Due to a fast time to establish equilibrium in the cluster fractions populations, the Gibbs energy for a mole of basic particles (the chemical potential), G, does not depend on their aggregate state: the molar Gibbs energy of basic particles in each cluster fraction, G_n, and in the monomer fraction, G_m, is the same and is equal to the total Gibbs energy of the gas: $G_n=G_m=G$ [17, 18]. This statement is correct only for equilibrium systems. In a no equilibrium situation, the basic particles' Gibbs energies for different cluster fractions may split, like the Fermi quasilevels for electrons and holes in semiconductors.

For atomic ideal gases, the molar Gibbs energy $G=-RT\ln(V/V_q)$, where V is the molar volume of gas and V_q is the molar quantum

volume of atoms. In molecular gases, we should add the part of the molar Gibbs energy responsible for the internal molecular movements: rotations of molecules and vibrations of their atoms, $G0$.

The monomer fraction in a gas behaves as an ideal gas with a molar volume $Vm=1/Dm$; therefore, the molar Gibbs energy G of basic particles is [18]:

$$G = G_m = G_0 + RT \ \ln\left(D_m V_q\right),$$ (1)

where V_q is the molar quantum volume for basic particles that is proportional to the third degree of the thermal de Broglie wavelength:

$$V_q = \frac{h^3 N_A^4}{(2\pi \ MRT)^{3/2}},$$ (2)

where h is the Plank's constant, M is molecular weight of basic particles in kg/mol, N_A is Avogadro number, and R is universal gas constant. The compact form of (1) combines in V_q the entropy dependence on atomic weight, temperature, and Plank constant.

Equation (1) is the thermodynamics-based definition of the monomer fraction density. This equation reminds the well-known equation for fugacity $f:G=(T)+RT\ln(f)$. The monomer fraction density is more evident: it has a clear statistical and mechanical sense. Its introduction may help in a better understanding of properties of widely used variables: fugacity and activity.

In this theory, G_0, like (T) in the theory of fugacity, is supposed to be independent on the density and aggregate state of basic particles. All possible changes in the internal movements' part of the Gibbs energy are accounted for by the pressure dependence of D_m.

G corresponds to the thermodynamics equation:

$$\left(\frac{\partial G}{\partial P}\right)\Big|_T = V,$$ (3)

that together with (1) leads to the differential equation for D_m:

$$\left(\frac{\partial D_m}{\partial P}\right)\Bigg|_T = \frac{D_m}{RTD}.$$

$$(4)$$

The numeric integration of (4) should start from such a small pressure ϖ_1, at which the difference between the real density D_1 and the ideal density $D_{p1}=\varpi_1/RT$ is small. Then, the initial condition for numeric integration of (1) may be $D_{m1}=2D_{p1}-D_1$. Equation (4) is valid for all fluid phases: gaseous, liquid, and supercritical. Figure 5 shows the D_m pressure dependence in comparison with the total density dependence at subcritical and supercritical temperatures in Nitrogen.
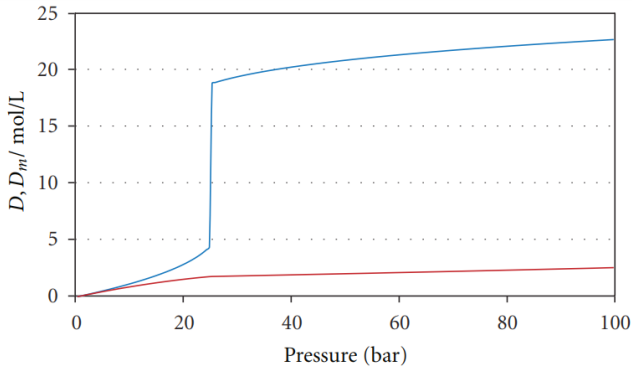
(a)
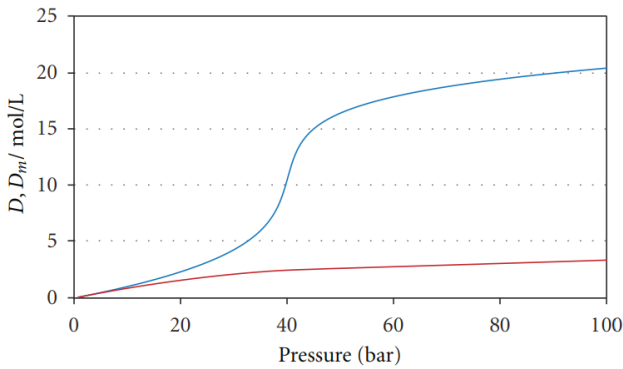
(b)

Figure 5. Density (blue lines) and monomer fraction density (red lines) versus pressure in gaseous, liquid, and supercritical Nitrogen at (a) subcritical temperature, $T=120$ K; (b) supercritical temperature, $T=130$ K.

The figure shows that the share of monomers in the total density falls with growing pressure, but still remains large both in liquid and supercritical media. The integration over the gas-liquid phase transition boundary does not put any problem, because the monomer fraction density does not change its value at the phase transition. When the monomer fraction density is found, it becomes possible to use it as an argument for other thermodynamics functions, such as the entropy or potential energy, and to use it as an argument in series expansions of different values for properties of real gases.

2.3.4 Generalization of the Sackur-Tetrode Equation for Real Gases

In spite of its applicability only to ideal atomic gases, it made a significant contribution both in thermal and quantum physics. The theory was confirmed experimentally by calculation of the entropy for dilute Neon gas taking into account the third law of thermodynamics. The measurements started from the near zero Kelvin temperature and included solid and liquid phases.

According to this theory, entropy of an ideal atomic gas with a molar volume V equals to

$$S = 2.5R + R\ln\left(\frac{V}{V_q}\right),$$

(5)

where V_q is the molar quantum volume given by (2).

Equation (5) with account of (1) and $G=H-TS$ can be transformed to

$$G - G_0 = RT \ \ln\left(D_m V_q\right) = H - H_0 - T(S - S_0),$$

(6)

where H_0 and S_0 are the enthalpy and entropy of the internal molecular movements: rotations and vibrations. Thus, we come to the Generalized Sackur-Tetrode equation [17–19]:

$$S = S_0 + \frac{H - H_0}{T} - R\ln\left(D_m V_q\right).$$

(7)

To test the developed here theory, we compared the experimental values for entropy of Water in gaseous and liquid phases with computed by (7) model values; D_m was found by integration of (4). All experimental data have been taken from the NIST database.

Figure 6 shows the pressure dependence of the Water entropy in gaseous and liquid phases at a temperature 350 K and the multiplied by factor 10^9 deviation of the model values from the experimental data. For H_0, the result of extrapolation to zero pressure of the experimental values for (P_i) was taken. For $S_0-R\ln(V_q)$ value, the averaged difference between experimental values for S and computed values for $(H-H_0)/T-R\ln(D_m)$ was taken. So this test estimates only the spread of computations. Nevertheless, the level of spread is nine orders of magnitude lower than the total entropy change that tells about correctness of the theory and about the high precision of computations. This high precision of computations results from remarkable features of the NIST database:(i)the experimental data have been interpolated with a very high precision;(ii)the data for different thermophysical properties have been mutually correlated.
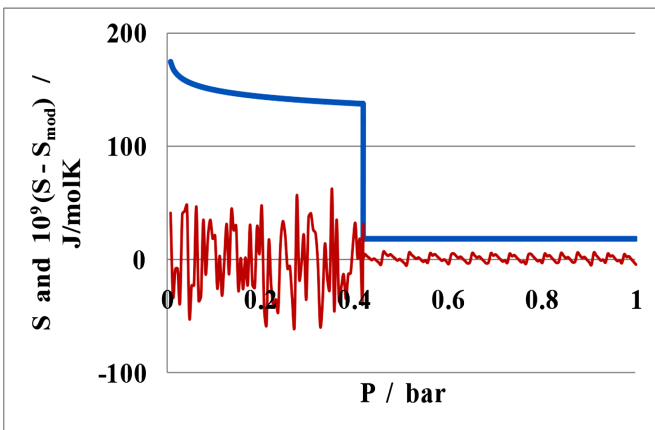
Figure 6. Confirmation of a high precision of the entropy computation by the generalized Sackur-Tetrode equation for Water in the gaseous

and liquid phases at temperature 350 K. Blue line: experimental and computed values for entropy; red line: multiplied by factor 10^9 deviations of the computed values from the experimental ones.

This test had been applied to a number of pure gases in different conditions, including gaseous, liquid, and supercritical phases, and the results confirm the high precision of computations of the $D_m(\odot,T)$ and $S(\odot,T)$ values. On this basis, the D_m values in a couple with the NIST tables permit to find the cluster fractions equilibrium constants and molecular interaction parameters for pure real gases with a good precision.

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3

EQUILIBRIA OF REACTIONS INVOLVING GASES

INTRODUCTION

A reaction is at equilibrium when the amounts of reactants or products no longer change. Chemical equilibrium is a dynamic process, meaning the rate of formation of products by the forward reaction is equal to the rate at which the products re-form reactants by the reverse reaction.

A chemical reaction is usually written in a way that suggests it proceeds in one direction, the direction in which we read, but all chemical reactions are reversible, and both the forward and reverse reaction occur to one degree or another depending on conditions. In a chemical equilibrium, the forward and reverse reactions occur at equal rates, and the concentrations of products and reactants remain constant. If we run a reaction in a closed system so that the products cannot escape, we often find the reaction does not

give a 100% yield of products. Instead, some reactants remain after the concentrations stop changing. At this point, when there is no further change in concentrations of reactants and products, we say the reaction is at equilibrium.

In beginning our study of the reactions of gases, you will assume a knowledge of the physical properties of gases as described by the Ideal Gas Law and an understanding of these properties as given by the postulates and conclusions of the Kinetic Molecular Theory. You have developed a dynamic model of phase equilibrium in terms of competing rates. You will also assume an understanding of the bonding, structure, and properties of individual molecules.

3.1 CONCEPT OF CHEMICAL REACTION EQUILIBRIA

Reaction chemistry forms the essence of chemical processes. The very distinctiveness of the chemical industry lies in its quest for transforming less useful substances to those which are useful to modern life. The perception of old art of 'alchemy' bordered on the magical; perhaps in today's world its role in the form of modern chemistry is in no sense any less. Almost everything that is of use to humans is manufactured through the route of chemical synthesis. Such reactive processes need to be characterized in terms of the maximum possible yield of the desired product at any given conditions, starting from the raw materials (i.e., reactants). The theory of chemical reactions indicates that rates of reactions are generally enhanced by increase of temperature. However, experience shows that the maximum quantum of conversion of reactants to products does not increase monotonically. Indeed for a vast majority the maximum conversion reaches a maximum with respect to reaction temperature and subsequently diminishes.

The reason behind this phenomenon lies in the molecular processes that occur during a reaction. Consider a typical reaction of the following form occurring in gas phase: $A(g) + B(g) \rightarrow C(g) + D(g)$. The reaction typically begins with the reactants being brought together

in a reactor. In the initial phases, molecules of A and B collide and form reactive complexes, which are eventually converted to the products C and D by means of molecular rearrangement. Clearly then the early phase of the reaction process is dominated by the presence and depletion of A and B. However, as the process continues, the fraction of C and D in the reactor increases, which in turn enhances the likelihood of these molecules colliding with each other and undergoing transformation into A and B. Thus, while initially the forward reaction dominates, in time the backward reaction becomes increasingly significant, which eventually results in the two rates becoming equal. After this point is reached the concentrations of each species in the reactor becomes fixed and displays no further propensity to change unless propelled by any externally imposed "disturbance" (say, by provision of heat). Under such a condition the reaction is said to be in a state of equilibrium. The magnitude of all measurable macroscopic variables (T, P and composition) characterizing the reaction remains constant. Clearly under the equilibrium state the percentage conversion of the reactants to products must be the maximum possible at the given temperature and pressure. Or else the reaction would progress further until the state of equilibrium is achieved. The principles of chemical reaction thermodynamics are aimed at the prediction of this equilibrium conversion.

The reason why the equilibrium conversion itself changes with variation of temperature may be appreciated easily. The rates of the forward and backward reactions both depend on temperature; however, an increase in temperature will, in general, have different impacts on the rates of each. Hence the extent of conversion at which they become identical will vary with temperature; this prompts a change in the equilibrium conversion. Reactions for which the conversion is 100% or nearly so are termed irreversible, while for those which never attains complete conversion are essentially reversible in nature. The fact that a maxima may occur in the conversion behavior (figure) suggests that for such reactions while the forward reaction rates dominate at lower temperatures, while at higher temperatures the backward reaction may be predominant. This is shown schematically in figure.
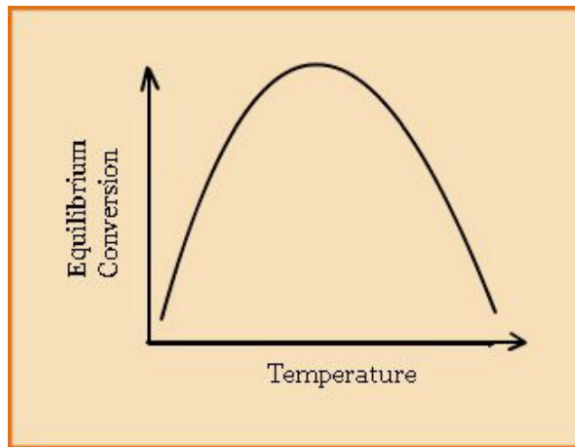
Schematic of Equilibrium Reaction vs. Temperature

The choice of the reaction conditions thus depends on the maximum (or equilibrium) conversion possible. Further, the knowledge of equilibrium conversions is essential to intensification of a process. Finally, it also sets the limit that can never be crossed in practice regardless of the process strategies. This forms a primary input to the determination of the economic viability of a manufacturing process. If reaction equilibria considerations suggest that the maximum possible conversion over practical ranges of temperature is lower than that required for commercial feasibility no further effort is useful in its further development. On the other hand if the absolute maximum conversion is high then the question of optimizing the process conditions attain significance. Exploration of the best strategy for conducting the reaction (in terms of temperature, pressure, rate enhancement by use of catalytic aids, etc.) then offers a critical challenge.

A mixture of reactants and products is found at equilibrium.

For example, when we place a sample of dinitrogen tetroxide (N_2O_4, a colorless gas) in a glass tube, it forms nitrogen dioxide (NO_2, a brown gas) by the reaction

$N_2O_{4(g)} \rightleftharpoons 2NO_2(g)$
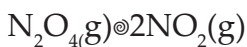
The color becomes darker as N_2O_4 is converted to NO_2. When the system reaches equilibrium, both N_2O_4 and NO_2 are present (Below Figure).
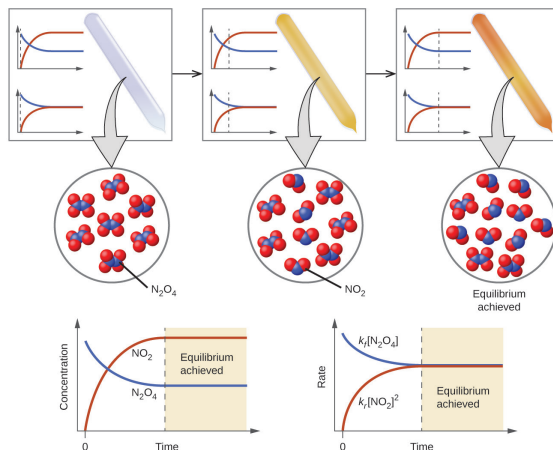
A mixture of NO_2 and N_2O_4 moves toward equilibrium. Colorless N_2O_4 reacts to form brown NO_2. As the reaction proceeds toward equilibrium, the color of the mixture darkens due to the increasing concentration of NO_2.

The formation of NO_2 from N_2O_4 is a reversible reaction, which is identified by the equilibrium arrow (). All reactions are reversible, but many reactions, for all practical purposes, proceed in one direction until the reactants are exhausted and will reverse only under certain conditions. Such reactions are often depicted with a one-way arrow from reactants to products. Many other reactions, such as the formation of NO_2 from N_2O_4, are reversible under more easily obtainable conditions and, therefore, are named as such. In a reversible reaction, the reactants can combine to form products and the products can react to form the reactants. Thus, not only can N_2O_4 decompose to form NO_2, but the NO_2 produced can react to form N_2O_4. As soon as the forward reaction produces any NO_2, the reverse reaction begins and NO_2 starts to react to form N_2O_4. At equilibrium, the concentrations of N_2O_4 and NO_2 no longer change because the rate of formation of NO_2 is exactly equal to the rate of consumption of NO_2, and the rate of formation of N_2O_4 is exactly equal to the rate of consumption of N_2O_4. *Chemical equilibrium is*

a dynamic process: As with the swimmers and the sunbathers, the numbers of each remain constant.

In a chemical equilibrium, the forward and reverse reactions do not stop, rather they continue to occur at the same rate, leading to constant concentrations of the reactants and the products. Plots showing how the reaction rates and concentrations change with respect to time are shown in Figure.

We can detect a state of equilibrium because the concentrations of reactants and products do not appear to change. However, it is important that we verify that the absence of change is due to equilibrium and not to a reaction rate that is so slow that changes in concentration are difficult to detect.

We use a double arrow when writing an equation for a reversible reaction. Such a reaction may or may not be at equilibrium. For example, Figure shows the reaction:

$N_2O_4(g) \rightleftharpoons 2NO_2(g)$
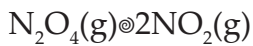
When we wish to speak about one particular component of a reversible reaction, we use a single arrow. For example, in the equilibrium shown in Figure, the rate of the forward reaction

$2NO_2(g) \rightarrow N_2O_4(g)$

is equal to the rate of the backward reaction

$N_2O_4(g) \rightarrow 2NO_2(g)$

3.1.1 The Stoichiometry of Chemical Reaction

Stoichiometry is the calculation of reactants and products in chemical reactions in chemistry. Stoichiometry is founded on the law of conservation of mass where the total mass of the reactants equals the total mass of the products, leading to the insight that the relations among quantities of reactants and products typically form a ratio of positive integers. This means that if the amounts of the separate reactants are known, then the amount of the product can be calculated. Conversely, if one reactant has a known quantity

and the quantity of the products can be empirically determined, then the amount of the other reactants can also be calculated.

$$CH_4 \quad + \quad 2O_2 \quad \longrightarrow \quad CO_2 \quad + \quad 2H_2O$$
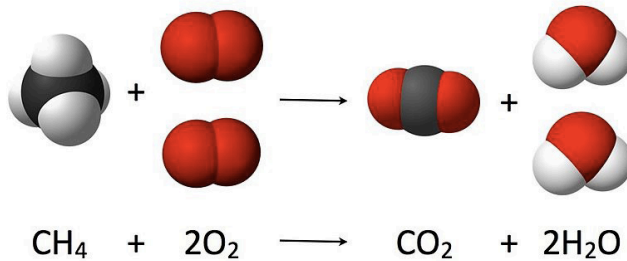
A stoichiometric diagram of the combustion reaction of methane

This is illustrated in the image here, where the balanced equation is:

$CH_4 + 2O_2 -> CO_2 + 2H_2O$
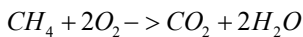
Here, one molecule of methane reacts with two molecules of oxygen gas to yield one molecule of carbon dioxide and two molecules of water. This particular chemical equation is an example of complete combustion. Stoichiometry measures these quantitative relationships, and is used to determine the amount of products and reactants that are produced or needed in a given reaction. Describing the quantitative relationships among substances as they participate in chemical reactions is known as reaction stoichiometry. In the example above, reaction stoichiometry measures the relationship between the quantities of methane and oxygen that react to form carbon dioxide and water.

Because of the well-known relationship of moles to atomic weights, the ratios that are arrived at by stoichiometry can be used to determine quantities by weight in a reaction described by a balanced equation. This is called composition stoichiometry.

Gas stoichiometry deals with reactions involving gases, where the gases are at a known temperature, pressure, and volume and can be assumed to be ideal gases. For gases, the volume ratio is ideally the same by the ideal gas law, but the mass ratio of a single reaction has to be calculated from the molecular masses of the reactants

and products. In practice, due to the existence of isotopes, molar masses are used instead when calculating the mass ratio.

3.1.2 Definition of Stoichiometry

A stoichiometric amount or stoichiometric ratio of a reagent is the optimum amount or ratio where, assuming that the reaction proceeds to completion:

- All of the reagent is consumed
- There is no deficiency of the reagent
- There is no excess of the reagent.

Stoichiometry rests upon the very basic laws that help to understand it better, i.e., law of conservation of mass, the law of definite proportions (i.e., the law of constant composition), the law of multiple proportions and the law of reciprocal proportions. In general, chemical reactions combine in definite ratios of chemicals. Since chemical reactions can neither create nor destroy matter, nor transmute one element into another, the amount of each element must be the same throughout the overall reaction. For example, the number of atoms of a given element X on the reactant side must equal the number of atoms of that element on the product side, whether or not all of those atoms are actually involved in a reaction.

Chemical reactions, as macroscopic unit operations, consist of simply a very large number of elementary reactions, where a single molecule reacts with another molecule. As the reacting molecules (or moieties) consist of a definite set of atoms in an integer ratio, the ratio between reactants in a complete reaction is also in integer ratio. A reaction may consume more than one molecule, and the stoichiometric number counts this number, defined as positive for products (added) and negative for reactants (removed).

Different elements have a different atomic mass, and as collections of single atoms, molecules have a definite molar mass, measured with the unit mole (6.02×10^{23} individual molecules, Avogadro's constant). By definition, carbon-12 has a molar mass of 12 g/

mol. Thus, to calculate the stoichiometry by mass, the number of molecules required for each reactant is expressed in moles and multiplied by the molar mass of each to give the mass of each reactant per mole of reaction. The mass ratios can be calculated by dividing each by the total in the whole reaction.

Elements in their natural state are mixtures of isotopes of differing mass, thus atomic masses and thus molar masses are not exactly integers. For instance, instead of an exact 14:3 proportion, 17.04 kg of ammonia consists of 14.01 kg of nitrogen and 3 × 1.01 kg of hydrogen, because natural nitrogen includes a small amount of nitrogen-15, and natural hydrogen includes hydrogen-2 (deuterium). A stoichiometric reactant is a reactant that is consumed in a reaction, as opposed to a catalytic reactant, which is not consumed in the overall reaction because it reacts in one step and is regenerated in another step.

3.2 EQUILIBRIUM CONSTANT EXPRESSIONS INVOLVING GASES

When calculating equilibrium constants of solutions, the concentrations of each component in the solution are used to calculate K, which is the equilibrium constant. When working with concentrations, the equilibrium constant is designated as K_c. However, when working with a mixture of gases, concentrations are not used, but instead the gases' partial pressures. By first calculating the equilibrium constant in terms of pressure, designated K_p, K_c can then be calculated by using a simple formula.

How do you begin writing the equilibrium constant for a mixture of gases?

To explain this clearly, let us look at a simple example, the reaction: $2NH_3(g) \longleftrightarrow N_2(g) + 3H_2(g)$.
   1)   First, each component of the mixture in the equilibrium constant is written in terms of their activities. The

activity of each component is the partial pressure of each component divided by their partial pressure "reference-states." Writing the equilibrium constant in terms of partial pressures requires it to be referred to as K_p.

$$K = ((a_{N2})(a_{H2})^3 / (a_{NH3})^2) \text{ eq}$$
$$a_{N2} = P_{N2}/P^o$$
$$a_{H2} = P_{H2}/P^o$$
$$a_{NH3} = P_{NH3}/P^o$$

2)   Next, take the activities, showed in terms of pressure, of the products raised to the power of their coefficients, and divided by the activities of the reactants. The activities of the reactants are also raised to the power of their coefficients. To simplify the expression, the partial pressure "reference-state" of each component can be divided out.

$$K_p = ((P_{N2}/P^o)(P_{H2}/P^o)^3 / (P_{NH3}/P^o)^2) \text{ eq}$$
$$P^o ((P_{N2})(P_{H2})^3/(P_{NH3})^2) \text{ eq}$$

3)   To relate the pressures of this expression to concentrations, the ideal gas law is used. The ideal gas law is **PV=nRT**, where P is the pressure, V is the volume, n is the number of moles of the substnace, R is the constant 0.08206 L atm/K mol, and T is the temperature in Kelvins. By inverting the ideal gas law equation and solving for the concentration, n/V, or moles per liter, the concentrations of the gases are expressed by their partial pressures divided by RT.

$$\{N2\} = n/v = P_{N2}/RT$$
$$\{H2\} = n/V = P_{H2}/RT$$
$$\{NH3\} = n/V = P_{NH3}/RT$$

4)   Now, since we have solved for the concentrations of each gas component, we write them in terms of concentration activities. This is the concentrations of each component divided by the concentration reference state.

$$a_{N2} = \{N2\}/c^o = (P_{N2}/RT)/c^o$$

$a_{H2} = \{H2\}/c^{o} = (P_{H2}/RT)/c^{o}$

$a_{NH3} = \{NH3\}/c^{o} = (P_{NH3}/RT)/c^{o}$

The last and final step is entering these activities into the expression we earlier derived in step 2 and dividing out RT.

$K_{p} = P^{o}((\{N2\}RT)(\{H2\}RT)^{3}/(\{NH3\}RT)^{2})$ eq

$K_{p} = (P^{o}/RT)(\{N2\}\{H2\}^{3}/\{NH3\}^{2})$ eq

This gives the equilibrium constant expression for a mixture of gases (K_{p}).

K_{p} and K_{c} can be related by setting the two equations equal to each other and divided out the reference states. This gives the simple formula:

$K_{p} = K_{c}(RT)^{\text{difference in coefficients of gas components only}}$

Please Note

P^{o} is the partial pressure reference-state and it equals about 1 atm

c^{o} is the concentration reference-state and it equals about 1mol/L

eq is the term used to indicate that the components are at equilibrium

$\{x\}$ is the concentration of the component x where x is a variable used to indicate a substance

Equilibrium constant expression do not include those components in a reaction that are pure solids or liquids

3.3 THE PROPERTIES OF GASES

Gases are the least dense and most mobile of the three phases of matter. Particles of matter in the gas phase are spaced far apart from one another and move rapidly and collide with each other often. Gases occupy much greater space than the same amount

of liquid or solid. This is because the gas particles are spaced apart from one another and are therefore compressible. Solid or liquid particles are spaced much closer and cannot be compressed further. Although gases are simple, both to describe and in terms of their internal structure, they are of immense importance. We spend our whole lives surrounded by gas in the form of air and the local variation in its properties is what we call the 'weather'. To understand the atmospheres of this and other planets we need to understand gases. As we breathe, we pump gas in and out of our lungs, where it changes composition and temperature. Many industrial processes involve gases, and both the outcome of the reaction and the design of the reaction vessels depend on a knowledge of their properties.

3.3.1 Equations of State

You can specify the state of any sample of substance by giving the values of the following properties:

V, the volume of the sample

p, the pressure of the sample

T, the temperature of the sample

n, the amount of substance in the sample

However, an astonishing experimental fact is that these four quantities are not independent of one another. For instance, we cannot arbitrarily choose to have a sample of 0.555 mol H_2O in a volume of 100 cm^3 at 100 kPa and 500 K: it is found experimentally that that state simply does not exist. If we select the amount, the volume, and the temperature, then we find that we have to accept a particular pressure (close to 23 MPa). The same is true of all substances, but the pressure in general will be different for each one. This experimental generalization is summarized by saying the substance obeys an equation of state, an equation of the form

$$p = f(n, V, T) \qquad\qquad\qquad (1)$$

This expression tells us that the pressure is some function of amount, volume, and temperature and that if we know those three variables, then the pressure can have only one value.

The equations of state of most substances are not known, so in general we cannot write down an explicit expression for the pressure in terms of the other variables. However, certain equations of state are known. In particular, the equation of state of a low-pressure gas is known, and proves to be very simple and very useful. This equation is used to describe the behavior of gases taking part in reactions, the behavior of the atmosphere, as a starting point for problems in chemical engineering, and even in the description of the structures of stars.

3.3.2 The Perfect Gas Equation of State

The equation of state of a low-pressure gas was among the first results to be established in physical chemistry. The original experiments were carried out by Robert Boyle in the seventeenth century and there was a resurgence in interest later in the century when people began to fly in balloons. This technological progress demanded more knowledge about the response of gases to changes of pressure and temperature and, like technological advances in other fields today, that interest stimulated a lot of experiments.

The experiments of Boyle and his successors led to the formulation of the following perfect gas equation of state:

$$pV = nRT \qquad\qquad\qquad (2)$$

In this equation (which has the form of equation 1 when we rearrange it into $p = nRT/V$), the gas constant, R, is an experimentally determined quantity that turns out to have the same value for all gases. It may be determined by evaluating $R = pV/nRT$ as the pressure is allowed to approach zero or by measuring the speed of sound (which depends on R). Values of R in different units are given in Table 1.

Table 1: The gas constant in various units

$R =$	8.314 47	$J\ K^{-1}\ mol^{-1}$
	8.314 47	$dm^3\ kPa\ K^{-1}\ mol^{-1}$
	$8.205\ 74 \times 10^{-2}$	$dm^3\ atm\ K^{-1}\ mol^{-1}$
	62.364	$dm^3\ Torr\ K^{-1}\ mol^{-1}$
	1.987 21	$cal\ K^{-1}\ mol^{-1}$

$1\ dm^3 = 10^{-3}\ m^3$
The text's website contains links to online databases of
properties of gases.

The perfect gas equation of state—more briefly, the 'perfect gas law'—is so-called because it is an idealization of the equations of state that gases actually obey. Specifically, it is found that all gases obey the equation ever more closely as the pressure is reduced towards zero. That is, equation 2 is an example of a limiting law, a law that becomes increasingly valid as the pressure is reduced and is obeyed exactly in the limit of zero pressure.

A hypothetical substance that obeys equation 2 at all pressures is called a perfect gas. From what has just been said, an actual gas, which is termed a real gas, behaves more and more like a perfect gas as its pressure is reduced towards zero. In practice, normal atmospheric pressure at sea level ($p \approx 100$ kPa) is already low enough for most real gases to behave almost perfectly, and unless stated otherwise we shall always assume in this text that the gases we encounter behave like a perfect gas. The reason why a real gas behaves differently from a perfect gas can be traced to the attractions and repulsions that exist between actual molecules and that are absent in a perfect gas.

The perfect gas law summarizes three sets of experimental observations. One is Boyle's law:

At constant temperature, the pressure of a fixed amount of gas is inversely proportional to its volume.

Mathematically:

Boyle's law: at constant temperature, $p \propto \dfrac{1}{V}$

We can easily verify that equation 2 is consistent with Boyle's law: by treating n and T as constants, the perfect gas law becomes $pV =$ constant, and hence $p \propto 1/V$. Boyle's law implies that if we compress (reduce the volume of) a fixed amount of gas at constant temperature into half its original volume, then its pressure will double. Figure 1 shows the graph obtained by plotting experimental values of p against V for a fixed amount of gas at different temperatures and the curves predicted by Boyle's law. Each curve is called an isotherm because it depicts the variation of a property (the pressure) at a single constant temperature. It is hard, from this graph, to judge how well Boyle's law is obeyed. However, when we plot p against 1/V, we get straight lines, just as we would expect from Boyle's law (Figure 2).
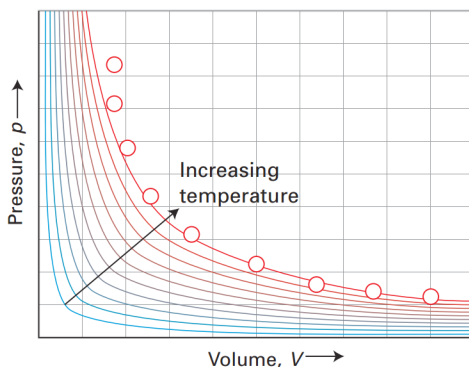
Figure 1: The volume of a gas decreases as the pressure on it is increased. For a sample that obeys Boyle's law and that is kept at constant temperature, the graph showing the dependence is a hyperbola. Each curve corresponds to a single temperature, and hence is an isotherm. The isotherms are hyperbolas, graphs of xy = constant, or y = constant/x.
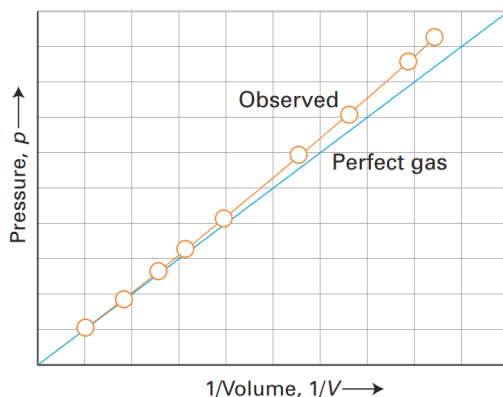
Figure 2: A good test of Boyle's law is to plot the pressure against 1/V (at constant temperature), when a straight line should be obtained. This diagram shows that the observed pressures (the blue line) approach a straight line as the volume is increased and the pressure reduced. A perfect gas would follow the straight line at all pressures; real gases obey Boyle's law in the limit of low pressures.

The second experimental observation summarized by equation 2 is Charles's law:

At constant pressure, the volume of a fixed amount of gas varies linearly with the temperature.

Mathematically:

Charles's law: at constant pressure, $V = A + B\theta$

where θ (theta) is the temperature on the Celsius scale and A and B are constants that depend on the amount of gas and the pressure. Figure 3 shows typical plots of volume against temperature for a series of samples of gases at different pressures and confirms that (at low pressures, and for temperatures that are not too low) the volume varies linearly with the Celsius temperature. We also see that all the volumes extrapolate to zero as θ approaches the same very low temperature ($-273.15°C$, in fact), regardless of the identity of the gas. Because a volume cannot be negative, this common temperature must represent the absolute zero of temperature, a temperature below which it is impossible to cool an object. Indeed,

the 'thermodynamic' scale ascribes the value T = 0 to this absolute zero of temperature. In terms of the thermodynamic temperature, therefore, Charles's law takes the simpler form

Charles's law: at constant pressure, $V \propto T$

It follows that doubling the temperature (such as from 300 K to 600 K, corresponding to an increase from 27°C to 327°C) doubles the volume, provided the pressure remains the same. Now we can see that equation 2 is consistent with Charles's law. First, we rearrange it into $V = nRT/p$, and then note that when the amount n and the pressure p are both constant, we can write $V \propto T$, as required.
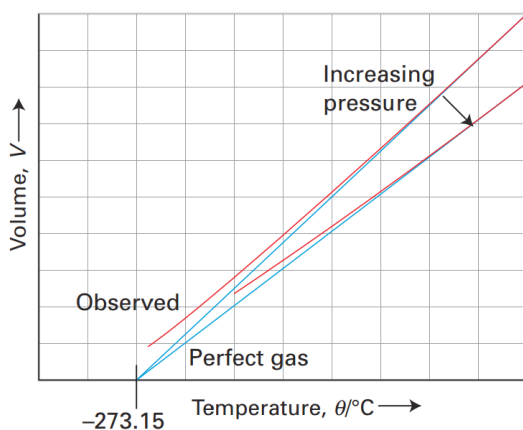
Figure 3: This diagram illustrates the content and implications of Charles's law, which asserts that the volume occupied by a gas (at constant pressure) varies linearly with the temperature. When plotted against Celsius temperatures (as here), all gases give straight lines that extrapolate to V = 0 at −273.15°C. This extrapolation suggests that −273.15°C is the lowest attainable temperature.

The third feature of gases summarized by equation 2 is Avogadro's principle:

At a given temperature and pressure, equal volumes of gas contain the same numbers of molecules.

That is, 1.00 dm³ of oxygen at 100 kPa and 300 K contains the same number of molecules as 1.00 dm³ of carbon dioxide, or any

other gas, at the same temperature and pressure. The principle implies that if we double the number of molecules, but keep the temperature and pressure constant, then the volume of the sample will double. We can therefore write:

Avogadro's principle: at constant temperature and pressure, $V \propto n$

This result follows easily from equation 2 if we treat p and T as constants. Avogadro's suggestion is a principle rather than a law (a direct summary of experience), because it is based on a model of a gas, in this case as a collection of molecules. Even though there is no longer any doubt that molecules exist, this relation remains a principle rather than a law.

The molar volume, V_m, of any substance (not just a gas) is the volume it occupies per mole of molecules. It is calculated by dividing the volume of the sample by the amount of molecules it contains:

$$V_m = \frac{V \quad \boxed{\text{Volume of sample}}}{n \quad \boxed{\text{Amount of substance in sample}}}$$

(3)

With volume in cubic decimeters and amount in moles, the units of molar volume are cubic decimeters per mole ($dm^3\ mol^{-1}$). The data in Table 2 show that this conclusion is approximately true for most gases under normal conditions (normal atmospheric pressure of about 100 kPa and room temperature).

Table 2: The molar volumes of gases at standard ambient temperature and pressure

Gas	$V_m/(dm^3\ mol^{-1})$
Perfect gas	24.7896*
Ammonia	24.8
Argon	24.4
Carbon dioxide	24.6
Nitrogen	24.8
Oxygen	24.8
Hydrogen	24.8
Helium	24.8

3.3.3 Using the Perfect Gas Law

Here we review three elementary applications of the perfect gas equation of state. The first is the prediction of the pressure of a gas given its temperature, its chemical amount, and the volume it occupies. The second is the prediction of the change in pressure arising from changes in the conditions. The third is the calculation of the molar volume of a perfect gas under any conditions. Calculations like these underlie more advanced considerations, including the way that meteorologists understand the changes in the atmosphere that we call the weather.

In some cases, we are given the pressure under one set of conditions and are asked to predict the pressure of the same sample under a different set of conditions. We use the perfect gas law as follows. Suppose the initial pressure is p_1, the initial temperature is T_1, and the initial volume is V_1. Then by dividing both sides of equation 2 by the temperature we can write

$$\frac{p_1 V_1}{T_1} = nR$$

Suppose now that the conditions are changed to T_2 and V_2, and the pressure changes to p_2 as a result. Then under the new conditions equation 2 tells us that

$$\frac{p_2 V_2}{T_2} = nR$$

The nR on the right of these two equations is the same in each case, because R is a constant and the amount of gas molecules has not changed. It follows that we can combine the two equations into a single equation:

$$\frac{p_1 V_1}{T_1} = \frac{p_2 V_2}{T_2} \tag{4}$$

This expression is known as the combined gas equation. We can rearrange it to calculate any one unknown (such as p_2, for instance) in terms of the other variables.

Finally, we see how to use the perfect gas law to calculate the molar volume of a perfect gas at any temperature and pressure. Equation 3 expresses the molar volume in terms of the volume of a sample; equation 2 in the form $V = nRT/p$ expresses the volume in terms of the pressure. When we combine the two, we get

$$V_m = \frac{V}{n} = \frac{nRT/p}{n} = \frac{RT}{p}$$

(5)

This expression lets us calculate the molar volume of any gas (provided it is behaving perfectly) from its pressure and its temperature. It also shows that, for a given temperature and pressure, provided they are behaving perfectly, all gases have the same molar volume.

Chemists have found it convenient to report much of their data at a particular set of 'standard' conditions. By standard ambient temperature and pressure (SATP) they mean a temperature of 25°C (more precisely, 298.15 K) and a pressure of exactly 1 bar (100 kPa). The standard pressure is denoted p, so p = 1 bar exactly. The molar volume of a perfect gas at SATP is 24.79 dm³ mol⁻¹, as can be verified by substituting the values of the temperature and pressure into equation 5. This value implies that at SATP, 1 mol of perfect gas molecules occupies about 25 dm³ (a cube of about 30 cm on a side). An earlier set of standard conditions, which is still encountered, is standard temperature and pressure (STP), namely 0°C and 1 atm. The molar volume of a perfect gas at STP is 22.41 dm³ mol⁻¹.

3.3.4 Mixtures of Gases: Partial Pressures

We are often concerned with mixtures of gases, such as when we are considering the properties of the atmosphere in meteorology, the composition of exhaled air in medicine, or the mixtures of hydrogen and nitrogen used in the industrial synthesis of ammonia. We need to be able to assess the contribution that each

component of a gaseous mixture makes to the total pressure.

In the early nineteenth century, John Dalton carried out a series of experiments that led him to formulate what has become known as Dalton's law:

The pressure exerted by a mixture of perfect gases is the sum of the pressures that each gas would exert if it were alone in the container at the same temperature:

$$p = p_A + p_B + ... \tag{6}$$

p_J is the pressure that the gas J would exert if it were alone in the container at the same temperature. Dalton's law is strictly valid only for mixtures of perfect gases (or for real gases at such low pressures that they are behaving perfectly), but it can be treated as valid under most conditions we encounter.

For any type of gas (real or perfect) in a mixture, the partial pressure, p_J, of the gas J is defined as

$$p_J = x_J p \tag{7}$$

where x_J is the mole fraction of the gas J in the mixture. The mole fraction of J is the amount of J molecules expressed as a fraction of the total amount of molecules in the mixture. In a mixture that consists of n_A A molecules, n_B B molecules, and so on (where the n_J are amounts in moles), the mole fraction of J (where J = A, B,...) is

$$x_J = \frac{n_J}{n} \quad \underset{\text{total amount of molecules in the mixture}}{\overset{\text{amount of J molecules in the mixture}}{}} \tag{8a}$$

where $n = n_A + n_B + ...$ Mole fractions are unitless because the unit mole in numerator and denominator cancels. For a binary mixture, one that consists of two species, this general expression becomes

$$x_A = \frac{n_A}{n_A + n_B} \quad x_B = \frac{n_B}{n_A + n_B} \quad x_A + x_B = 1 \tag{8b}$$

When only A is present, $x_A = 1$ and $x_B = 0$. When only B is present, $x_B = 1$ and $x_A = 0$. When both are present in the same amounts, x_A

$= \dfrac{1}{2}$ and $x_B = \dfrac{1}{2}$.

For a mixture of perfect gases, we can identify the partial pressure of J with the contribution that J makes to the total pressure. Thus, if we introduce $p = nRT/V$ into equation 7, we get

$$p_J = x_J p = x_J \times \underset{\text{Definition}}{\underbrace{\frac{nRT}{V}}} = (nx_J) \times \frac{RT}{V} = n_J \times \frac{RT}{V}$$

(with annotations: $p = nRT/V$ over nRT/V; n_J over nx_J)

The value of $n_J RT/V$ is the pressure that an amount n_J of J would exert in the otherwise empty container. That is, the partial pressure of J as defined by equation 7 is the pressure of J used in Dalton's law, provided all the gases in the mixture behave perfectly. If the gases are real, their partial pressures are still given by equation 7, for that definition applies to all gases, and the sum of these partial pressures is the total pressure (because the sum of all the mole fractions is 1); however, each partial pressure is no longer the pressure that the gas would exert when alone in the container.

3.4 THE KINETIC MODEL OF GASES

We remarked in the Introduction that a gas may be pictured as a collection of particles in ceaseless, random motion (Figure 4). Now we develop this model of the gaseous state of matter to see how it accounts for the perfect gas law. One of the most important functions of physical chemistry is to convert qualitative notions into quantitative statements that can be tested experimentally by making measurements and comparing the results with predictions. Indeed, an important component of science as a whole is its technique of proposing a qualitative model and then expressing that model mathematically. The 'kinetic model' (or the 'kinetic molecular theory', KMT) of gases is an excellent example of this procedure: the model is very simple, and the quantitative prediction (the perfect gas law) is experimentally verifiable.
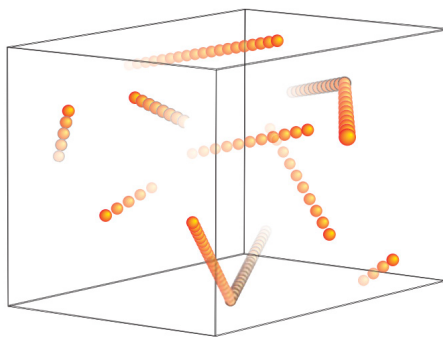
Figure 4: The model used for discussing the molecular basis of the physical properties of a perfect gas. The point-like molecules move randomly with a wide range of speeds and in random directions, both of which change when they collide with the walls or with other molecules.

The kinetic model of gases is based on three assumptions:

1. A gas consists of molecules in ceaseless random motion.
2. The size of the molecules is negligible in the sense that their diameters are much smaller than the average distance travelled between collisions.
3. The molecules do not interact, except during collisions.

The assumption that the molecules do not interact unless they are in contact implies that the potential energy of the molecules (their energy due to their position) is independent of their separation and may be set equal to zero. The total energy of a sample of gas is therefore the sum of the kinetic energies (the energy due to motion) of all the molecules present in it. It follows that the faster the molecules travel (and hence the greater their kinetic energy), the greater the total energy of the gas.

3.4.1 The Pressure of a Gas According To the Kinetic Model

The kinetic model accounts for the steady pressure exerted by a gas in terms of the collisions the molecules make with the walls of

the container. Each impact gives rise to a brief force on the wall, but as billions of collisions take place every second, the walls experience a virtually constant force, and hence the gas exerts a steady pressure. On the basis of this model, the pressure exerted by a gas of molar mass M in a volume V is

$$p = \frac{nMc^2}{3V}$$

(9)

Here c is the root-mean-square speed (rms speed) of the molecules. This quantity is defined as the square root of the mean value of the squares of the speeds, v, of the molecules. That is, for a sample consisting of N molecules with speeds v_1, v_2, ..., v_N, we square each speed, add the squares together, divide by the total number of molecules (to get the mean, denoted by $\langle ... \rangle$), and finally take the square root of the result:

$$c = \langle v^2 \rangle^{1/2} = \left(\frac{v_1^2 + v_2^2 + \cdots + v_N^2}{N} \right)^{1/2}$$

(10)

The rms speed might at first sight seem to be a rather peculiar measure of the mean speeds of the molecules, but its significance becomes clear when we make use of the fact that the kinetic energy of a molecule of mass m travelling at a speed v is $E_k = \frac{1}{2}mv^2$, which implies that the mean kinetic energy, $\langle E_k \rangle$, is the average of this quantity, or $-mc$. It follows from the relation $\frac{1}{2}mv^2 = \langle E_k \rangle$ that

$$c = \left(\frac{2\langle E_k \rangle}{m} \right)^{1/2}$$

(11)

Therefore, wherever c appears, we can think of it as a measure of the mean kinetic energy of the molecules of the gas. The rms speed is quite close in value to another and more readily visualized measure of molecular speed, the mean speed, $\bar{c}$, of the molecules:

$$\bar{c} = \frac{v_1 + v_2 + \cdots + v_N}{N}$$

(12)

For samples consisting of large numbers of molecules, the mean speed is slightly smaller than the rms speed. The precise relation is

$$\bar{c} = \left(\frac{8}{3\pi}\right)^{1/2} c \approx 0.921c$$

(13)

For elementary purposes, and for qualitative arguments, we do not need to distinguish between the two measures of average speed, but for precise work the distinction is important.

Equation 9 already resembles the perfect gas equation of state, for we can rearrange it into

$$pV = \tfrac{1}{3}nMc^2$$

(14)

and compare it to pV = nRT. This conclusion is a major success of the kinetic model, for the model implies an experimentally verified result

3.4.2 The Average Speed of Gas Molecules

We now suppose that the expression for pV derived from the kinetic model is indeed the equation of state of a perfect gas. That being so, we can equate the expression on the right of equation 14 to nRT,

$$\boxed{pV} = \boxed{nRT}$$
$$\boxed{pV} = \boxed{\tfrac{1}{3}nMc^2}$$

which gives

$$\tfrac{1}{3}nMc^2 = nRT$$

The ns now cancel, to give

$$\tfrac{1}{3}Mc^2 = RT$$

The great usefulness of this expression is that we can rearrange it into a formula for the rms speed of the gas molecules at any temperature:

$$c = \left(\frac{3RT}{M}\right)^{1/2}$$

(15)

Substitution of the molar mass of O_2 (32.0 g mol^{-1}) and a temperature corresponding to 25°C (that is, 298 K) gives an rms speed for these molecules of 482 m s^{-1}. The same calculation for nitrogen molecules gives 515 m s^{-1}. Both these values are not far off the speed of sound in air (346 m s^{-1} at 25°C). That similarity is reasonable, because sound is a wave of pressure variation transmitted by the movement of molecules, so the speed of propagation of a wave should be approximately the same as the speed at which molecules can adjust their locations.

The important conclusion to draw from equation 15 is that

The rms speed of molecules in a gas is proportional to the square root of the temperature.

Because the mean speed is proportional to the rms speed, the same is true of the mean speed too (because the two quantities are proportional to each other). Therefore, doubling the thermodynamic temperature (that is, doubling the temperature on the Kelvin scale) increases the mean and the rms speed of molecules by a factor of $2^{1/2} = 1.414....$

3.4.3 The Maxwell Distribution of Speeds

So far, we have dealt only with the average speed of molecules in a gas. Not all molecules, however, travel at the same speed: some move more slowly than the average (until they collide, and get accelerated to a high speed, like the impact of a bat on a ball), and others may briefly move at much higher speeds than the average, but be brought to a sudden stop when they collide. There

is a ceaseless redistribution of speeds among molecules as they undergo collisions. Each molecule collides once every nanosecond (1 ns = 10^{-9} s) or so in a gas under normal conditions.

The mathematical expression that tells us the fraction of molecules that have a particular speed at any instant is called the distribution of molecular speeds. Thus, the distribution might tell us that at 20°C 19 out of 1000 O_2 molecules have a speed in the range between 300 and 310 m s^{-1}, that 21 out of 1000 have a speed in the range 400 to 410 m s^{-1}, and so on. The precise form of the distribution was worked out by James Clerk Maxwell towards the end of the nineteenth century, and his expression is known as the Maxwell distribution of speeds. According to Maxwell, the fraction f of molecules that have a speed in a narrow range between s and s + Δs (for example, between 300 m s^{-1} and 310 m s^{-1}, corresponding to s = 300 m s^{-1} and Δs = 10 m s^{-1}) is

$$f = F(s)\Delta s \quad \text{with} \quad F(s) = 4\pi \left(\frac{M}{2\pi RT} \right)^{3/2} s^2 e^{-Ms^2/2RT}$$

(16)

This formula was used to calculate the numbers quoted above.

Although equation 16 looks complicated, its features can be picked out quite readily. One of the skills to develop in physical chemistry is the ability to interpret the message carried by equations. Equations convey information, and it is far more important to be able to read that information than simply to remember the equation. Let's read the information in equation 16 piece by piece.

Before we begin, and in preparation for their occurrence throughout the text, it will be useful to know the shape of exponential functions. Here, we deal with two types, e^{-ax} and e^{-ax^2}.

- An exponential function, a function of the form e^{-ax}, starts off at 1 when x = 0 and decays toward zero, which it reaches as x approaches infinity (Figure 5). This function approaches zero more rapidly as an increases.
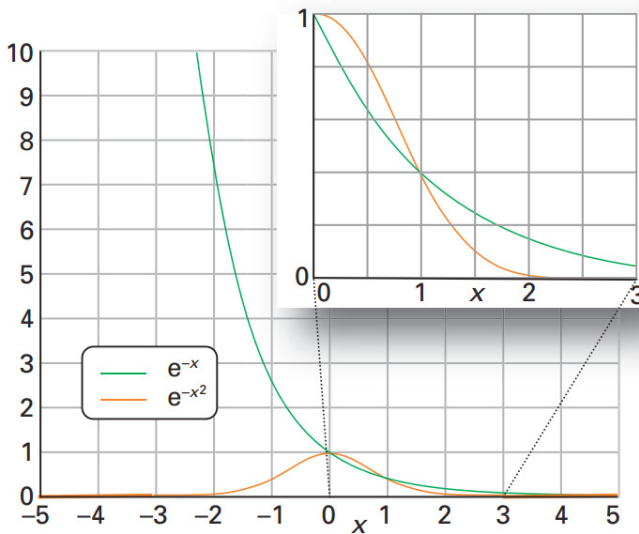
Figure 5: The exponential function, e^{-x}, and the bell-shaped Gaussian function, e^{-x^2}. Note that both are equal to 1 at $x = 0$ but the exponential function rises to infinity as $x \circledcirc -\infty$.

- A Gaussian function, a function of the form e^{-ax^2}, also starts off at 1 when $x = 0$ and decays to zero as x increases, however, its decay is initially slower but then plunges down to zero more rapidly than an exponential function (Figure 5).

The illustration also shows the behavior of the two functions for negative values of x. The exponential function e^{-ax} rises rapidly to infinity, but the Gaussian function falls back to zero and traces out a bell-shaped curve.

Now let's consider the content of equation 16.

- Because f is proportional to the range of speeds Δs, we see that the fraction in the range Δs increases in proportion to the width of the range. If at a given speed we double

the range of interest (but still ensure that it is narrow), then the fraction of molecules in that range doubles too.

- Equation 16 includes a decaying exponential function, the term $F(s) = 4\pi(M/2\pi RT)^{3/2} s^2 \boxed{e^{-Ms^2/2RT}}$ Its presence implies that the fraction of molecules with very high speeds will be very small because e^{-x^2} becomes very small when x^2 is large.

- The factor M/2RT multiplying s^2 in the exponent, $F(s) = 4\pi(M/2\pi RT)^{3/2} s^2 \ e^{-\boxed{Ms^2/2RT}}$, is large when the molar mass, M, is large, so the exponential factor goes most rapidly towards zero when M is large. That tells us that heavy molecules are unlikely to be found with very high speeds.

- The opposite is true when the temperature, T, is high: then the factor M/2RT in the exponent is small, so the exponential factor falls towards zero relatively slowly as s increases. This tells us that at high temperatures, a greater fraction of the molecules can be expected to have high speeds than at low temperatures.

- A factor s^2 $(F(s) = 4\pi(M/2\pi RT)^{3/2} \boxed{s^2} e^{-Ms^2/2RT})$ multiplies the exponential. This factor goes to zero as s goes to zero, so the fraction of molecules with very low speeds will also be very small.

- The remaining factors (the term $F(s) = \boxed{4\pi(M/2\pi RT)^{3/2}} s^2 \ e^{-Ms^2/2RT})$ simply ensure that when we add together the fractions over the entire range of speeds from zero to infinity, then we get 1.
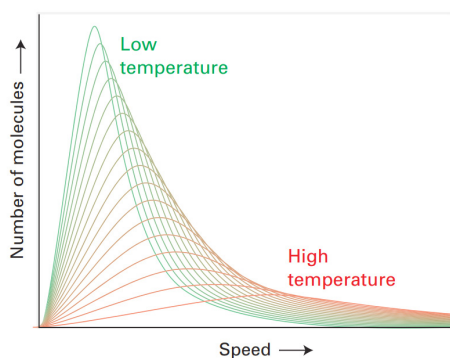
Figure 6: The Maxwell distribution of speeds and its variation with the temperature. Note the broadening of the distribution and the shift of the rms speed to higher values as the temperature is increased.

Figure 6 is a graph of the Maxwell distribution, and shows these features pictorially for the same gas (the same value of M) but different temperatures. As we deduced from the equation, we see that only small fractions of molecules in the sample have very low or very high speeds. However, the fraction with very high speeds increases sharply as the temperature is raised, as the tail of the distribution reaches up to higher speeds. This feature plays an important role in the rates of gas-phase chemical reactions, for, the rate of a reaction in the gas phase depends on the energy with which two molecules crash together, which in turn depends on their speeds.
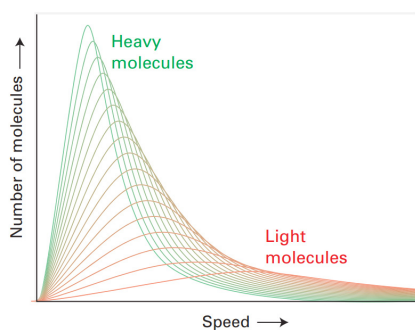
Figure 7: The Maxwell distribution of speeds also depends on the molar mass of the molecules. Molecules of low molar mass have a broad spread

of speeds, and a significant fraction may be found travelling much faster than the rms speed. The distribution is much narrower for heavy molecules, and most of them travel with speeds close to the rms value.

Figure 7 is a plot of the Maxwell distribution for molecules with different molar masses at the same temperature. As can be seen, not only do heavy molecules have lower average speeds than light molecules at a given temperature, but they also have a significantly narrower spread of speeds. That narrow spread means that most molecules will be found with speeds close to the average. In contrast, light molecules (such as H_2) have high average speeds and a wide spread of speeds: many molecules will be found travelling either much more slowly or much more quickly than the average. This feature plays an important role in determining the composition of planetary atmospheres, because it means that a significant fraction of light molecules travel at sufficiently high speeds to escape from the planet's gravitational attraction. The ability of light molecules to escape is one reason why hydrogen (molar mass 2.02 g mol^{-1}) and helium (4.00 g mol^{-1}) are very rare in the Earth's atmosphere.

The Maxwell distribution has been verified experimentally by passing a beam of molecules from an oven at a given temperature through a series of coaxial slotted disks. The speed of rotation of the disks brings the slots into line for molecules travelling at a particular speed, so only molecules with that speed pass through and are detected. By varying the rotation speed, the shape of the speed distribution can be explored and is found to match that predicted by equation 16.

Diffusion and Effusion

Diffusion is the process by which the molecules of different substances mingle with each other. The atoms of two solids diffuse into each other when the two solids are in contact, but the process is very slow. The diffusion of a solid through a liquid solvent is much faster but mixing normally needs to be encouraged by stirring or shaking the solid in the liquid (the process is then no longer

pure diffusion). Gaseous diffusion is much faster. It accounts for the largely uniform composition of the atmosphere, for if a gas is produced by a localized source (such as carbon dioxide from the respiration of animals, oxygen from photosynthesis by green plants, and pollutants from vehicles and industrial sources), then the molecules of gas will diffuse from the source and in due course be distributed throughout the atmosphere. In practice, the process of mixing is accelerated by winds: such bulk motion of matter is called convection. The process of effusion is the escape of a gas through a small hole, as in a puncture in an inflated balloon or tyre (Figure 8).
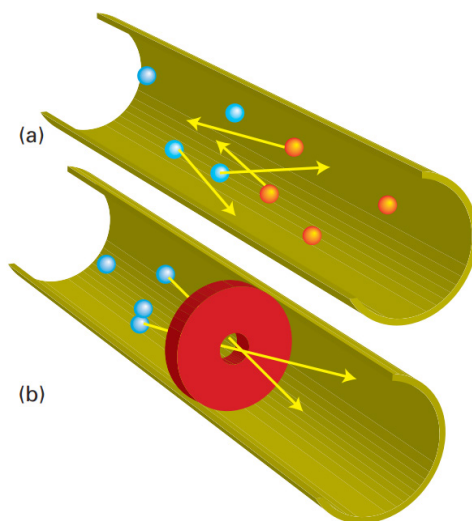
Figure 8: (a) Diffusion is the spreading of the molecules of one substance into the region initially occupied by another species. Note that molecules of both substances move, and each substance diffuses into the other. (b) Effusion is the escape of molecules through a small hole in a confining wall.

The rates of diffusion and effusion of gases increase with increasing temperature, as both processes depend on the motion of molecules, and molecular speeds increase with temperature. The rates also decrease with increasing molar mass, as molecular speeds decrease with increasing molar mass. The dependence on

molar mass, however, is simple only in the case of effusion. In effusion, only a single substance is in motion, not the two or more intermingling gases involved in diffusion.

The experimental observations on the dependence of the rate of effusion of a gas on its molar mass are summarized by Graham's law of effusion, proposed by Thomas Graham in 1833:

At a given pressure and temperature, the rate of effusion of a gas is inversely proportional to the square root of its molar mass:

$$\text{Rate of effusion} \propto \frac{1}{M^{1/2}}$$

(17)

Rate in this context means the number (or number of moles) of molecules that escape per second.

The high rate of effusion of hydrogen and helium is one reason why these two gases leak from containers and through rubber diaphragms so readily. The different rates of effusion through a porous barrier are employed in the separation of uranium-235 from the more abundant and less useful uranium-238 in the processing of nuclear fuel. The process depends on the formation of uranium hexafluoride, a volatile solid. However, because the ratio of the molar masses of $^{238}UF_6$ and $^{235}UF_6$ is only 1.008, the ratio of the rates of effusion is only $(1.008)^{1/2} = 1.004$. Thousands of successive effusion stages are therefore required to achieve a significant separation. The rate of effusion of gases was once used to determine molar mass by comparison of the rate of effusion of a gas or vapor with that of a gas of known molar mass. However, there are now much more precise methods available, such as mass spectrometry.

Graham's law is explained by noting that the rms speed of molecules of a gas is inversely proportional to the square root of the molar mass (equation 15). Because the rate of effusion through a hole in a container is proportional to the rate at which molecules pass through the hole, it follows that the rate should be inversely proportional to $M^{1/2}$, which is in accord with Graham's law.

Molecular Collisions

The average distance that a molecule travels between collisions is called its mean free path, λ (lambda). The mean free path in a liquid is less than the diameter of the molecules, because a molecule in a liquid meets a neighbor even if it moves only a fraction of a diameter. However, in gases, the mean free paths of molecules can be several hundred molecular diameters. If we think of a molecule as the size of a tennis ball, then the mean free path in a typical gas would be about the length of a tennis court.

The collision frequency, z, is the average rate of collisions made by one molecule. Specifically, z is the average number of collisions one molecule makes in a given time interval divided by the length of the interval. It follows that the inverse of the collision frequency, 1/z, is the time of flight, the average time that a molecule spends in flight between two collisions (for instance, if there are 10 collisions per second, so the collision frequency is 10 s^{-1}, then the average time between collisions is $\frac{1}{10}$ of a second and the time of flight is $\frac{1}{10}$ s). The collision frequency in a typical gas is about 10^9 s^{-1} at 1 atm and room temperature, so the time of flight in a gas is typically 1 ns.

Because speed is distance travelled divided by the time taken for the journey, the rms speed c, which we can loosely think of as the average speed, is the average length of the flight of a molecule between collisions (that is, the mean free path, λ) divided by the time of flight (1/z). It follows that the mean free path and the collision frequency are related by

$$c = \frac{\text{mean free path}}{\text{time of flight}} = \frac{\lambda}{1/z} = \lambda z \qquad (18)$$

Therefore, if we can calculate either λ or z, then we can find the other from this equation and the value of c given in equation 15.
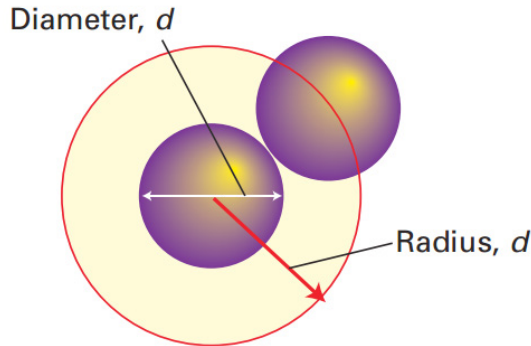
Figure 9: To calculate features of a perfect gas that are related to collisions, a point is regarded as being surrounded by a sphere of diameter d. A molecule will hit another molecule if the center of the former lies within a circle of radius d. The collision cross-section is the target area, πd^2.

To find expressions for λ and z we need a slightly more elaborate version of the kinetic model. The basic kinetic model supposes that the molecules are effectively point-like; however, to obtain collisions, we need to assume that two 'points' score a hit whenever they come within a certain range d of each other, where d can be thought of as the diameter of the molecules (Figure 9). The collision cross-section, σ (sigma), the target area presented by one molecule to another, is therefore the area of a circle of radius d, so $\sigma = \pi d^2$. When this quantity is built into the kinetic model, it is possible to show that

$$\lambda = \frac{RT}{2^{1/2}N_A\sigma p} \qquad \boxed{\text{Use } z = c/\lambda} \qquad z = \frac{2^{1/2}N_A\sigma c p}{RT} \tag{19}$$

Table 3 lists the collision cross-sections of some common atoms and molecules.

Table 3: Collision cross-sections of atoms and molecules

Species	σ/nm^2
Argon, Ar	0.36
Benzene, C_6H_6	0.88
Carbon dioxide, CO_2	0.52
Chlorine, Cl_2	0.93
Ethene, C_2H_4	0.64
Helium, He	0.21
Hydrogen, H_2	0.27
Methane, CH_4	0.46
Nitrogen, N_2	0.43
Oxygen, O_2	0.40
Sulfur dioxide, SO_2	0.58

$1 \ nm^2 = 10^{-18} \ m^2$.

Once again, we should interpret the essence of the two expressions in equation 19 rather than trying to remember them.

Because $\lambda \propto 1/p$, we see that the mean free path decreases as the pressure increases.

This decrease is a result of the increase in the number of molecules present in a given volume as the pressure is increased, so each molecule travels a shorter distance before it collides with a neighbor. For example, the mean free path of an O_2 molecule decreases from 73 nm to 36 nm when the pressure is increased from 1.0 bar to 2.0 bar at 25°C.

Because $\lambda \propto 1/\sigma$, the mean free path is shorter for molecules with large collision cross-sections.

For instance, the collision cross-section of a benzene molecule (0.88 nm²) is about four times greater than that of a helium atom (0.21 nm²), and at the same pressure and temperature its mean free path is four times shorter.

Because $z \propto p$, the collision frequency increases with the pressure of the gas.

This dependence follows from the fact that, provided the temperature is the same, the molecule takes less time to travel to its neighbor in a denser, higher-pressure gas. For example, although the collision frequency for an O_2 molecule in oxygen gas at SATP is 6.2×10^9 s^{-1}, at 2.0 bar and the same temperature the collision frequency is doubled, to 1.2×10^{10} s^{-1}.

Because equation 19 shows that $z \propto c$, and we know that $c \propto 1/M^{1/2}$, heavy molecules have lower collision frequencies than light molecules, providing their collision cross-sections are the same.

Heavy molecules travel more slowly on average than light molecules do (at the same temperature), so they collide with other molecules less frequently.

3.4.4 Real Gases

So far, everything we have said applies to perfect gases, in which the average separation of the molecules is so great that they move independently of one another. A perfect gas is a gas for which the mean free path, λ, of the molecules in the sample is much greater than d, the separation at which they are regarded as being in contact:

Condition for perfect-gas behavior: $\lambda \gg d$

As a result of this large average separation, a perfect gas is a gas in which the only contribution to the energy comes from the kinetic energy of the motion of the molecules and there is no contribution to the total energy from the potential energy arising from the interaction of the molecules with one another.

However, in fact all molecules do interact with one another provided they are close enough together, so the 'kinetic energy only' model is only an approximation. Nevertheless, under most conditions the criterion $\lambda \gg d$ is satisfied and the gas can be treated as though it is perfect.

Molecular Interactions

There are two types of contribution to the interaction between molecules. At relatively large separations (a few molecular diameters), molecules attract each other. This attraction is responsible for the condensation of gases into liquids at low temperatures. At low enough temperatures the molecules of a gas have insufficient kinetic energy to escape from each other's attraction and they stick together. Second, although molecules attract each other when they are a few diameters apart, as soon as they come into contact they repel each other. This repulsion is responsible for the fact that liquids and solids have a definite bulk and do not collapse to an infinitesimal point.

Molecular interactions—the attractions and repulsions between molecules—give rise to a potential energy that contributes to the total energy of a gas.
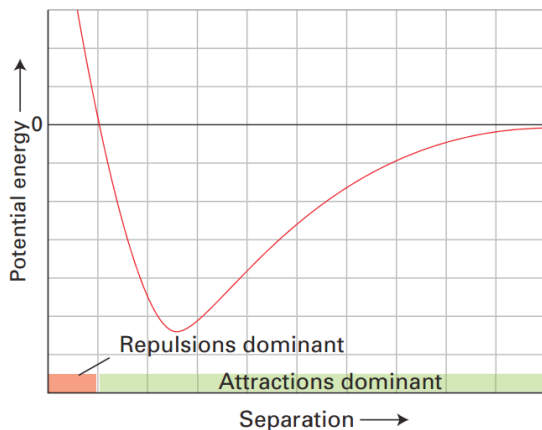
Figure 10: The variation of the potential energy of two molecules with their separation. High positive potential energy (at very small separations) indicates that the interactions between them are strongly repulsive at these distances. At intermediate separations, where the potential energy is negative, the attractive interactions dominate. At large separations (on the right) the potential energy is zero and there is no interaction between the molecules.

Because attractions correspond to a lowering of total energy as molecules get closer together, they make a negative contribution to the potential energy. On the other hand, repulsions make a positive contribution to the total energy as the molecules squash together. Figure 10 illustrates the general form of the variation of the intermolecular potential energy. At large separations, the energy-lowering interactions are dominant, but at short distances the energy-raising repulsions dominate.

Molecular interactions affect the bulk properties of a gas and, in particular, their equations of state. For example, the isotherms of real gases have shapes that differ from those implied by Boyle's law, particularly at high pressures and low temperatures when the interactions are most important. Figure 11 shows a set of experimental isotherms for carbon dioxide. They should be compared with the perfect-gas isotherms shown in Figure 1. Although the experimental isotherms resemble the perfect-gas isotherms at high temperatures (and at low pressures, off the scale on the right of the graph), there are very striking differences between the two at temperatures below about 50°C and at pressures above about 1 bar.
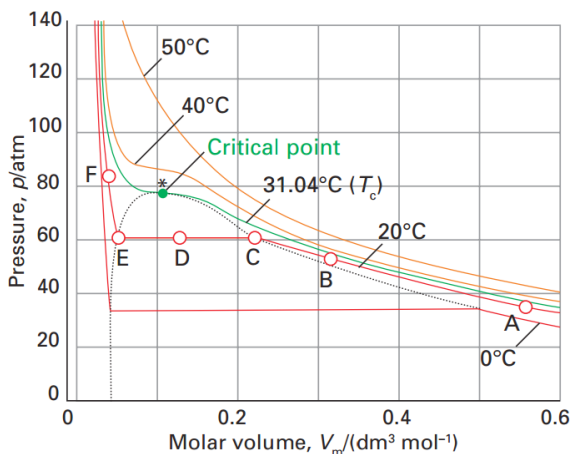
Figure 11: The experimental isotherms of carbon dioxide at several temperatures. The critical isotherm is at 31.04°C.

3.4.5 The Critical Temperature

To understand the significance of the isotherms in Figure 11, let's begin with the isotherm at 20°C. At point A the sample of carbon dioxide is a gas. As the sample is compressed to B by pressing in a piston, the pressure increases broadly in agreement with Boyle's law, and the increase continues until the sample reaches point C. Beyond this point, we find that the piston can be pushed in without any further increase in pressure, through D to E. The reduction in volume from E to F requires a very large increase in pressure. This variation of pressure with volume is exactly what we expect if the gas at C condenses to a compact liquid at E. Indeed, if we could observe the sample we would see it begin to condense to a liquid at C, and the condensation would be complete when the piston was pushed in to E. At E, the piston is resting on the surface of the liquid. The subsequent reduction in volume, from E to F, corresponds to the very high pressure needed to compress a liquid into a smaller volume. In terms of intermolecular interactions, the step from C to E corresponds to the molecules being so close on average that they attract each other and cohere into a liquid. The step from E to F represents the effect of trying to force the molecules even closer together when they are already in contact, and hence trying to overcome the strong repulsive interactions between them.

If we could look inside the container at point D, we would see a liquid separated from the remaining gas by a sharp surface (Figure 12). At a slightly higher temperature (at 30°C, for instance), a liquid forms, but a higher pressure is needed to produce it. It might be difficult to make out the surface because the remaining gas is at such a high pressure that its density is similar to that of the liquid. At the special temperature of 31.04°C (304.19 K) the gaseous state of carbon dioxide appears to transform continuously into the condensed state and at no stage is there a visible surface between the two states of matter. At this temperature (which is 304.19 K for carbon dioxide but varies from substance to substance), called the critical temperature, T_c, and at all higher temperatures, a single form of matter fills the container at all stages of the compression

and there is no separation of a liquid from the gas. We have to conclude that a gas cannot be condensed to a liquid by the application of pressure unless the temperature is below the critical temperature.

Figure 12 also shows that in the critical isotherm, the isotherm at the critical temperature, the volumes at each end of the horizontal part of the isotherm have merged to a single point, the critical point of the gas. The pressure and molar volume at the critical point are called the critical pressure, pc, and critical molar volume, V_c, of the substance. Collectively, p_c, V_c, and T_c are the critical constants of a substance. Table 4 lists the critical temperatures of some common gases. The data there imply, for example, that liquid nitrogen cannot be formed by the application of pressure unless the temperature is below 126 K (−147°C). The critical temperature is sometimes used to distinguish the terms 'vapor' and 'gas': a vapor is the gaseous phase of a substance below its critical temperature (and which can therefore be liquefied by compression); a gas is the gaseous phase of a substance above its critical temperature (and that cannot therefore be liquefied by compression alone). Oxygen at room temperature is therefore a true gas; the gaseous phase of water at room temperature is a vapor.

Increasing temperature ⟶
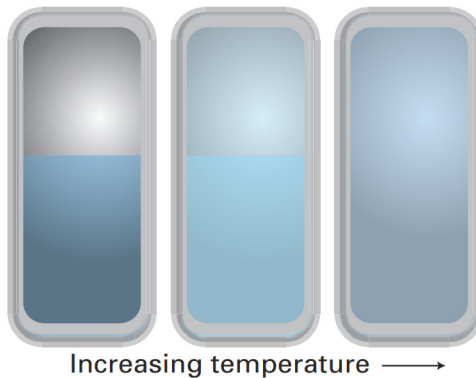
Figure 12: When a liquid is heated in a sealed container, the density of the vapor phase increases and that of the liquid phase decreases, as depicted here by the changing density of shading. There comes a stage at which the two densities are equal and the interface between the two fluids disappears. This disappearance occurs at the critical temperature.

The container needs to be strong: the critical temperature of water is at 373°C and the vapor pressure is then 218 atm.

Table 4: The critical temperatures of gases

	Critical temperature/°C
Noble gases	
Helium, He	−268 (5.2 K)
Neon, Ne	−229
Argon, Ar	−123
Krypton, Kr	−64
Xenon, Xe	17
Halogens	
Chlorine, Cl_2	144
Bromine, Br_2	311
Small inorganic molecules	
Ammonia, NH_3	132
Carbon dioxide, CO_2	31
Hydrogen, H_2	−240
Nitrogen, N_2	−147
Oxygen, O_2	−118
Water, H_2O	374
Organic compounds	
Benzene, C_6H_6	289
Methane, CH_4	−83
Tetrachloromethane, CCl_4	283

The dense fluid obtained by compressing a gas when its temperature is higher than its critical temperature is not a true liquid, but it behaves like a liquid in many respects—it has a density similar to that of a liquid, for instance, and can act as a solvent. However, despite its density, the fluid is not strictly a liquid because it never possesses a surface that separates it from a vapor phase. Nor is it much like a gas, because it is so dense. It is an example of a supercritical fluid. Supercritical fluids (SCF) are currently being used as solvents. For example, supercritical carbon dioxide is used to extract caffeine in the manufacture of decaffeinated coffee where, unlike organic solvents, it does not result in the formation of an unpleasant and possibly toxic residue. Supercritical fluids are also currently of great interest in industrial processes, as they can be used instead of chlorofluorocarbons (CFC) and hence avoid the environmental damage that CFCs are known to cause. Because supercritical carbon dioxide is obtained either from the atmosphere or from renewable organic sources (by fermentation), its use does not increase the net load of atmospheric carbon dioxide.

The Compression Factor

A useful quantity for discussing the properties of real gases is the compression factor, Z, which is the ratio of the actual molar volume of a gas to the molar volume of a perfect gas under the same conditions:

$$Z = \frac{V_m}{V_m^o}$$ Molar volume of the gas
Molar volume of a perfect gas

$$\text{(20a)}$$

The molar volume of a perfect gas is RT/p (recall equation 1.3), so we can rewrite this definition as

Definition

$$Z = \frac{V_m}{V_m^o} = \frac{V_m}{RT/p} = \frac{pV_m}{RT}$$

$V_m^o = RT/p$

$$\text{(20b)}$$

where V_m is the molar volume of the gas we are studying. For a perfect gas, $Z = 1$, so deviations of Z from 1 are a measure of how far a real gas departs from behaving perfectly.

When Z is measured for real gases, it is found to vary with pressure as shown in Figure 13. At low pressures, some gases (methane, ethane, and ammonia, for instance) have $Z < 1$. That is, their molar volumes are smaller than that of a perfect gas, suggesting that the molecules are pulled together slightly. We can conclude that for these molecules and these conditions, the attractive interactions are dominant. The compression factor rises above 1 at high pressures whatever the identity of the gas, and for some gases (hydrogen in the illustration) $Z > 1$ at all pressures. The type of behavior exhibited depends on the temperature. The observation that $Z > 1$ tells us that the molar volume of the gas is now greater than that expected for a perfect gas of the same temperature and pressure, so the molecules are pushed apart slightly. This behavior indicates that the repulsive forces are dominant. For hydrogen, the attractive interactions are so weak that the repulsive interactions dominate even at low pressures.
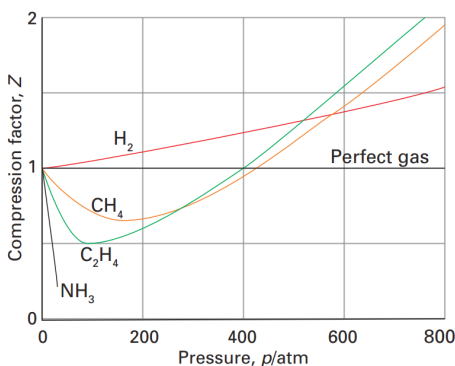
Figure 13: The variation of the compression factor, Z, with pressure for several gases at 0°C. A perfect gas has $Z = 1$ at all pressures. Of the gases shown, hydrogen shows positive deviations at all pressures (at this temperature); all the other gases show negative deviations initially but positive deviations at high pressures. The negative deviations are a result of the attractive interactions between molecules and the positive deviations are a result of the repulsive interactions.

The Virial Equation of State

We can use the deviation of Z from its 'perfect' value of 1 to construct an empirical (observation-based) equation of state. To do so, we suppose that, for real gases, the relation $Z = 1$ is only the first term of a lengthier expression, and write instead

$$Z = 1 + \frac{B}{V_m} + \frac{C}{V_m^2} + \cdots$$

$$(21)$$

The coefficients B, C,..., are called virial coefficients; B is the second virial coefficient, C, the third, and so on; the unwritten $A = 1$ is the first. The word 'virial' comes from the Latin word for force, and it reflects the fact that intermolecular forces are now significant. The virial coefficients, which are also denoted B_2, B_3, etc. in place of B, C, etc., vary from gas to gas and depend on the temperature. This technique, of taking a limiting expression ($Z = 1$, which applies to gases at very large molar volumes) and supposing that it is the first term of a more complicated expression, is quite

common in physical chemistry. The limiting expression is the first approximation to the true expression, whatever that may be, and the additional terms progressively take into account the secondary effects that the limiting expression ignores.

The most important additional term on the right in equation 21 is the one proportional to B (because under most conditions $C/V_m^2 \ll B/V_m$ and C/V_m^2 can be neglected). From the graphs in Fig 15, it follows that, for the temperature to which the data apply, B must be positive for hydrogen (so that Z > 1) but negative for methane, ethane, and ammonia (so that for them Z < 1). However, regardless of the sign of B, the positive term C/V_m^2 becomes large for highly compressed gases (when V_m^2 is very small) and the right-hand side of equation 21 becomes greater than 1, just as in the curves for the other gases in Figure 13. The values of the virial coefficients for many gases are known from measurements of Z over a range of molar volumes and using mathematical software to fit the data to equation 21 by varying the coefficients until a good match is obtained.

To convert equation 21 into an equation of state, we combine it with equation 20b ($Z = pV_m /RT$), which gives

$$\frac{pV_m}{RT} = 1 + \frac{B}{V_m} + \frac{C}{V_m^2} + \cdots$$

We then multiply both sides by RT/V_m we obtain

$$p = \frac{RT}{V_m}\left(1 + \frac{B}{V_m} + \frac{C}{V_m^2} + \cdots\right)$$

Next, we replace V_m by V/n throughout to get p as a function of n, V, and T:

$$p = \frac{nRT}{V}\left(1 + \frac{nB}{V} + \frac{n^2C}{V^2} + \cdots\right)$$

(22)

Equation 22 is the virial equation of state. When the molar volume is very large, the terms B/V_m and C/V_m^2 are both very small, and only the 1 inside the parentheses survives. In this limit, the equation of state approaches that of a perfect gas.

3.4.6 The Van Der Waals Equation of State

Although it is the most reliable equation of state, the virial equation does not give us much immediate insight into the behavior of gases and their condensation to liquids. The van der Waals equation, which was proposed in 1873 by the Dutch physicist Johannes van der Waals, is only an approximate equation of state but it has the advantage of showing how the intermolecular interactions contribute to the deviations of a gas from the perfect gas law. We can view the van der Waals equation as another example of taking a soundly based qualitative idea and building up a mathematical expression that can be tested quantitatively.

The repulsive interaction between two molecules implies that they cannot come closer than a certain distance. Therefore, instead of being free to travel anywhere in a volume V, the actual volume in which the molecules can travel is reduced to an extent proportional to the number of molecules present and the volume they each exclude (Figure 16). We can therefore model the effect of the repulsive, volume-excluding forces by changing V in the perfect gas equation to V − nb, where b is the proportionality constant between the reduction in volume and the amount of molecules present in the container.

Excluded volume
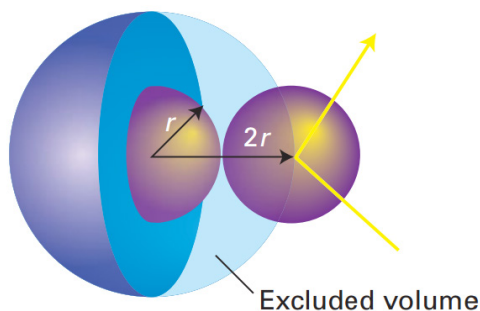
Figure 14: When two molecules, each of radius r and volume $V_{mol} = \frac{4}{3}\pi r^3$ approach each other, the center of one of them cannot penetrate into a sphere of radius 2r and therefore volume $8V_{mol}$ surrounding the other molecule.

So far, the perfect gas equation of state changes from $p = nRT/V$ to

$$p = \frac{nRT}{V - nb}$$

This equation of state—it is not yet the full van der Waals equation—should describe a gas in which repulsions are important. Note that when the pressure is low, the volume is large compared with the volume excluded by the molecules (which we write $V \gg nb$). The nb can then be ignored in the denominator and the equation reduces to the perfect gas equation of state. It is always a good plan to verify that an equation reduces to a known form when a plausible physical approximation is made.

The effect of the attractive interactions between molecules is to reduce the pressure that the gas exerts. We can model the effect by supposing that the attraction experienced by a given molecule is proportional to the concentration, n/V, of molecules in the container. Because the attractions slow the molecules down, the molecules strike the walls less frequently and strike it with a weaker impact. (This slowing does not mean that the gas is cooler close to the walls: the simple relation between T and mean speed in equation 15 is valid only in the absence of intermolecular forces.) We can therefore expect the reduction in pressure to be proportional to the square of the molar concentration, one factor of n/V reflecting the reduction in frequency of collisions and the other factor the reduction in the strength of their impulse. If the constant of proportionality is written a, we can write

$$\text{Reduction in pressure} = a \times \left(\frac{n}{V}\right)^2$$

It follows that the equation of state allowing for both repulsions and attractions is

$$p = \frac{nRT}{V - nb} - a\left(\frac{n}{V}\right)^2 \tag{23a}$$

This expression is the van der Waals equation of state. To show the resemblance of this equation to the perfect gas equation $pV =$

nRT, equation 23a is sometimes rearranged by bringing the term proportional to a to the left and multiplying throughout by V − nb:

$$\left(p + \frac{an^2}{V^2}\right)(V - nb) = nRT$$

(23b)

We have built the van der Waals equation by using physical arguments about the volumes of molecules and the effects of forces between them. It can be derived in other ways, but the present method has the advantage of showing how to derive the form of an equation out of general ideas. The derivation also has the advantage of keeping imprecise the significance of the van der Waals parameters, the constants a and b: they are much better regarded as empirical parameters than as precisely defined molecular properties. The van der Waals parameters depend on the gas, but are taken as independent of temperature (Table 5). It follows from the way we have constructed the equation that a (the parameter representing the role of attractions) can be expected to be large when the molecules attract each other strongly, whereas b (the parameter representing the role of repulsions) can be expected to be large when the molecules are large.

Table 5: van der Waals parameters of gases

Substance	$a/(\text{atm dm}^6 \text{ mol}^{-2})$	$b/(10^{-2} \text{ dm}^3 \text{ mol}^{-1})$
Air	1.4	0.039
Ammonia, NH_3	4.225	3.71
Argon, Ar	1.337	3.20
Carbon dioxide, CO_2	3.610	4.29
Ethane, C_2H_6	5.507	6.51
Ethene, C_2H_4	4.552	5.82
Helium, He	0.0341	2.38
Hydrogen, H_2	0.2420	2.65
Nitrogen, N_2	1.352	3.87
Oxygen, O_2	1.364	3.19
Xenon, Xe	4.137	5.16

You can judge the reliability of the van der Waals equation by comparing the isotherms it predicts, which are shown in Figure 15, with the experimental isotherms already shown in Figure 11. Apart from the waves below the critical temperature they do resemble experimental isotherms quite well. The waves, which are called van der Waals' loops, are unrealistic because they suggest

that under some conditions compression results in a decrease of pressure. The loops are therefore trimmed away and replaced by horizontal lines (Figure 16). The van der Waals parameters in Table 5 were found by fitting the calculated curves to experimental isotherms.

Two important features of the van der Waals equation should be noted. First, perfect-gas isotherms are obtained from the van der Waals equation at high temperatures and low pressures. To confirm this remark, we need to note that when the temperature is high, RT may be so large that the first term on the right in equation 23a greatly exceeds the second, so the latter may be ignored. Furthermore, at low pressures, the molar volume is so large that V − nb can be replaced by V. Hence, under these conditions (of high temperature and low pressure), equation 23a reduces to p = nRT/V, the perfect gas equation. The critical constants are related to the van der Waals coefficients as follows:
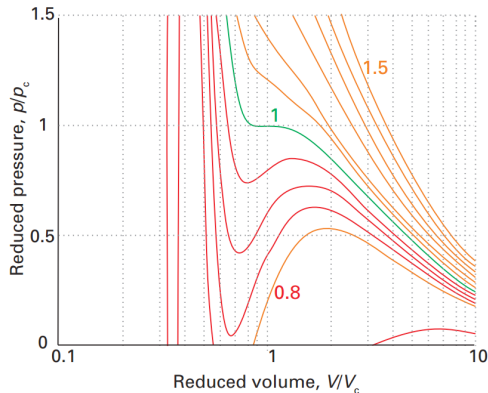
Figure 15: Isotherms calculated by using the van der Waals equation of state. The axes are labelled with the 'reduced pressure', p/p_c, and 'reduced volume', V/V_c, where $p_c = a/27b^2$ and $V_c = 3b$. The individual isotherms are labelled with the 'reduced temperature', T/T_c, where $T_c = 8a/27Rb$. The isotherm labelled 1 is the critical isotherm (the isotherm at the critical temperature).
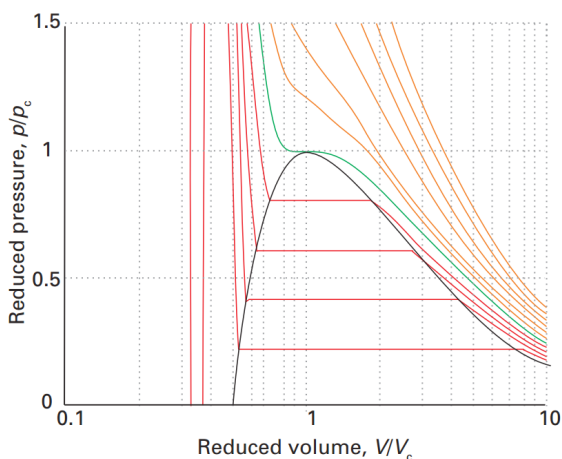
Figure 16: The unphysical van der Waals loops are eliminated by drawing straight lines that divide the loops into areas of equal size. With this procedure, the isotherms strongly resemble the observed isotherms.

$$V_c = 3b \qquad T_c = \frac{8a}{27Rb} \qquad p_c = \frac{a}{27b^2}$$

(24)

The first of these relations shows that the critical volume is about three times the volume occupied by the molecules themselves.

3.4.7 The Liquefaction of Gases

A gas may be liquefied by cooling it below its boiling point at the pressure of the experiment. For example, chlorine at 1 atm can be liquefied by cooling it to below −34°C in a bath cooled with dry ice (solid carbon dioxide). For gases with very low boiling points (such as oxygen and nitrogen, at −183°C and −186°C, respectively), such a simple technique is not practicable unless an even colder bath is available.

We saw earlier that the rms speed of molecules in a gas is proportional to the square root of the temperature (equation 15). It follows that reducing the rms speed of the molecules is equivalent to cooling the gas. If the speed of the molecules can

be reduced to the point that neighbors can capture each other by their intermolecular attractions, then the cooled gas will condense to a liquid.

To slow the gas molecules, we make use of an effect similar to that seen when a ball is thrown into the air: as it rises it slows in response to the gravitational attraction of the Earth and its kinetic energy is converted into potential energy. Molecules attract each other, as we have seen (the attraction is not gravitational, but the effect is the same), and if we can cause them to move apart from each other, like a ball rising from a planet, then they should slow. It is very easy to move molecules apart from each other: we simply allow the gas to expand, which increases the average separation of the molecules. To cool a gas, therefore, we allow it to expand without allowing any heat to enter from outside. As it does so, the molecules move apart to fill the available volume, struggling as they do so against the attraction of their neighbors. Because some kinetic energy must be converted into potential energy to reach greater separations, the molecules travel more slowly as their separation increases. Therefore, because the average speed of the molecules has been reduced, the gas is now cooler than before the expansion. This process of cooling a real gas by expansion through a narrow opening called a 'throttle' is called the Joule–Thomson effect. The effect was first observed and analyzed by James Joule (whose name is commemorated in the unit of energy) and William Thomson (who later became Lord Kelvin). The procedure works only for real gases in which the attractive interactions are dominant, because the molecules have to climb apart against the attractive force in order for them to travel more slowly. For molecules under conditions when repulsions are dominant (corresponding to $Z > 1$), the Joule– Thomson effect results in the gas becoming warmer.

The gas is allowed to expand several times by recirculating it through a device called a Linde refrigerator (Figure 17). On each successive expansion the gas becomes cooler, and as it flows past the incoming gas, the latter is cooled further. After several successive expansions, the gas becomes so cold that it condenses to a liquid.
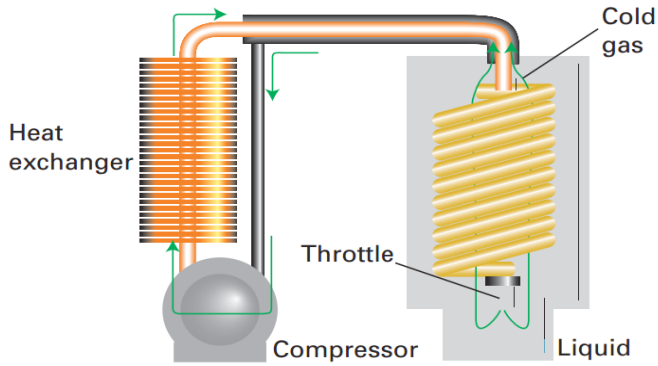
Figure 17: The principle of the Linde refrigerator. The gas is recircu-
lated and cools the gas that is about to undergo expansion through the
throttle. The expanding gas cools still further. Eventually, liquefied gas
drips from the throttle.

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PHASE RULE

INTRODUCTION

A phase is defined as any homogeneous and physically distinct part of a system bounded by a surface and is mechanically separable from other parts of the system.

A phase may be gaseous, liquid or solid. It is perfectly homogeneous and distinct from every other phase that is present in the system. There must be a definite boundary between any two phases. This boundary is known as the interface.

Air constitutes a single phase only as it contains a mixture of nitrogen, oxygen, carbon dioxide, water vapour etc. A system consisting of only one phase is said to be homogeneous.

A mixture of two immiscible liquids such as water and benzene, will exist in two distinct liquid phases and in addition there will

be a vapour phase. Thus there will be three phases each separated from the other by a well-defined bounding surface.

A system consisting of more than one phase is said to be heterogeneous. When various phases are in equilibrium with one another in a heterogeneous system, there can be no transfer of energy or mass from one phase to another. This means that at equilibrium, the various phases must have the same temperature and pressure and their respective compositions must remain constant all along.

The homogeneous reversible reactions can be studied using the law of mass action. For heterogeneous reversible reactions , the phase rule given by Williard Gibbs is used.

4.1 PHASE RULE STATEMENT

Phase rule states that " If the equilibrium between any number of phases is not influenced by gravity, or electrical, or magnetic forces, or by surface action but are influenced only by temperature, pressure and concentration , then the number of degrees of freedom (F) of the system is related to the number of components (C) and number of phases (P) by the following phase rule equation :

$$F = C - P + 2$$

4.1.1 Phase (P)

A phase is defined as " an homogeneous, physically distinct and mechanically separable portion of system, which is separated from other such parts of the system by definite boundary surfaces"

Example :

1. *Liquid phase :-* The number of liquid phase depends on the number of liquids present and their miscibility.

i)   If two liquids are immiscible, they will form two separate liquid phases.

Example : benzene and water

ii)   If two liquids are miscible they will form one liquid phase only.

Example : alcohol and water

2.   *Solid phase :-* Each solid forms a separate phase. The number of solid phase depends on the number of solids present in it.

Example : Many forms of sulphur can exist together, but these are all separate phases.

3.   *Gaseous phase :-* Since a gaseous mixture are thoroughly miscible in all proportions, it will form one phase only.

Example : a mixture of N_2 and H_2 forms one phse only.

4.   A solution of a substance in a solvent consists of one phase only, e.g. glucose solution.

5.   A heterogeneous mixture like:

$$CaCO_{3(s)} \rightleftharpoons CaO_{(s)} + CO_{2(g)}$$
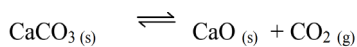
consists of three phases (i.e., two solids and one gaseous).

In the equilibrium reaction,

$$Fe_{(s)} + H_2O_{(g)} \rightleftharpoons FeO_{(s)} + H_{2(g)}$$
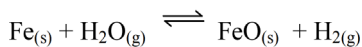
There are two solid phases, Fe and FeO and one gaseous phase consisting of $H_2O_{(g)}$ and $H_{2(g)}$. Thus three phases exists in equilibrium.

6.   At freezing point, water consists of three phases:

$$Ice_{(s)} \rightleftharpoons Water_{(l)} \rightleftharpoons Water\ vapour_{(g)}$$
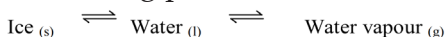
7.   A homogeneous solid solution of a salt forms a single phase.

Example : Mohr's salt [$FeSO_4$. $(NH_4)_2SO_4.6H_2O$] solution has a single phase.

4.1.2 Component (C)

Component is defined as " the smallest number of independently variable constituents, by means of which the composition of each phase can be expressed in the form of a chemical equation".

Example :

i)   In the water system,

$$Ice_{(s)} \rightleftharpoons Water_{(l)} \rightleftharpoons Water\ vapour_{(g)}$$
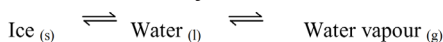
The chemical component of all the three phases is H_2O and therefore it is one component system.

ii)   Sulphur exists in four phases namely rhombic, monoclinic, liquid and vapour, but the chemical composition of all phases is S. Thus is an one component system.

iii)   A system of saturated solution of NaCl consists of solid salt, salt solution and water vapour. The chemical composition of all the three phases can be expressed in terms of NaCl and H_2O. Therefore it is a two component system.

iv)   In the thermal decomposition of $CaCO_3$,

$$CaCO_{3\ (s)} \rightleftharpoons CaO_{(s)} + CO_{2\ (g)}$$
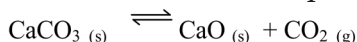
The composition of each of the three phases can be expressed in terms of at least any two of the independent variable constituents, $CaCO_3$, CaO and CO_2. Suppose $CaCO_3$ and CaO are chosen as the two components, then the composition of different phases is represented as follows:

Phase : $CaCO_3 = CaCO_3 + 0CaO$

Phase : $CaO = 0CaCO_3 + CaO$

Phase : $CO_2 = CaCO_3 - CaO$

Thus, it is a two component system.

v)   In   the   equilibrium, $Fe_{(s)} + H_2O_{(g)} \rightleftharpoons FeO_{(s)} + H_2{(g)}$, the minimum components required to express the composition of each phase is three. Thus it is a three component system.

vi)   In the dissociation of NH_4Cl, the following equilibrium occurs:

$$NH_4Cl_{(s)} \rightleftharpoons NH_{3(g)} + HCl_{(g)}$$

The system consists of two phass namely solid NH_4Cl and the gaseous mixture containing NH_3+HCl.

When NH_3 and HCl are present in equivalent quantities the composition of both the phases can be represented by the same chemical compound NH4Cl and hence the system will be a one component system.

4.1.3 Degree Of Freedom

Degree of freedom is defined as the minimum number of independent variable factors such as temperature, pressure and concentration of the phases, which must be fixed in order to define the condition of a system completely.

A system having 1,2,3 or 0 degrees of freedom is called univariant, bivariant, trivariant and nonvariant respectively.

Example :

i)   Consider the water system,

$Ice_{(s)} \rightleftharpoons Water_{(l)} \rightleftharpoons Water\ vapour_{(g)}$
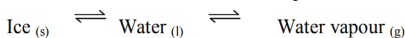
The three phases can be in equilibrium only at particular temperature and pressure.

Therefore, when all the three phases are present in equilibrium, then no condition need to be specified. The system is therefore

zero variant or invariant or has no degree of freedom.

In this system if pressure or temperature is altered , three phases will not remain in equilibrium and one of the phases disappears.

ii)   Consider a system consisting of water in contact with its vapour,

Water $_{(l)}$ $\rightleftharpoons$ Water vapour $_{(g)}$
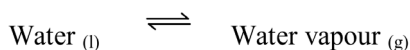
To define this system completely, we must state either the temperature or pressure Thus degree of freedom is one and the system is univariant.

iii)   For a system consisting of water vapour phase only, we must state the values of both the temperature and pressure in order to define the system completely. Hence the system is bivariant or has two degrees of freedom.

iv)   For a gaseous mixture of N_2 and H_2, we must state both the pressure and temperature, because if pressure and temperature are fixed, the volume automatically becomes definite. Hence, for a gaseous system, two factors must be stated in order to define it completely and thus, it has two degrees of freedom or bivariant system.

v)   Consider a system consisting of

NaCl $_{(s)}$ $\rightleftharpoons$ NaCl-water $_{(aq)}$ $\rightleftharpoons$ Water vapour $_{(g)}$
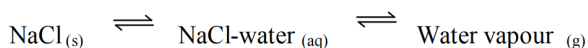
we must state either the temperature or pressure, because the saturation solubility is fixed at a particular temperature or pressure. Hence the system is univariant.

Consider a system in an equilibrium state. In this state, the system has one or more phases; each phase contains one or more species; and intensive properties such as T, p, and the mole fraction of a species in a phase have definite values. Starting with the system in this state, we can make changes that place the system in a new equilibrium state having the same kinds of phases and the same species, but different values of some of the intensive properties. The number of different independent intensive variables

that we may change in this way is the number of degrees of freedom or variance, F, of the system.

Clearly, the system remains in equilibrium if we change the *amount* of a phase without changing its temperature, pressure, or composition. This, however, is the change of an extensive variable and is not counted as a degree of freedom.

The phase rule, in the form to be derived, applies to a system that continues to have complete thermal, mechanical, and transfer equilibrium as intensive variables change. This means different phases are not separated by adiabatic or rigid partitions, or by semipermeable or impermeable membranes. Furthermore, every conceivable reaction among the species is either at reaction equilibrium or else is frozen at a fixed advancement during the time period we observe the system.

The number of degrees of freedom is the maximum number of intensive properties of the equilibrium system we may independently vary, or fix at arbitrary values, without causing a change in the number and kinds of phases and species. We cannot, of course, change one of these properties to just any value whatever. We are able to vary the value only within a certain finite (sometimes quite narrow) range before a phase disappears or a new one appears.

The number of degrees of freedom is also the number of independent intensive variables needed to specify the equilibrium state in all necessary completeness, aside from the amount of each phase. In other words, when we specify values of F different independent intensive variables, then the values of all other intensive variables of the equilibrium state have definite values determined by the physical nature of the system.

Just as for a one-component system, we can use the terms bivariant, univariant, and invariant depending on the value of F.

4.1.4 Species Approach to the Phase Rule

This section derives an expression for the number of degrees of freedom, F, based on *species*. an expression based on *components*. Both approaches yield equivalent versions of the phase rule.

Recall that a *species* is an entity, uncharged or charged, distinguished from other species by its chemical formula. Thus, CO_2 and CO_3^{2-} are different species, but $CO_2(aq)$ and $CO_2(g)$ is the same species in different phases.

Consider an equilibrium system of P phases, each of which contains the same set of species. Let the number of different species be s. If we could make changes while the system remains in thermal and mechanical equilibrium, but not necessarily in transfer equilibrium, we could independently vary the temperature and pressure of the system as a whole and the amount of each species in each phase; there would then be 2+Ps independent variables.

The equilibrium system is, however, in transfer equilibrium, which requires each species to have the same chemical potential in each phase: $\mu_i^\beta = \mu_i^\alpha, \mu_i^\gamma = \mu_i^\alpha$, and so on. There are P−1 independent relations like this for each species, and a total of s(P−1) independent relations for all species. Each such independent relation introduces a constraint and reduces the number of independent variables by one. Accordingly, taking transfer equilibrium into account, the number of independent variables is 2+Ps−s(P−1)=2+s.

We obtain the same result if a species present in one phase is totally excluded from another. For example, solvent molecules of a solution are not found in a pure perfectly-ordered crystal of the solute, undissociated molecules of a volatile strong acid such as HCl can exist in a gas phase but not in aqueous solution, and ions of an electrolyte solute are usually not found in a gas phase. For each such species absent from a phase, there is one fewer amount variable and also one fewer relation for transfer equilibrium; on balance, the number of independent variables is still 2+s.

Next, we consider the possibility that further independent relations exist among intensive variables in addition to the relations needed

for thermal, mechanical, and transfer equilibrium. (Relations such as $\sum_i p_i = p$ for a gas phase or $\sum_i x_i = 1$ for a phase in general have already been accounted for in the derivation by the specification of p and the amount of each species.) If there are r of these additional relations, the total number of independent variables is reduced to 2+s−r. These relations may come from

1. reaction equilibria,
2. the requirement of electroneutrality in a phase containing ions, and
3. initial conditions determined by the way the system is prepared.

In the case of a reaction equilibrium, the relation is $\Delta_r G = \sum_i \nu_i \mu_i = 0$, or the equivalent relation $K = \prod_i (a_i)^{\nu_i}$ for the thermodynamic equilibrium constant. Thus, r is the sum of the number of independent reaction equilibria, the number of phases containing ions, and the number of independent initial conditions.

There is an infinite variety of possible choices of the independent variables (both extensive and intensive) for the equilibrium system, but the total *number* of independent variables is fixed at 2+s−r. Keeping intensive properties fixed, we can always vary how much of each phase is present (e.g., its volume, mass, or amount) without destroying the equilibrium. Thus, at least P of the independent variables, one for each phase, must be extensive. It follows that the maximum number of independent *intensive* variables is the difference (2+s−r)−P.

It may be that initial conditions establish relations among the amounts of phases. If present, these are relations among *extensive* variables that are not counted in r. Each such independent relation decreases the total number of independent variables without changing the number of independent intensive variables calculated from (2+s−r)−P. Since the maximum number of independent intensive variables is the number of degrees of freedom, our expression for F based on species is

F=2+s−r−P

4.1.5 Components Approach to the Phase Rule

The derivation of the phase rule in this section uses the concept of components. The number of components, C, is the minimum number of substances or mixtures of fixed composition from which we could in principle prepare each individual phase of an equilibrium state of the system, using methods that may be hypothetical. These methods include the addition or removal of one or more of the substances or fixed-composition mixtures, and the conversion of some of the substances into others by means of a reaction that is at equilibrium in the actual system. It is not always easy to decide on the number of components of an equilibrium system. The number of components may be less than the number of substances present, on account of the existence of reaction equilibria that produce some substances from others. When we use a reaction to prepare a phase, nothing must remain unused. For instance, consider a system consisting of solid phases of $CaCO_3$ and CaO and a gas phase of CO_2. Assume the reaction $CaCO_3(s) \rightarrow\rightarrow CaO(s) + CO_2(g)$ is at equilibrium. We could prepare the $CaCO_3$ phase from CaO and CO_2 by the reverse of this reaction, but we can only prepare the CaO and CO_2 phases from the individual substances. We could not use $CaCO_3$ to prepare either the CaO phase or the CO_2 phase, because CO_2 or CaO would be left over. Thus this system has three substances but only two components, namely CaO and CO_2.

In deriving the phase rule by the components approach, it is convenient to consider only intensive variables. Suppose we have a system of P phases in which each substance present is a component (i.e., there are no reactions) and each of the C components is present in each phase. If we make changes to the system while it remains in thermal and mechanical equilibrium, but not necessarily in transfer equilibrium, we can independently vary the temperature and pressure of the whole system, and for each phase we can independently vary the mole fraction of all but one of the substances (the value of the omitted mole fraction comes from the relation $\sum_i x_i = 1$). This is a total of $2 + P(C-1)$ independent intensive variables.

When there also exist transfer and reaction equilibria, not all of these variables are independent. Each substance in the system is either a component, or else can be formed from components by a reaction that is in reaction equilibrium in the system. Transfer equilibria establish P−1 independent relations for each component ($\mu_i^\beta = \mu_i^\alpha$, $\mu_i^\gamma = \mu_i^\alpha$, etc.) and a total of C(P−1) relations for all components. Since these are relations among chemical potentials, which are intensive properties, each relation reduces the number of independent intensive variables by one. The resulting number of independent intensive variables is

F=[2+P(C−1)]−C(P−1)=2+C−P

If the equilibrium system lacks a particular component in one phase, there is one fewer mole fraction variable and one fewer relation for transfer equilibrium. These changes cancel in the calculation of F, which is still equal to 2+C−P. If a phase contains a substance that is formed from components by a reaction, there is an additional mole fraction variable and also the additional relation $\sum_i v_i \mu_i = 0$ for the reaction; again the changes cancel. We may need to *remove* a component from a phase to achieve the final composition. Note that it is not necessary to consider additional relations for electroneutrality or initial conditions; they are implicit in the definitions of the components. For instance, since each component is a substance of zero electric charge, the electrical neutrality of the phase is assured. We conclude that, regardless of the kind of system, the expression for F based on components is given by F=2+C−P. By comparing this expression and F=2+s−r−P, we see that the number of components is related to the number of species by

C=s−r

4.1.6 Merits of the Phase rule

1. It is applicable to both physical and chemical equilibria.
2. It requires no information regarding molecular/ microstructure, since it is applicable to macroscopic systems.

3. It is a convenient method of classifying equilibrium states in terms of phases, components and degrees of freedom.

4. It helps us to predict the behaviour of a system, under different sets of variables.

5. It indicates that different systems with same degree of freedom behave similarly.

6. It helps in deciding whether under a given set of conditions :

    a. various substances would exist together in equilibrium (or)

    b. some of the substances present would be interconverted or (c) some of the substances present would be eliminated.

4.1.7 Limitations of Phase rule

1. It can be applied only for system in equilibrium. Consequently, it is of little value in case of very slow equilibrium state attaining system.

2. It applies only to a single equilibrium system; and provide no information regarding any other possible equilibria in the system.

3. It requires at most care in deciding the number of phases existing in an equilibrium state, since it considers only the number of phases, rather than their amounts. Thus even if a trace of phase is present, it accounts towards the total number of phases.

4. It conditions that all phases of the system must be present simultaneously under the identical conditions of temperature and pressure.

5. It conditions that solid and liquid phases must not be in finely-divided state; otherwise deviations occurs.

4.2 APPLICATIONS OF PHASE RULE TO ONE COMPONENT SYSTEM (WATER SYSTEM)

The water system is a one component system

Ice $\rightleftharpoons$ Water $\rightleftharpoons$ Vapour
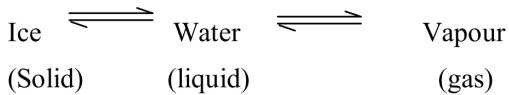
(Solid)   (liquid)   (gas)

Since water exists in three possible phases such as solid, liquid and vapour, there are three forms of equilibria :

Liquid – vapour , solid vapour and solid liquid

i.e.,

Liquid $\rightleftharpoons$ Vapour

Solid $\rightleftharpoons$ Vapour

Solid $\rightleftharpoons$ Liquid
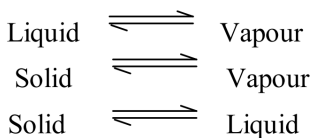
Each equilibrium involves two phases. The nature of these phases which exist in equilibrium at any time depends on the conditions of temperature and pressure. These conditions have been determined and summarized in the pressure-temperature diagram in which pressure is treated as independent variable and is plotted along y – axis whereas temperature is plotted along xaxis.

The phase diagram for the water system is shown in Fig 1.

The phase diagram consists of

1.   *Curves :* There are three curves OA, OB and OC.

2.   *Areas :* Three curves OA , OB and OC divide the diagram into three areas AOB, AOC and BOC.

3.   *Triple point :* The above three curves meet at the point O and is known as triple point.

4.   *Metastable equilibrium :* The curve OA represents the metastable equilibrium.

4.2.1 Curve OA

The curve OA is called vapourisation curve, it represents the equilibrium between water and vapour. At any point on the curve the following equilibrium will exist.

Water $\rightleftharpoons$ Water vapour
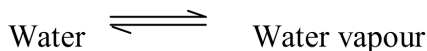
The degree of freedom of the system is one, i.e, univariant. Thus applying phase rule equation,

$F = C - P + 2 = 1 - 2 + 2 ; \quad F = 1$

This equilibrium (i.e, line OA) will extend upto the critical temperature (374^0C). Beyond the critical temperature the equilibrium will disappear only water vapour will exist.

4.2.2 Curve OB

The curve OB is called sublimation curve of ice, it represents the equilibrium between ice and vapour. At any point on the curve the following equilibrium will exist.

Ice $\rightleftharpoons$ Vapour
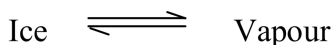
The degree of freedom of the system is one, i.e., univariant.

This is predicted by the phase rule.

$F = C - P + 2 ; \quad F = 1 - 2 + 2 ; \quad F = 1$

This equilibrium line will extend upto the absolute zero($- 273^0$C) where no vapour can be present and only ice will exist.

4.2.3 Curve OC

The curve OC is called melting point curve of ice, it represents the equilibrium between ice and water. At any point on the curve the following equilibrium will exist.

Ice $\rightleftharpoons$ Water
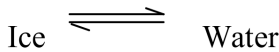
The curve OC is slightly inclined towards pressure axis. This shows that melting point of ice decreases with increase of pressure.

The degree of freedom of the system is one. i.e., univariant.
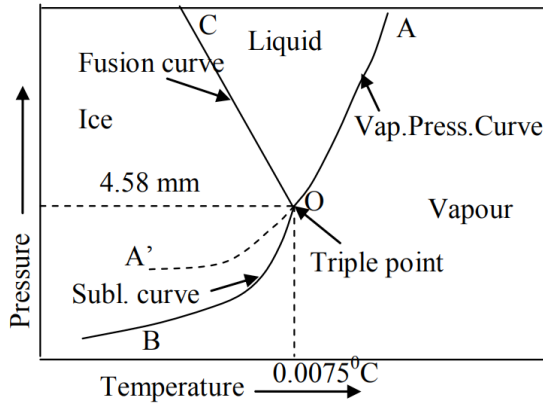
Figure 1: Water System.

4.2.4 Triple Point (Point 'O')

At triple point all the three phases namely ice, water and vapour coexist. Thus the value of P is 3. Applying phase rule equation, the degree of freedom at this point is zero. It means that three phases can coexist in equilibrium only at a definite temperature and pressure. The values are 0.0075^{0}C and 4.58 mm respectively.

At this triple point, neither pressure nor temperature can be altered even slightly without causing the disappearance of one of the phases. The triple point is not the same as the ordinary melting point of ice (i.e, 0^{0}C). It's value has been increased due to the fact that 0^{0}C is the melting point of ice at 760mm of mercury and a decrease of 4.58 mm will rise the melting point to 0.0075^{0}C.

4.2.5 Curve OB (Metastable Equilibrium)

The curve OB is called vapour pressure curve of the super-cool water or metastable equilibrium.

Where the following equilibrium will exist.

Super-cool water $\rightleftharpoons$ Vapour
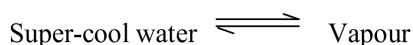
Sometimes water can be cooled below 0^0C without the formation of ice, this water is called super-cooled water. Supercooled water is unstable and it can be converted into solid by 'seeding' or by slight disturbance.

4.2.6 Areas

Area AOC, BOC , AOB represents water ice and vapour respectively. In order to define the system at any point in the areas, it is essential to specify both temperature and pressure. The degree of freedom of the system is two. i.e., Bivariant.

This is predicted by the phase rule

$$F = C - P + 2; \ F = 1 - 1 + 2 ; \ F = 2$$

4.3 THE GIBBS PHASE RULE FOR MULTICOMPONENT SYSTEMS

the Gibbs phase rule for a pure substance was written F=3−P. We now consider a system of more than one substance and more than one phase in an equilibrium state. The phase rule assumes the system is at thermal and mechanical equilibrium. We shall assume furthermore that in addition to the temperature and pressure, the only other state functions needed to describe the state are the amounts of the species in each phase; this means for instance that surface effects are ignored.

The derivations to follow will show that the phase rule may be written either in the form

F=2+C−P(13.1.1)

or

F=2+s−r−P

where the symbols have the following meanings:

F= the number of degrees of freedom (or variance) the maximum number of intensive variables that can be varied independently while the system remains in an equilibrium state;

C= the number of components the minimum number of substances (or fixed-composition mixtures of substances) that could be used to prepare each phase individually;

P= the number of different phases;

s= the number of different species;

r= the number of independent relations among intensive variables of individual phases other than relations needed for thermal, mechanical, and transfer equilibrium.

If we subdivide a phase, that does not change the number of phases P. That is, we treat noncontiguous regions of the system that have identical intensive properties as parts of the same phase.

4.4 PHASE DIAGRAM

Phase diagram is a graph obtained by plotting one degree of freedom against another.

If the phase diagram is plotted between temperature against pressure, the diagram is called P-T diagram. P-T diagram is used for one component system. If the phase diagram is drawn between temperature against composition, the diagram is called T-C diagram. T-C diagram is used for two component system.

4.4.1 Uses of Phase diagram

1.   From the phase diagram, it is possible to predict whether an eutectic alloy or a solid solution is formed on cooling a homogeneous liquid containing mixture of two metals.

2.   The phase diagrams are useful in understanding the properties of materials in the heterogeneous equilibrium system.

3.   The study of low melting eutectic alloys, used in soldering, can be carried out using phase diagrams.

4.4.2 Two Component (Binary) Phase Diagrams

As an example, we're going to look at how one might go about determining the stability of a mixture of 2 mineral phases, A and B. To perform these experiments we start with pure minerals A and B and then make mixtures in varying proportions. Each one of these mixtures, plus the pure A and pure B represent different compositions. In this case, we are only going to look at how the stability varies as with temperature and composition, holding Pressure constant at 1 atmosphere.

This type of experiment can be done in a furnace with controlled temperature. Pressure does not have to be controlled because the phase relations will be determined at atmospheric pressure. The various compositions are placed in a capsule that will not react with any of the phases produced.

Usually this would be Platinum. Each mixture is then placed in the furnace, the temperature is raised to some point and held at that temperature long enough for equilibrium between all of the phases to occur.

The capsules are then quickly removed from the furnace and quenched rapidly. The rapid decrease in temperature that occurs during quenching helps to assure that no further reactions take place and the phase assemblage that was present at the higher temperature is preserved at room temperature. During quenching,

any liquid that may have been present at high temperature is found to be glass.

After quenching, each capsule is opened and the phases present are determined using a microscope. In the example shown, we use different symbols to represent the mineral phase assemblages present for each composition run. In this set of experiments 6 different assemblages are found, and are plotted on a diagram with Temperature of the experiment plotted on the vertical axis, and composition in terms of %A or %B plotted on the horizontal axis.
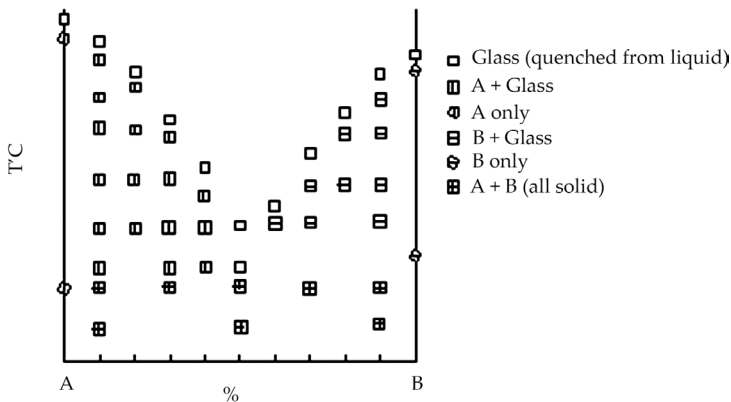
Note that pure A plots at 100% A which corresponds to 0% B, and pure B plots at 100%B, which corresponds to 0% A.

Note also that no experiments were run at temperatures higher than those where the first complete liquid appeared for each composition.

Once the points are plotted, we can then draw best-fit curves or lines between the data points to determine the Temperature - Composition stability fields for the various phase assemblages. These curves/lines are shown here, and the stability fields for each phase assemblage are labeled. the resulting phase diagram is called a binary eutectic diagram. Not all binary melting diagrams look like this, but this is the simplest and the type that we will discuss first.
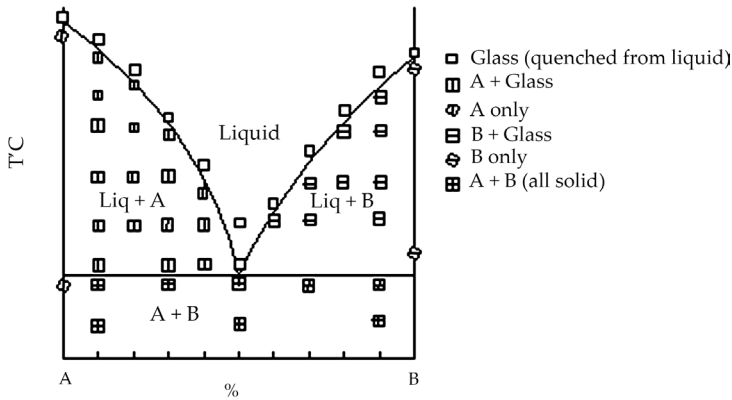
4.4.3 Two Component Eutectic Systems

Figure 1 shows the simplest of two component phase diagrams. The components are A and B, and the possible phases are pure crystals of A, pure crystals of B, and liquid with compositions ranging between pure A and pure B.

Compositions are plotted across the bottom of the diagram. Note that composition can be expressed as either a percentage of A or a percentage of B, since the total percentage must add up to 100. (Compositions might also be expressed as mole fraction of A or B, in which case the total must add up to 1). Temperature or pressure is plotted on the vertical axis. For the case shown, we consider pressure to be constant, and therefore have plotted temperature on the vertical axis.

The curves separating the fields of A + Liquid from Liquid and B + Liquid from Liquid are termed liquidus curves. The horizontal line separating the fields of A + Liquid and B + Liquid from A + B all solid, is termed the solidus.

The point, E, where the liquidus curves and solidus intersect, is termed the eutectic point. At the eutectic point in this two component system, all three phases, that is Liquid, crystals of A and crystals of B, all exist in equilibrium. Note that the eutectic is the only point on the diagram where this is true.
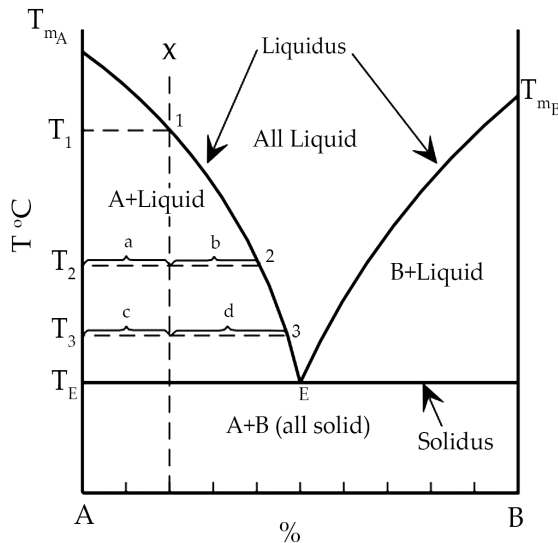
Figure 1.

Since we looking at a system at constant pressure, the phase rule in this case is F = C +1 - P. The eutectic point is therefore an invariant point. If we change the composition of the liquid or the temperature, the number of phases will be reduced to 2.

If the system contains only pure A, then the system is a one component system and phase A melts at only one temperature, the melting temperature of pure A, T_{mA}. If the system contains only pure B, then it is a one component system and B melts only at the melting temperature of pure B, T_{mB}.

For all compositions between pure A and pure B, the melting temperature is drastically reduced, and melting begins at the eutectic temperature T_E. Note that for all compositions between A and B the melting also occurs over a range of temperatures between the solidus and the liquidus. This is true for all compositions except one, that of the eutectic. The eutectic composition melts at only one temperature, T_E.

We will now consider the crystallization of a liquid with composition X in Figure 1. First, however, we must state the following rule, which must always be obeyed:

Rule 1 - In equilibrium crystallization or melting in a closed system, the final composition of the system will be identical to the initial composition of the system.

Therefore, according to rule 1, composition X, which is made up of a mixture of 80% A and 20% B, will have, as its final crystalline product a mixture of 80% crystals of A and 20% crystals of B.

Composition X will be all liquid above the temperature T1, because it will lie in the field of all Liquid. If the temperature is lowered to T_1, at T_1 crystals of A begin to form.

Further lowering of the temperature causes more crystals of A to form. As a result, the liquid composition must become more enriched in B as more crystals of A form out of the liquid. Thus, with lowering of temperature, the liquid composition will change from point 1 to point 2 to point 3 to point E as the temperature is lowered from T_1 to T_2 to T_3 to T_E respectively. At all temperatures between T_1 and T_E, two phases will be present in the system; liquid and crystals of A. At the eutectic temperature, T_E, crystals of B will begin to form, and three phases will coexist; crystals of A, crystals of B, and liquid. The temperature must remain at T_E until one of the phases disappears. Thus when the liquid crystallizes completely, only pure solid A and pure solid B will remain and mixture of these two solid phases will be in the proportions of the original mixture, that is 80% A and 20% B.

The crystallization history of composition X can be written in abbreviated form as follows:

$T > T_1$ -- all liquid

T_1 - T_E -- liquid + A

at T_E -- liquid + A + B

$T < T_E$ -- A + B all solid

If we were to stop the crystallization process at any point during crystallization and observe how much of each phase is present we can use the following example to determine what we would see.

For example, at a temperature T_2 the amount of crystals of A and liquid (the only two phases present at this temperature) could be determined by measuring the distances a and b on figure 1. The percentages would then be given by the lever rule:

% crystals of A = b/(a + b) x 100

% liquid = a/(a + b) x 100

Note that since the amount of crystals must increase with falling temperature the proportional distance between the vertical line which marks the initial composition and the liquidus increases as temperature falls. Thus the distance used to calculate the amount of solid is always measured toward the liquid side of the initial composition.

At the temperature T_3, note that more crystals must have formed since the proportional distance d/(c+d) is greater than the proportional distance b/(a+b). Thus at T_3 the lever rule gives:

% crystals of A = d/(d + c) x 100

% liquid = c/(c + d) x 100

At T_3, note that the composition of the liquid is given at point 3, i.e. 53% A, the composition of the solid is pure A, and the composition of the system is still 80% A and 20% B. Make sure you understand the difference between composition of the phases and the amount or percentages of the phases.

The melting process is exactly the reverse of the crystallization process. That is if we started with composition X at some temperature below T_E the first liquid would form at T_E. The temperature would remain constant at T_E until all of the crystals of B were melted. The liquid composition would then change along the liquidus curve from E to point 1 as temperature increased until the temperature T_1 was reached. Above T_1 the system would contain only liquid with a composition of 80% A and 20% B. The melting process in abbreviated form is listed below:

$T < T_E$ -- all solid A + B

at T_E -- Liquid + A + B

T_E - T_1 -- Liquid + A

$T > T_1$ -- all Liquid

4.4.4 Incongruent Melting

Liquidus - The line separating the field of all liquid from that of liquid plus crystals.

Solidus - The line separating the field of all solid from that of liquid plus crystals.

Eutectic point - the point on a phase diagram where the maximum number of allowable phases are in equilibrium. When this point is reached, the temperature must remain constant until one of the phases disappears. A eutectic is an invariant point.

Peritectic point - The point on a phase diagram where a reaction takes place between a previously precipitated phase and the liquid to produce a new solid phase. When this point is reached, the temperature must remain constant until the reaction has run to completion. A peritectic is also an invariant point.

Intermediate compound - A phase that has a composition intermediate between two other phases.

Congruent melting - melting wherein a phase melts to a liquid with the same composition as the solid.

Incongruent melting - melting wherein a phase melts to a liquid with a composition different from the solid and produces a solid of different composition to the original solid.

For the case of incongruent melting, we will use the system forsterite (Mg_2SiO_4) - silica (SiO_2), which has an intermediate compound, enstatite ($MgSiO_3$). This system is a prime example of the phenomena of incongruent melting in rocks, and therefore gives insights into many aspects of mineral formation.

A simplified version of the system forsterite - silica with its intermediate compound enstatite is shown in Figure 2. The crystallization histories for compositions X, Y, and Z will be documented in the following discussion. Each of these compositions behaves in a slightly different manner

4.4.5 Crystallization of Composition X

Composition X is a mixture of 13 wt. % SiO_2 and 87 wt. % Mg_2SiO_4. Because this composition falls between the compositions of pure forsterite and pure enstatite, it must end its crystallization history containing only crystals of forsterite and enstatite. i.e. no quartz will occur in the final crystalline mixture.

If a mixture such as composition X is taken to a temperature above its liquidus (i.e. above 1800°C in Figure 2) it will be in an all liquid state. We now trace the cooling history of composition X.
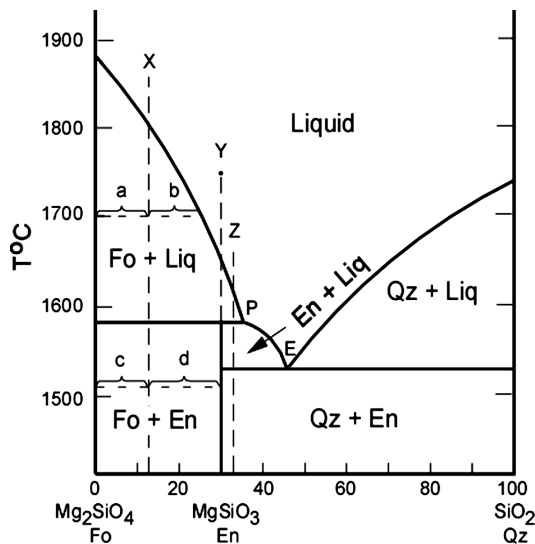
Figure 2.

As a liquid of composition X is cooled, nothing will happen until the temperature is equal to the liquidus temperature at 1800°. At this point crystals of forsterite (Fo) begin to precipitate out of the

liquid. As the temperature is further lowered, the composition of the liquid will change along the liquidus toward the peritectic (P), and the crystals forming from the liquid will always be pure Fo until P is reached. At the temperature of the peritectic, about 1580°, note that three phases must be in equilibrium, Fo, liquid, and enstatite (En). At this point some of the crystals of Fo react with the liquid to produce crystals of En. The reaction that takes place can be written as follows:

$Mg_2SiO_4 + SiO_2 = 2MgSiO_3$

Fo + liq = 2En

(Where SiO_2 in the reaction refers to the component of SiO_2 in liquid with composition P).

After all of the liquid is consumed by this reaction, only crystals of Fo and En will remain. The proportions of Fo and En in the final crystalline product can be found by applying the lever rule.

%Fo crystals = [d/(c + d)] x 100

%En crystals = [c/(c + d)] x 100

At any intermediate stage in the process, such as at 1700° the proportion of all phases present (Fo and liquid in this case) can similarly be found by applying the lever rule.

at 1700°C

%Fo crystals = [b/(a + b)] x 100

%liquid = [a/(a + b)] x 100

Note that melting of composition X is exactly the reverse of crystallization. Mixture X will begin to melt at the peritectic temperature. At this point En will melt to crystals of Fo plus liquid (incongruent melting). As soon as all of the En crystals have been consumed by this reaction, the temperature can be increased until it reaches 1800° at which point all of the Fo crystals will have been consumed and the only phase left will be liquid with a composition of the starting material.

4.4.6 Crystallization of Composition Y

Composition Y is equivalent to pure En. Thus only En may appear in the final crystalline product if perfect equilibrium is maintained.

If composition Y is cooled from an all liquid state it first begins to crystallize at about 1650°. At 1650° crystals of Fo will begin to precipitate from the liquid. This will continue with further cooling until the temperature of the peritectic is reached. In this interval, the composition of the liquid must become more enriched in SiO_2 and will thus change along the liquidus until it has the composition of the peritectic, P. At the peritectic temperature (1580°) all of the remaining liquid will react with all of the previously precipitated Fo to produce crystals of En. The temperature will remain constant until this reaction has gone to completion, after which the only phase present will be pure En.

Thus, it can be seen that enstatite melts incongruently. If pure enstatite is heated to a temperature of 1580° it melts to Fo plus liquid.

4.4.7 Crystallization of Composition Z

Since composition Z lies between En and SiO_2, it must end up with crystals of En and Qz (Quartz). If such a composition were cooled from some high temperature where it is in the all liquid state, it would remain all liquid until it reached the liquidus temperature at about 1600°. At this temperature crystals of Fo would begin to precipitate and the composition of the liquid would begin to change along the liquidus toward the peritectic, P. At P, all of the Fo previously precipitated would react with the liquid to produce crystals of En. After this reaction has run to completion, and all of the previously precipitated Fo is consumed, there would still remain some liquid. With decreasing temperature, more crystals of En would form, and the liquid composition would change along the liquidus toward the eutectic, E. At E crystals of Qz would begin to form, the temperature would remain constant until all of the liquid was used up, leaving crystals of Qz and En

as the final solid. Note that because composition Z lies very close to the composition of pure En, the final crystalline product would consist mostly of En with a very small amount of Qz.

For all compositions between P and 100% SiO_2 the system would behave in an identical fashion to the simple Eutectic system discussed previously.

4.4.8 Fractional Crystallization in the System

Up to this point we have always been discussing the case of equilibrium crystallization. That is all solids remain in contact with the liquid until any reaction that takes place has run to completion. As is often the case in natural systems crystals can somehow become separated from the system so that they will not react at reaction points such as P. This is the case of fractional crystallization. Under fractional crystallization conditions the cooling and crystallization histories will be drastically different. In particular, the rule that the final composition must equal the initial composition will not be followed.

As an example of this phenomena we will examine the fractional crystallization of composition X. Furthermore, we will look at the case of perfect fractional crystallization. During perfect fractional crystallization of composition X all of the Fo that is precipitated will be somehow removed from the system. (In nature this can occur by crystals sinking to the bottom of the liquid due to the fact that crystals generally tend to be more dense than liquids.) Note that if only some of the crystals are removed from the liquid we will have a case intermediate between perfect fractional crystallization and equilibrium crystallization.

Cooling a liquid of composition X to the liquidus at 1800° will cause Fo to precipitate as before. With further cooling the liquid composition will change along the liquidus and more Fo will be precipitated. In this case, however, all of the Fo will be removed from the system as it crystallizes. Since the Fo is no longer present, the composition of the system will have the composition of the liquid

(the Fo removed can no longer contribute to the composition of the system). Therefore, when the temperature reaches the peritectic temperature, 1580°, there will be no Fo available to react with the liquid, and the liquid (and system) will have a composition, P. Thus the liquid will now precipitate crystals of En and continue cooling to the eutectic, E, where crystals of Qz will form. The final crystalline product will consist of Qz and En.

Compare this case with the previously discussed case of equilibrium crystallization of composition X. Note that under equilibrium conditions the final crystalline product of composition X contained crystals of Fo and En, while in the fractional crystallization case the final product contains En and Qz. Thus fractional crystallization has allowed an originally Fo rich composition to produce an SiO_2 rich liquid and Qz appears in the final crystalline product.

If you go back and look at simple eutectic systems, or look at fractional crystallization of composition Z in the more complex system, you should be able to see that fractional crystallization will have no effect on the phases produced in the final crystalline product, but will only change the proportions of the phases produced. Fractional crystallization is only effective in producing a different final phase assemblage if there is a reaction relationship of one of the phases to the liquid.

4.4.9 Solid Solution Systems

In the systems we've discussed so far, all of the mineral or solid phases have been pure phases, that is they have one and only one possible composition. This is not usually the case in nature, since substitution of one element for another often occurs due to the fact that some elements behave in a chemically similar fashion to other elements. When such substitutions occur, the phase can have a range of possible compositions, depending on the amount of substitution that takes place. Such solids that can have various amounts of elemental substitution are called solid solutions. A good example of a solid solution mineral is the mineral olivine. The general chemical formula for olivine is $(Mg,Fe)_2SiO_4$. Since

Mg^{+2} and Fe^{+2} are about the same size and have the same charge, they may substitute for one another in the crystal structure of olivine. Thus olivine may have a composition anywhere between the pure Mg end member, forsterite (Mg_2SiO_4), and the pure Fe end member, fayalite (Fe_2SiO_4). When all compositions between two end members are possible, the solid solution is said to be a complete solid solution.

Another good example of a complete solid solution is displayed in the plagioclase feldspars. In this case the solid solution is between the end members albite ($NaAlSi_3O_8$) and anorthite ($CaAl_2Si_2O_8$). In order to maintain charge balance we cannot simply substitute Na+ for Ca^{+2}, so this solid solution is what is called a coupled solid solution. In this case Na+Si+4 is substituted for $Ca^{+2}Al^{+3}$ in the plagioclase structure to produce intermediate compositions of plagioclase.

Because the elements that substitute are not exactly the same size (they are similar in size) the amount of substitution is dependent on temperature and pressure and the solid solutions behave in a somewhat orderly fashion as illustrated below.

Since plagioclase is one of the most common minerals in the earth's crust, we will discuss the phase diagram for the plagioclase system. The phase relations in the plagioclase system are shown in Figure 3 at constant pressure equal to that of the atmosphere (atmospheric pressure is 1 bar). In Figure 3 the upper curve is called the liquidus and the lower curve is called the solidus. At temperatures above the liquidus everything is liquid, below the solidus everything is solid (crystals of plagioclase solid solution). At temperatures between the solidus and liquidus crystals of plagioclase solid solution coexist in equilibrium with liquid.

Pure albite melts (or crystallizes) at 1118°C, and pure anorthite melts (or crystallizes) at 1500°C. Note that any composition of plagioclase between the two end members melts or crystallizes over a range of temperatures unlike the pure end members which have only one melting point. Thus we can read from the diagram that a solid solution containing 50% albite and 50% anorthite

(Ab$_{50}$An$_{50}$) begins to melt at 1220°, point F, and the melting is complete at 1410°, point A. Inversely, if a melt of composition Ab$_{50}$An$_{50}$ is cooled it will begin to crystallize at 1410° and will be completely crystalline at 1220°.
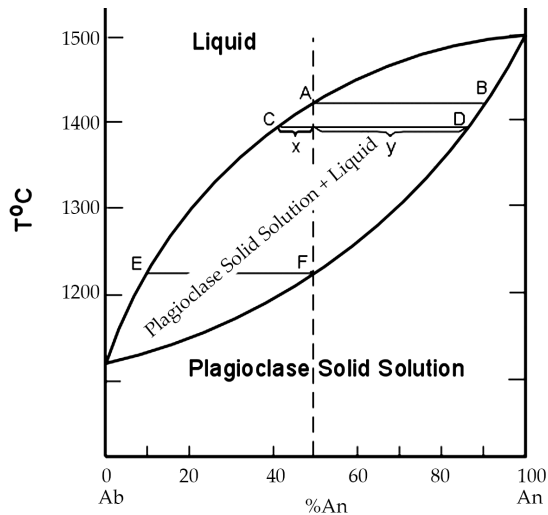
Figure 3.

We will now trace the crystallization history of composition X, which is Ab$_{50}$An$_{50}$. Composition X is completely liquid above the liquidus (above 1410°). Cooling to the liquidus at point A results in the crystallization of a small amount of plagioclase solid solution. The composition of this plagioclase can be found by drawing an isotherm (line of constant temperature, a horizontal line in this diagram) through the temperature 1410°. Where this isotherm intersects the solidus (at point B), the composition of the solid can be found by drawing a vertical line to the base of the diagram. Thus it is seen that the first crystals precipitated from composition X will have the composition Ab$_{10}$An$_{90}$. Note that in this diagram crystals that are in equilibrium with liquid will always be enriched in anorthite component relative to the liquid. As crystallization continues with lowering of temperature the composition of the plagioclase will change along the solidus, continually reacting with the liquid to produce crystals more enriched in the Ab component. Meanwhile, the composition of the liquid will change along the

liquidus, thus also becoming more enriched in the Ab component. At a temperature of 1395° the liquid composition will be at point C, while the solid composition will be at point D. Crystallization proceeds until a temperature of about 1220°, at which point the last remaining liquid will have a composition at E, and the solid will have a composition equal to the original starting composition at point F.

At this point all of the liquid will be consumed and the final crystalline product will have the composition $Ab_{50}An_{50}$.

During crystallization the proportion of the solid continually increases while that of the liquid continually decreases. Thus as the composition of the liquid becomes more sodic, approaching E, its volume steadily decreases. Thus it can be seen that the amount of liquid in equilibrium with the solid of composition F will be extremely small.

If at any point during the crystallization we wish to determine the amount of solid and liquid, we can apply the lever rule. As an example, we will determine the proportions of liquid and solid in the system at a temperature of 1395°. At this point, we measure the distances oC, oD, and CD. The percentages of liquid and solid are then given as follows:

% solid (with composition D) = [x/(x + y)] x 100

% liquid (with composition C) = [y/(x + y)] x 100

The foregoing discussion assumes that equilibrium is maintained throughout the course of crystallization. This means that with falling temperature and continuing crystallization, the earlier-formed, more calcic crystals must react continuously with the liquid to produce homogeneous crystals that will become continuously more enriched in the sodic component. If this equilibrium cannot be maintained, then fractional crystallization will take place.

We will distinguish between three contrasting conditions.
1.   In equilibrium crystallization, the crystals remain suspended in the melt, and cooling and crystallization

are slow enough to allow continuous, complete reaction between crystals and melt. The early formed crystals will, on cooling, react with the melt continuously and thereby gradually change their composition along the solidus from B to F, while simultaneously the liquid changes from A to E. In such circumstances the crystals will not change composition beyond F, and the end product is a homogeneous mixed crystal (solid solution) having the same composition as the initial melt.

2. Assume that the crystals are continuously removed from the melt, by sinking or some natural filtering process. Reaction of crystals with the melt is prevented, and the composition of the liquid will continue to change along the liquidus curve toward the sodic feldspar component. The only limit to this change of composition of the liquid is the composition of the pure Na feldspar, but the relative amount of very sodic liquid would be very small. As the liquid phase changed composition with continuing removal of crystals, the successively formed crystals would become continuously more sodic; the final product would be pure albite, but it would constitute a very small proportion of the initial amount.

3. If the crystals remain suspended in the liquid, but relatively rapid crystallization does not allow complete reaction between crystals and liquid, the effect will be somewhat different. In effect, failure to react completely partially removes the already formed crystals from the system. The melt becomes increasingly more sodic, and earlier formed more calcic crystals serve as nuclei on which increasingly more sodic feldspar crystallizes. The resulting crystal contain zones of differing composition; the inner zones being more calcic, and the outer zones more sodic. The bulk (average) composition of the zoned crystal is that of the initial system, but the range of composition between the inner and outer zones might theoretically be as large as from B to pure Ab in the example shown for composition X.

4.4.10 Exsolution

Many minerals that show complete solid solution at higher temperatures do not show such solid solution at lower temperatures. When this is the case, the phenomenon of exsolution occurs. Since solid solutions are really one mineral phase dissolved in another mineral phase to form a single mineral phase, exsolution implies that one or the other of the mineral phases in the solution must "exsolve" or come out of solution with the other mineral phase.

Figure 4 illustrates a phase diagram (much simplified) of the alkali feldspar system which exhibits such exsolution behavior at low temperatures. At high temperatures the diagram shows that albite (Ab) or $NaAlSi_3O_8$ and orthoclase (Or) or $KAlSi_3O_8$ form a complete solid solution series. This solid solution series is different from the plagioclase solid solution series only in that it has a minimum composition in the middle rather than at the composition of one of the pure end members. At temperatures just below the solidus, alkali feldspar solid solutions are stable. At lower temperatures, along the curve labeled "solvus" the solid solution is no longer stable.
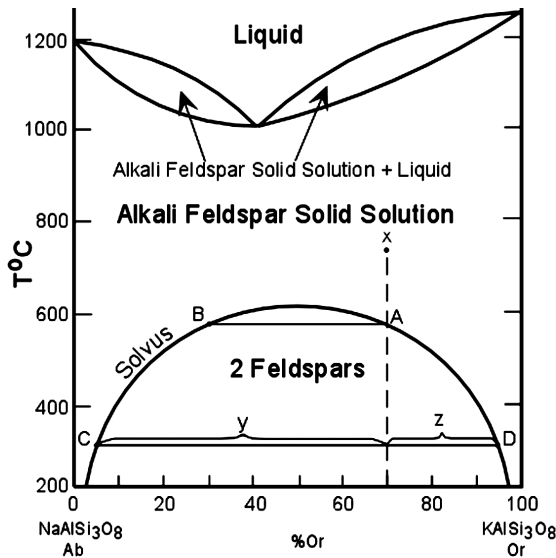

Figure 4.

In this case the exsolution phenomena occurs below the solidus and so is a "sub-solidus" reaction. In order to see what happens during exsolution we will examine what happens to a composition labeled X in Figure 4. We will start at a temperature of $750°$ in the region where alkali feldspar solid solutions are stable. At $750°$ the composition of the alkali feldspar solid solution is 70% orthoclase and 30% albite ($Or_{70}Ab_{30}$).

This solid solution remains stable with lowering of temperature until the temperature of the solvus is obtained at point A (a temperature of about $590°$). At this temperature the solid solution is no longer stable and begins to exsolve. The composition of coexisting exsolved phases can be found by drawing an isotherm until it intersects the solvus. Such an isotherm at $590°$ shows that at this temperature a solid solution having the composition of point B ($Or_{32}Ab_{68}$) coexists with an alkali feldspar solid solution with the composition of point A ($Or_{70}Ab_{30}$). With further lowering of temperature further exsolution occurs. At a temperature of 300o our original composition X has exsolved into two alkali feldspar solid solutions, one with the composition of point C and one with a composition of point D. To find the relative proportions or percentages of each of the solid solutions, the lever rule can once again be applied. For example at 300o for composition X the percentage of the albite-rich solid solution is [z/(z+y)] x 100, while that of the orthoclase-rich solid solution is [y/(z+y)] x 100. With further lowering of temperature all of the albite and orthoclase in the two solid solutions could exsolve completely to produce a pure albite phase and a pure orthoclase phase. Such complete exsolution does occur in nature, but only if the temperature is lowered very slowly. Complete exsolution is only common in metamorphic rocks. More often, especially in granitic rocks, the two exsolved phases do not separate as individual crystals, but occur as intergrown crystals with exsolution lamellae of one crystal occurring within the other crystal. In the alkali feldspars containing such exsolution lamellae the result is to produce a texture called perthitic or perthite.

4.5 PHASE TRANSITIONS

We witness and utilize changes of physical state, or phase transitions, in a great number of ways. As one example of global significance, consider the evaporation, condensation, freezing, and melting of water. These changes of state are essential aspects of our earth's water cycle as well as many other natural phenomena and technological processes of central importance to our lives. In this module, the essential aspects of phase transitions are explored.

4.5.1 Vaporization and Condensation

When a liquid vaporizes in a closed container, gas molecules cannot escape. As these gas phase molecules move randomly about, they will occasionally collide with the surface of the condensed phase, and in some cases, these collisions will result in the molecules re-entering the condensed phase. The change from the gas phase to the liquid is called condensation. When the rate of condensation becomes equal to the rate of vaporization, neither the amount of the liquid nor the amount of the vapor in the container changes. The vapor in the container is then said to be *in equilibrium* with the liquid. Keep in mind that this is not a static situation, as molecules are continually exchanged between the condensed and gaseous phases. Such is an example of a dynamic equilibrium, the status of a system in which reciprocal processes (for example, vaporization and condensation) occur at equal rates. The pressure exerted by the vapor in equilibrium with a liquid in a closed container at a given temperature is called the liquid's vapor pressure (or equilibrium vapor pressure). The area of the surface of the liquid in contact with a vapor and the size of the vessel have no effect on the vapor pressure, although they do affect the time required for the equilibrium to be reached. We can measure the vapor pressure of a liquid by placing a sample in a closed container, like that illustrated in Figure 1, and using a manometer to measure the increase in pressure that is due to the vapor in equilibrium with the condensed phase.

(a)   (b)   (c)
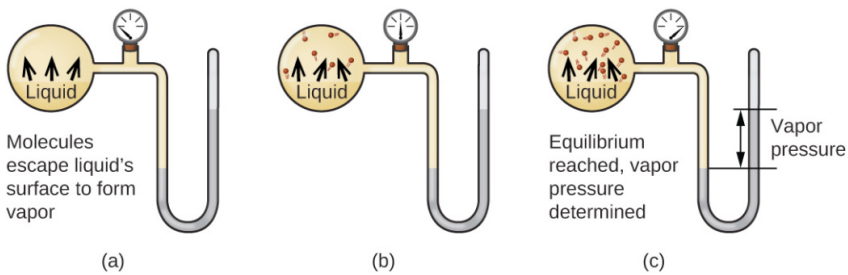
Figure 1: In a closed container, dynamic equilibrium is reached when (a) the rate of molecules escaping from the liquid to become the gas (b) increases and eventually (c) equals the rate of gas molecules entering the liquid. When this equilibrium is reached, the vapor pressure of the gas is constant, although the vaporization and condensation processes continue.

The chemical identities of the molecules in a liquid determine the types (and strengths) of intermolecular attractions possible; consequently, different substances will exhibit different equilibrium vapor pressures. Relatively strong intermolecular attractive forces will serve to impede vaporization as well as favoring "recapture" of gas-phase molecules when they collide with the liquid surface, resulting in a relatively low vapor pressure. Weak intermolecular attractions present less of a barrier to vaporization, and a reduced likelihood of gas recapture, yielding relatively high vapor pressures. The following example illustrates this dependence of vapor pressure on intermolecular attractive forces.

Example 1: explaining vapor pressure in terms of imfs

Given the shown structural formulas for these four compounds, explain their relative vapor pressures in terms of types and extents of IMFs:
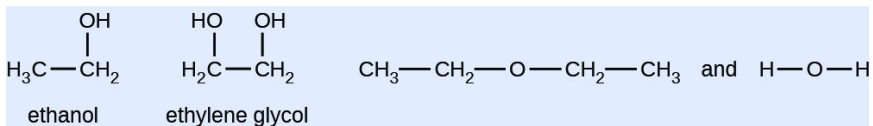
At 20 °C, the vapor pressures of several alcohols are given in this table. Explain these vapor pressures in terms of types and extents of IMFs for these alcohols:

| Compound	methanol CH_3OH	ethanol C_2H_5OH	propanol C_3H_7OH	butanol C_4H_9OH
Vapor Pressure at 25 °C	11.9 kPa	5.95 kPa	2.67 kPa	0.56 kPa

As temperature increases, the vapor pressure of a liquid also increases due to the increased average KE of its molecules. Recall that at any given temperature, the molecules of a substance experience a range of kinetic energies, with a certain fraction of molecules having a sufficient energy to overcome IMF and escape the liquid (vaporize). At a higher temperature, a greater fraction of molecules have enough energy to escape from the liquid, as shown in Figure 2. The escape of more molecules per unit of time and the greater average speed of the molecules that escape both contribute to the higher vapor pressure.
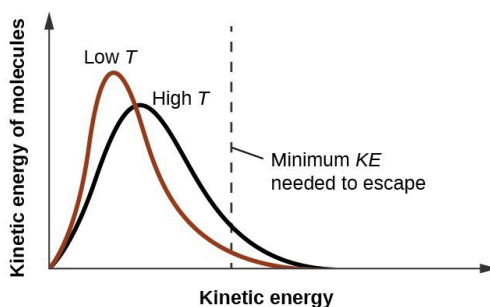
Figure 2: Temperature affects the distribution of kinetic energies for the molecules in a liquid. At the higher temperature, more molecules have the necessary kinetic energy, KE, to escape from the liquid into the gas phase.

4.5.2 Boiling Points

When the vapor pressure increases enough to equal the external atmospheric pressure, the liquid reaches its boiling point. The boiling point of a liquid is the temperature at which its equilibrium vapor pressure is equal to the pressure exerted on the liquid by its gaseous surroundings. For liquids in open containers,

this pressure is that due to the earth's atmosphere. The normal boiling point of a liquid is defined as its boiling point when surrounding pressure is equal to 1 atm (101.3 kPa). Figure 3 shows the variation in vapor pressure with temperature for several different substances. Considering the definition of boiling point, these curves may be seen as depicting the dependence of a liquid's boiling point on surrounding pressure.
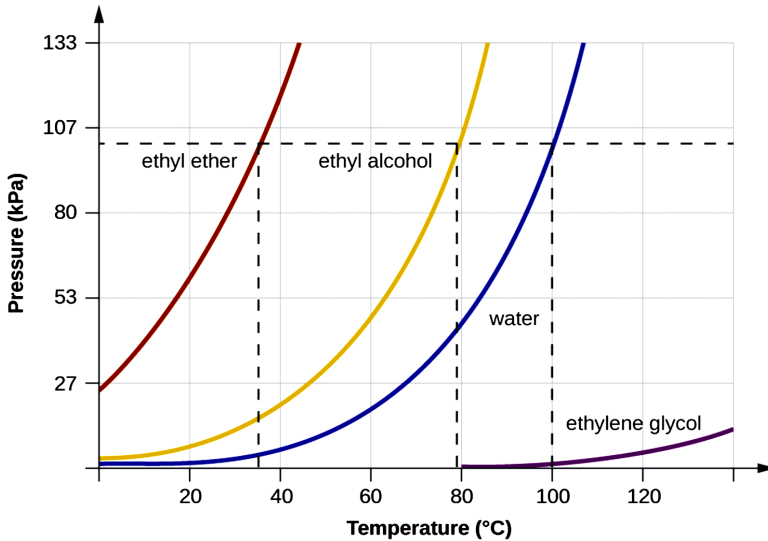
Figure 3: The boiling points of liquids are the temperatures at which their equilibrium vapor pressures equal the pressure of the surrounding atmosphere. Normal boiling points are those corresponding to a pressure of 1 atm (101.3 kPa.)

The quantitative relation between a substance's vapor pressure and its temperature is described by the Clausius-Clapeyron equation:

$$P = Ae^{-\Delta H_{vap}/RT}$$

where ΔH_{vap} is the enthalpy of vaporization for the liquid, R is the gas constant, and ln A is a constant whose value depends on the chemical identity of the substance. This equation is often rearranged into logarithmic form to yield the linear equation:

$$\ln P = \frac{\Delta H_{vap}}{RT} \ln A$$

This linear equation may be expressed in a two-point format that is convenient for use in various computations, as demonstrated in the example exercises that follow. If at temperature T_1, the vapor pressure is P_1, and at temperature T_2, the vapor pressure is T_2, the corresponding linear equations are:

$$\ln P_1 = \frac{\Delta H_{vap}}{RT_1} \ln A$$

and

$$\ln P_2 = \frac{\Delta H_{vap}}{RT_2} \ln A$$

Since the constant, $\ln A$, is the same, these two equations may be rearranged to isolate $\ln A$ and then set them equal to one another:

$$\ln P_1 + \frac{\Delta H_{vap}}{RT_1} = \ln P_2 + \frac{\Delta H_{vap}}{RT_2}$$

which can be combined into:

$$lp\left(\frac{P_2}{P_1}\right) = \frac{\Delta H_{vap}}{R}\left(\frac{1}{T_1} - \frac{1}{T_2}\right)$$

4.5.3 Enthalpy of Vaporization

Vaporization is an endothermic process. The cooling effect can be evident when you leave a swimming pool or a shower. When the water on your skin evaporates, it removes heat from your skin and causes you to feel cold. The energy change associated with the vaporization process is the enthalpy of vaporization, ΔH_{vap}. For example, the vaporization of water at standard temperature is represented by:

$$H_2O(l) \rightarrow H_2O(g) \qquad \Delta H_{vap} = 44.01 kJ \, / \, mol$$

the reverse of an endothermic process is exothermic. And so, the condensation of a gas releases heat:

$$H_2O(g) \rightarrow H_2O(l) \qquad \Delta H_{con} = \Delta H_{vap} = 44.01 kJ \, / \, mol$$

4.5.4 Melting and Freezing

When we heat a crystalline solid, we increase the average energy of its atoms, molecules, or ions and the solid gets hotter. At some point, the added energy becomes large enough to partially overcome the forces holding the molecules or ions of the solid in their fixed positions, and the solid begins the process of transitioning to the liquid state, or melting. At this point, the temperature of the solid stops rising, despite the continual input of heat, and it remains constant until all of the solid is melted. Only after all of the solid has melted will continued heating increase the temperature of the liquid (Figure 5).

(a)   (b)   (c)   (d)
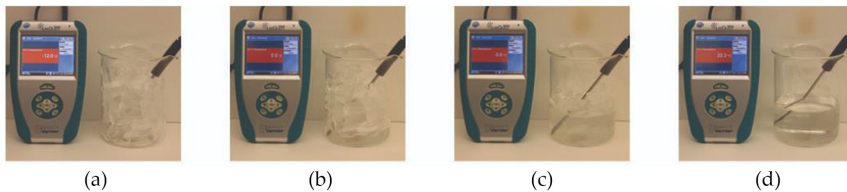
Figure 5: (a) This beaker of ice has a temperature of −12.0 °C. (b) After 10 minutes the ice has absorbed enough heat from the air to warm to 0 °C. A small amount has melted. (c) Thirty minutes later, the ice has absorbed more heat, but its temperature is still 0 °C. The ice melts without changing its temperature. (d) Only after all the ice has melted does the heat absorbed cause the temperature to increase to 22.2 °C.

If we stop heating during melting and place the mixture of solid and liquid in a perfectly insulated container so no heat can enter or escape, the solid and liquid phases remain in equilibrium. This is almost the situation with a mixture of ice and water in a very

good thermos bottle; almost no heat gets in or out, and the mixture of solid ice and liquid water remains for hours. In a mixture of solid and liquid at equilibrium, the reciprocal process of melting and freezing occur at equal rates, and the quantities of solid and liquid therefore remain constant. The temperature at which the solid and liquid phases of a given substance are in equilibrium is called the melting point of the solid or the freezing point of the liquid. Use of one term or the other is normally dictated by the direction of the phase transition being considered, for example, solid to liquid (melting) or liquid to solid (freezing).

The enthalpy of fusion and the melting point of a crystalline solid depend on the strength of the attractive forces between the units present in the crystal. Molecules with weak attractive forces form crystals with low melting points. Crystals consisting of particles with stronger attractive forces melt at higher temperatures.

The amount of heat required to change one mole of a substance from the solid state to the liquid state is the enthalpy of fusion, ΔH_{fus} of the substance. The enthalpy of fusion of ice is 6.0 kJ/mol at 0 °C. Fusion (melting) is an endothermic process:

$$H_2O(s) \rightarrow H_2O(l) \quad \Delta H_{fus} = 6.01 kJ / mol$$
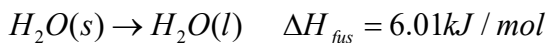
The reciprocal process, freezing, is an exothermic process whose enthalpy change is −6.0 kJ/mol at 0 °C:

$$H_2O(l) \rightarrow H_2O(s) \quad \Delta H_{frz} = \Delta H_{fus} = -6.01 kJ / mol$$
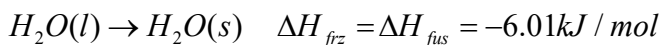
4.5.5 Sublimation and Deposition

Some solids can transition directly into the gaseous state, bypassing the liquid state, via a process known as sublimation. At room temperature and standard pressure, a piece of dry ice (solid CO_2) sublimes, appearing to gradually disappear without ever forming any liquid. Snow and ice sublime at temperatures below the melting point of water, a slow process that may be accelerated by winds and the reduced atmospheric pressures at high altitudes. When

solid iodine is warmed, the solid sublimes and a vivid purple vapor forms (Figure 6). The reverse of sublimation is called deposition, a process in which gaseous substances condense directly into the solid state, bypassing the liquid state. The formation of frost is an example of deposition.

Like vaporization, the process of sublimation requires an input of energy to overcome intermolecular attractions. The enthalpy of sublimation, ΔH_{sub}, is the energy required to convert one mole of a substance from the solid to the gaseous state. For example, the sublimation of carbon dioxide is represented by:

$$CO_2(s) \rightarrow CO_2(g) \quad \Delta H_{sub} = 26.1 kJ / mol$$
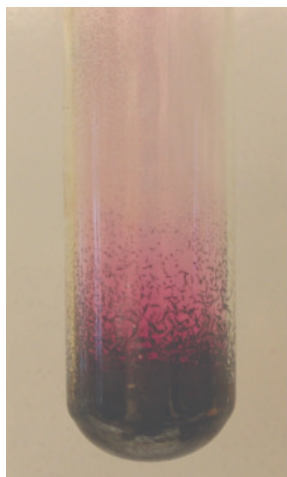
Figure 6: Sublimation of solid iodine in the bottom of the tube produces a purple gas that subsequently deposits as solid iodine on the colder part of the tube above.

Likewise, the enthalpy change for the reverse process of deposition is equal in magnitude but opposite in sign to that for sublimation:

$$CO_2(g) \rightarrow CO_2(s) \quad \Delta H_{dep} = \Delta H_{sub} = -26.1 kJ / mol$$
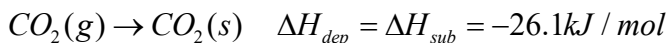
Consider the extent to which intermolecular attractions must be overcome to achieve a given phase transition. Converting a solid into a liquid requires that these attractions be only partially

overcome; transition to the gaseous state requires that they be completely overcome. As a result, the enthalpy of fusion for a substance is less than its enthalpy of vaporization. This same logic can be used to derive an approximate relation between the enthalpies of all phase changes for a given substance. Though not an entirely accurate description, sublimation may be conveniently modeled as a sequential two-step process of melting followed by vaporization in order to apply Hess's Law. Viewed in this manner, the enthalpy of sublimation for a substance may be estimated as the sum of its enthalpies of fusion and vaporization, as illustrated in Figure 7. For example:

$solid \rightarrow liquid \qquad \Delta H_{fus}$

$liquid \rightarrow gas \qquad \Delta H_{vap}$

$$solid \rightarrow gas \qquad \Delta H_{sub} = \Delta H_{fus} + \Delta H_{vap}$$
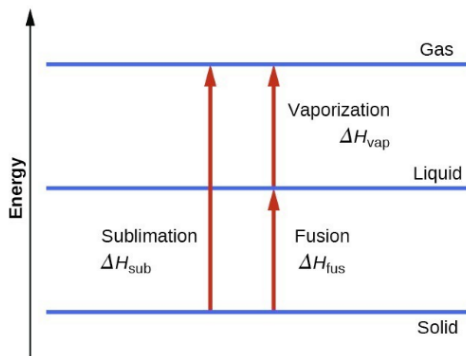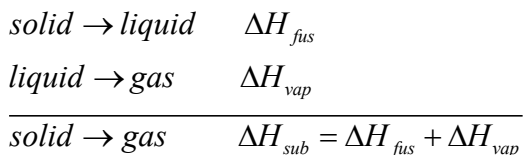
Figure 7: For a given substance, the sum of its enthalpy of fusion and enthalpy of vaporization is approximately equal to its enthalpy of sublimation.

4.5.6 Heating and Cooling Curves

In the chapter on thermochemistry, the relation between the amount of heat absorbed or related by a substance, q, and its accompanying temperature change, ΔT, was introduced:

$q = mc\Delta T$

where m is the mass of the substance and c is its specific heat. The relation applies to matter being heated or cooled, but not undergoing a change in state. When a substance being heated or cooled reaches a temperature corresponding to one of its phase transitions, further gain or loss of heat is a result of diminishing or enhancing intermolecular attractions, instead of increasing or decreasing molecular kinetic energies. While a substance is undergoing a change in state, its temperature remains constant. Figure 8 shows a typical heating curve.

Consider the example of heating a pot of water to boiling. A stove burner will supply heat at a roughly constant rate; initially, this heat serves to increase the water's temperature. When the water reaches its boiling point, the temperature remains constant despite the continued input of heat from the stove burner. This same temperature is maintained by the water as long as it is boiling. If the burner setting is increased to provide heat at a greater rate, the water temperature does not rise, but instead the boiling becomes more vigorous (rapid). This behavior is observed for other phase transitions as well: For example, temperature remains constant while the change of state is in progress.
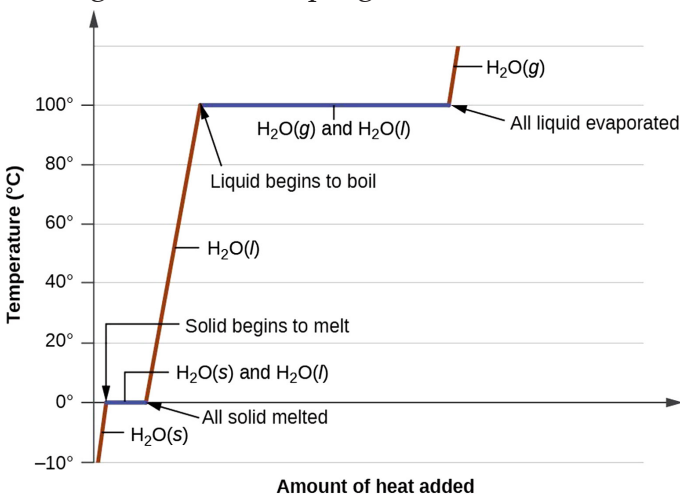
Figure 8: A typical heating curve for a substance depicts changes in temperature that result as the substance absorbs increasing amounts of heat. Plateaus in the curve (regions of constant temperature) are exhibited when the substance undergoes phase transitions.

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PHASE EQUILIBRIA IN SINGLE COMPONENT SYSTEMS

INTRODUCTION

Phase equilibria is the application of the principles of thermodynamics to the study of equilibrium relationships within or between phases, corresponding to homogeneous and heterogeneous phase equilibria, respectively. These phases may be minerals within a rock, a fluid percolating through the pore space of a sediment, or a gas, or a combination of these. The study of phase equilibria is used to constrain the stability of individual minerals and assemblages of minerals in pressure–temperature–composition space, to obtain estimates of pressure or temperature of equilibration of metamorphic and igneous rocks, and to evaluate conditions of origin of various magmas.

The study of phase equilibria is firmly rooted in thermodynamics as formulated by J.W. Gibbs in the late 19th century. In phase

equilibria, the problem is to determine the conditions at which a given portion of the universe – a system – is at equilibrium, with minimum energy. If the thermodynamic properties of the system, including the Gibbs free energy, enthalpy, entropy, molar volume, heat capacity, isothermal compressibility, thermal expansivity and the activity–composition relationships for all multi-component phases in the system, are all known, then the phase equilibria may be calculated. In practice, however, some of this information is usually lacking, and so techniques for the graphical analysis of phase equilibria have been developed to allow evaluation of heterogeneous equilibria based on limited experimental data.

Here, we shall first define some terms to provide a common terminology. Second, we shall look at the fundamental constraints on phase equilibria provided by thermodynamics by applying the phase rule and by looking at the inter-relationship of free energy, pressure, temperature, and composition that gives rise to phase diagrams. Finally, we will examine graphical analysis of phase equilibria, concentrating on Schreinemakers' analysis of the arrangement of univariant curves about an invariant point.

5.1 DEFINITIONS

The portion of the universe under consideration. The choice of how the system is defined is the observer's choice. Several types of systems are commonly defined. An isolated system is one in which no energy or matter is transferred into or out of the system. A closed system is one in which energy but no matter may be transferred into or out of the system. An open system is one in which both energy and matter may be transferred into or out of the system.

5.1.1 Component (c)

Components make up the minimum set of chemical constituents necessary to describe the chemical variation in the system. These constituents need not correspond to physical entities such as

mineral endmembers. The selection of components must allow for all possible chemical variations in phases in the system. For example, if the system is a crystal of potassium feldspar, $KAISi_3O_8$, at atmospheric pressure, then one component ($c = 1$) will suffice if temperatures are less than ⊚1150°C. At ⊚1150°C, the crystal will melt incongruently to a SiO_2– enriched liquid and crystalline leucite ($KAISi_2O_6$). At this point, two components ($c = 2$) are necessary to describe the chemical variation in the system. These two components could be $KAISi_2O_6$ and SiO_2; $KAIO_2$ and SiO_2; $KAIO_2$ and $Si(KAI)_{-1}$; or $KAISi_3O_8$ and either $KAIO_2$ or SiO_2, or any other combination that encompasses the chemical variability present in the system.

5.1.2 Phase (p)

A chemically homogeneous, uniform portion of the system that is mechanically separable from the rest of the system, at least in principle. Each phase is bounded by physical interfaces. Each phase may occur in different places in a system. For example, if the system is a rock containing quartz and feldspar crystals, all of the quartz crystals constitute a single phase. If all the feldspar crystals have the same composition they too would be a single phase. Another example is a mixture of oil and water at room temperature, two liquids that do not intermix but rather remain immiscible, although the scale of physical domains may be small. All the droplets of oil are the same phase, as is all of the surrounding water phase.

5.1.3 State Variable

A property of a system that has a fixed value at equilibrium. Extensive state variables are those that depend on the amount of matter in the system, such as volume and total internal energy. Intensive state variables are those that are independent of the amount of matter, and include density, temperature, pressure, concentration, among others. Extensive state variables may be converted to intensive state variables by dividing by the number

of moles (or grams) of material, to calculate molar (or specific) volume from total volume, for example.

5.1.4 Variance or Degrees Of Freedom (f)

The number of independent intensive variables that must be fixed to define uniquely the equilibrium state. If a system has no degrees of freedom ($f = 0$), it is invariant; if it has one degree of freedom ($f = 1$), it is univariant; and if it has two degrees of freedom ($f = 2$), it is divariant or bivariant.

5.1.5 Gibbs phase rule

The phase rule is an elegant, simple equation that results from the conditions of equilibrium between phases in a system. The phase rule may be expressed as:

$$f+p=c+2 \tag{1}$$

5.2 HOMOGENEOUS PHASE EQUILIBRIA

Equilibria within single phases involves the thermodynamic requirements for equilibrium, which are that the pressure and temperature must be uniform throughout the phase, and the free energy of the phase must be at a minimum. To formulate the free energy for the phase as a function of composition, pressure, and temperature, a model for the activities of the components of the phase must be formulated. Different aspects of homogeneous phase equilibria are considered in the entries under Activity and activity coefficients, Aqueous solutions, and Equilibrium.

5.2.1 Heterogeneous Phase Equilibria

Equilibria between phases is the realm of heterogeneous phase equilibria, and phase relationships in systems of increasing complexity will be considered in turn.

One-component Systems

From the phase rule, a one-component system may contain one, two or three co-existing phases, with variances of two, one and zero, respectively. As an example, consider the system with the single component SiO_2 (Figure 1). The $P–T$ diagram consists of three fields, labeled coesite, low quartz and high quartz, respectively, which represent the stability fields for these three polymorphs of SiO_2. Application of the phase rule to these fields, with $c = 1$ and $p = 1$, yields a variance of two, which requires that both the intensive variables pressure and temperature be specified to determine the state of the system. Graphically, this may be visualized by looking at point A (Figure 1), which is located in the divariant low quartz field. From A, both pressure and temperature may be varied independently (as shown by the arrows) and the system would remain single phase, with only low quartz present. In order to know exactly where A is requires both pressure and temperature to be specified.
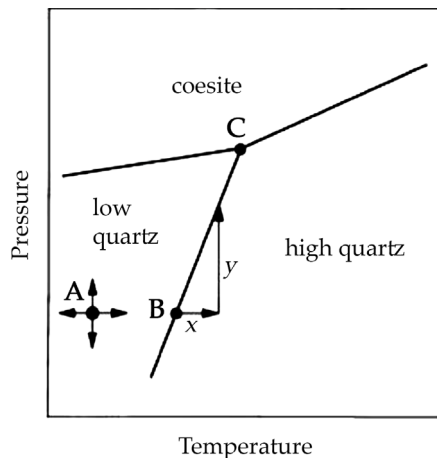
Figure 1: Schematic pressure–temperature projection of phase relations in the system SiO_2. Points A, B and C are discussed in the text.

In contrast, along the curve separating the fields of low quartz and high quartz, these two phases co-exist. Therefore, this curve represents the conditions of pressure and temperature at which these two phases are in equilibrium. Application of the phase

rule with $c = 1$ and $p = 2$ yields a variance of one, which means that only one intensive variable need be specified to define the system of co-existing low quartz and high quartz completely. This situation may be illustrated graphically by considering the point B on the univariant curve (Figure 1). A change in T of x requires a corresponding change in P of y to remain on the equilibrium boundary as required to preserve the co-existence of low quartz and high quartz. Therefore, only one of the intensive variables is independent, with the other being a dependent variable.

For the system to be invariant ($f = 0$) requires three phases co-existing in equilibrium. Such a situation exists at point C (Figure 1), where low quartz, high quartz, and coesite all co-exist. In this situation, neither pressure nor temperature may be specified independently; they are dictated by the pressure and temperature of the unique point on the P–T diagram where the system of three phases can exist.

Two-component (binary) Systems

Systems with two components introduce composition as a variable, with the compositions of all phases constrained to be co-linear in composition space. Phases may either have fixed composition (e.g. quartz SiO_2) or variable composition (e.g. plagioclase, with composition between $NaAISi_3O_8$ and $CaAI_2Si_2O_8$). Three dimensions are required to illustrate the phase relationships in terms of P, T, and X (composition).

Application of the phase rule leads to four possible situations:

- $f = 0$ (invariant), with four phases co-existing
- $f = 1$ (univariant), with three phases co-existing
- $f = 2$ (divariant), with two phases co-existing
- $f = 3$, with one phase present. Analogous to the one-component case, invariant situations plot as points on P–T projections, univariant situations as lines, and $f \geq 2$ as fields.

Three-component (ternary) Systems

Systems with three components introduce another compositional variable. The compositions of all phases, either fixed or variable in composition, must be co-planar in a three-component composition space. It is customary to illustrate these compositional relationships in an equilateral triangle, with each component occupying an apex (Figure 2). Because of the added compositional variable, four dimensions are required to illustrate the phase relationships in terms of *P, T,* and composition. Projections and sections of the phase relationships into three or two dimensions are therefore customary.

Application of the phase rule leads to five possible situations:

- $f = 0$ (invariant), with five phases co-existing
- $f = 1$ (univariant), with four phases co-existing
- $f = 2$ (divariant), with three phases co-existing
- $f = 3$, with two phases present, and
- $f = 4$, with one phase present. In *P–T* projection, invariant situations plot as points on *P–T* projections, univariant reactions as lines, and $f \geq 2$ as fields
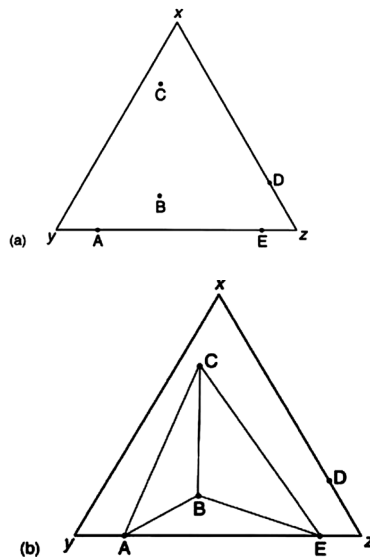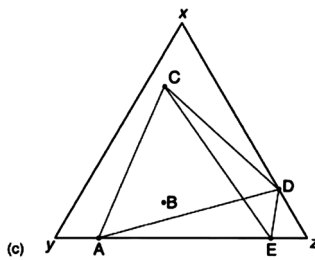
Figure 2: (a) Ternary composition space represented with an equilateral triangle. Components of the system are *x, y,* and *z.* Phases present are A, B, C, D, E. (b) Tielines for the eutectic-like ternary reaction A + C + E = B in the system *x, y, z.* (c) Tielines for the join-crossing trenary reaction A + D = C + E in the system *x, y, z.*

The possible univariant reactions are of two types, depending on the compositions of the phases involved. The first type is a eutectic-like reaction (also called a terminal stability reaction) such as: A + C + E = B (Figure 2b). In this type of reaction, the composition of the terminal phase (B) lies in the interior of the triangle defined by the compositions of the other three phases. The other type of reaction is a joint–crossing reaction such as: A + D = C + E (Figure 2c). In this reaction, the composition of the fourth phase lies exterior to the triangle formed by the other three phases.

Free energy diagrams in three-component systems

If one or more phases have variable compositions (solid or liquid solutions), the equilibrium case occurs when the planes defined by the free energies of the phases of fixed composition are tangential to the curved surfaces representing the free energies of the variable composition phases.

Systems with four or more components

Four components require three dimensions (and considerable artistic talent) to portray the compositional relationships alone. It is customary to represent the composition space with a terahedron, with each component represented at an apex. Often, the

compositions will be projected from one component apex onto an equilateral triangle to facilitate representation in two dimensions. From the phase rule, six phases co-exist at an invariant point, and five phases are involved in univariant reactions.

The two types of univariant reactions discussed above for ternary systems have analogs in quaternary systems. The eutectic-like reaction has the composition of the fifth phase interior to the polyhedron whose apices are the compositions of the other four phases. Algebraically, this type of reaction would be expressed: A + B + C + D = E. The join-crossing reaction would have the composition of the fifth phase exterior to the polyhedron whose apices are the compositions of the other four phases. Algebrically, the reaction stoichiometry would be A + B + C = D + E. Because one join that is being crossed is a three-phase join (A + B + C in the example above; geometrically a plane) this type of reaction is referred to as a plane-piercing reaction.

The principles outlined in the previous sections hold equally well for systems with more components, with the added complexity in illustrating or conceptualizing the relationships between phases. For these reasons, algebraic or analytical techniques, rather than graphical, are used for these systems.

The arrangement of univariant curves about an invariant point

For a system of c components, $c + 2$ phases co-exist at an invariant point. From this point, $c + 2$ univariant curves radiate outward in variable space. F. A. Schreinemakers, in a series of articles from 1915 to 1925, developed a method for determining systematically the arrangement of these univariant curves requiring only the compositions of the $c + 2$ phases co-existing at the invariant point.

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1915 to 1925, developed a method for determining systematically the arrangement of these univariant curves requiring only the compositions of the $c + 2$ phases co-existing at the invariant point.

Terminology

Each univariant reaction is denoted by the phase not participating in the reaction, surrounded by parentheses. In a similar fashion, divariant fields are denoted by the phases not present. For example, in the binary system illustrated in Figure 3, the reaction $A + C = B$ would be denoted (D), and the divariant assemblage $A + C$ would be denoted by (B, D).

Components: x, y
Phases: A, B, C, D

x A   B   C   D y
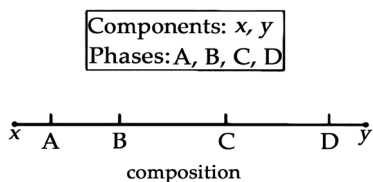
composition

Figure 3: The binary system x, y with the compositions of phases A, B, C, and D plotted. See text for discussion.

These univariant curves would represent the reactions:

- $B + D = C$ (A)
- $A + D = C$ (B)
- $A + D = B$ (C)
- $A + C = B$ (D) and the divariant assemblages would be:
- $A + B$ (C, D)
- $A + C$ (B, D)
- $A + D$ (B, C)
- $B + C$ (A, D)
- $B + D$ (A, C)
- $C + D$ (A, B) Several rules summarize Schreinemakers' method.

Rule 1 (the fundamental postulate)

A univariant curve, either stable or metastable, separates two divariant assemblages. On one side of this curve, one of the two divariant assemblages is more stable than the other assemblage. On the other side of the curve, the relative stabilities of the two assemblages are reversed.

This rule may be understood readily by considering the free energy surfaces (or curves) for the divariant assemblages. Returning to the simple one-component case of SiO_2 (Figure 4a), three univariant reactions are labeled (cs), (lq) and (hq), which represent coesite, low quartz, and high quartz, respectively. The reaction (hq) separates the divariant assemblages of coesite and low quartz. In the missing-phase notation, these divariant assemblages are (lq, hq) and (hq, cs) respectively. At P_1 (Figure 4b), coesite is more stable (i.e. has a lower free energy) than is low quartz at $T < T_1$. At $T > T_1$, the relative stabilities are reversed.
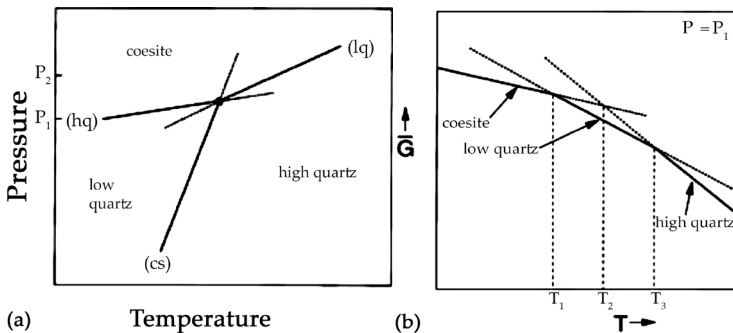
Figure 4: (a) Schematic P–T projection for the system SiO_2. The univariant reactions have been labeled with the 'missing-phase' notation. (b) Schematic $\bar{G}$ –T diagram corresponding to pressure P_1 of (a).

The logic applies equally well to metastable reactions. Consider the reaction (lq), coesite = high quartz, which is metastable at P_1. Coesite is more stable (less metastable) than is high quartz at $T < T_2$, high quartz is more stable (less metastable) than is coesite at $T > T_2$. In both situations, both coesite and high quartz are metastable relative to low quartz.

Rule 2

A divariant assemblage (A, B) occurs in a region of ≤180° about the invariant point between the univariant curves (A) and (B). The consequence of this rule is that the angle between neighboring stable univariant curves is ≤180°. This rule is used extensively to determine the stable fields of divariant assemblages.

Rule 3

Any divariant assemblage that extends across the univariant curve (X) contains the phase X. This rule holds for both stable and metastable curves.

Use of Schreinemakers' analysis in arranging univariant curves

An extremely powerful method for quickly and accurately deriving the arrangement of univariant curves about an invariant point uses Schreinemakers' system of notation that capitalizes on the correspondence between the stoichiometry of the univariant reactions and the arrangement of the corresponding univariant curves. This point is best illustrated by example. In the binary system x–y (Figure 3a), the reaction (D) may be written $A + C = B$.

The steps of the procedure for determining the arrangement of univariant reactions about an invariant point may be illustrated for a binary system. The same procedure applies to systems with more components.

- Write the reactions and the corresponding univariant schemes. From Figure 3, we see that the reactions are:

1. (A)

    $B + D = C$

2. (B)

    $A + D = C$

3. (C)

    $A + D = B$

4. (D)

A + C = B and the corresponding univariant schemes are:

(B)(D)|(A)|(C)
(A)(D)|(B)|(C)
(A)(D)|(C)|(B)
(A)(C)|(D)|(B)

- Begin by drawing (A), and indicate allowable locations for (B), (D) and (C) as shown by the arcs in Figure 5a.

(a) (A)

(b) (A)

(b) (A)

(c) (A)

(d) (A)
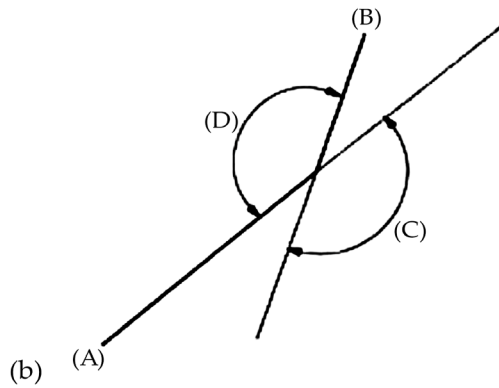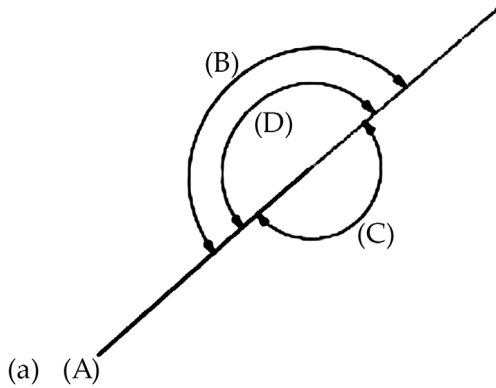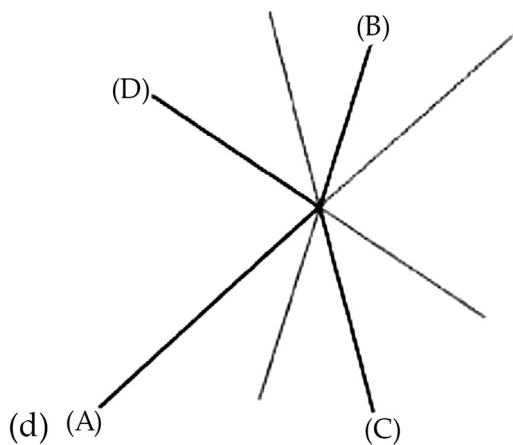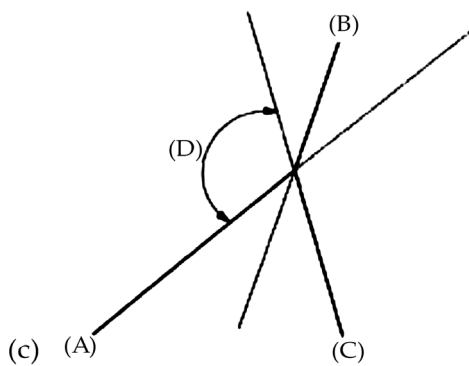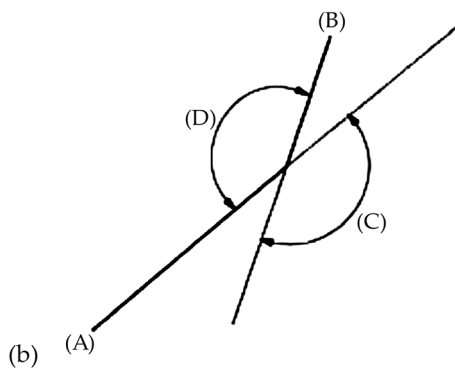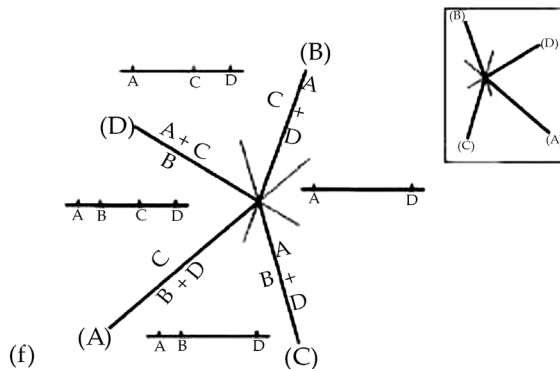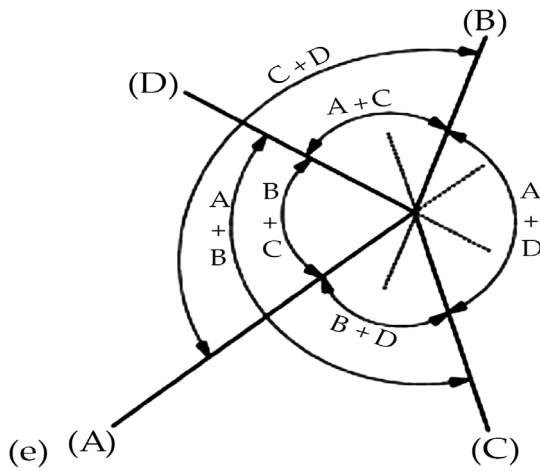
Figure 5: Construction of univariant curves about an invariant point for a binary system.

- Draw (B) in its permissible sector (Figure 5b). Using the univariant scheme for (B), narrow down the allowable locations for (C) and (D).
- Draw (C) in its permissible sector (Figure 5c), between the metastable extensions of (A) and (B). Using the univariant scheme for (C), narrow down the allowable sector for (D) to between the stable part of (A) and the metastable extension of (C).
- Draw (D) (Figure 5d).

- Indicate the fields of stability for the six divariant assemblages:

Assemblage	Missing-phase notation	Stable between univariant curves
A + B	(C, D)	(C), (D)
A + C	(B, D)	(B), (D)
A + D	(B, C)	(B), (C)
B + C	(A, D)	(A), (D)
B + D	(A, C)	(A), (C)
C + D	(A, B)	(A), (B)

as shown in Figure 5e.

Labeling the univariant curves with the appropriate reactions is now straightforward, because the divariant (two-phase) assemblage involved in each reaction is stable only on one side of the reaction. This labeling, and the use of the compositional join rather than arrows to represent permissible divariant assemblages, cleans up the diagram and yields the finished product (Figure 5f). Note that two mirror image (enantiomorphic) possibilities exist (Figure 5f and inset), and selection of the correct one, as well as the correct orientation in P–T space, requires additional information.

5.3 APPLICATION OF SCHREINEMAKERS' ANALYSIS TO BINARY SYSTEMS

The example worked above illustrates the principles of the application of this method to binary systems. A complication is introduced by degeneracy, where the compositions of two of the phases are the same. The logic outlined above still applies, but two of the unvariant reactions overlap in either their stable portions, or such that the stable portion of one overlaps with the metastable extension of the other. Two examples of such degenerate situations are illustrated in Figure 6.
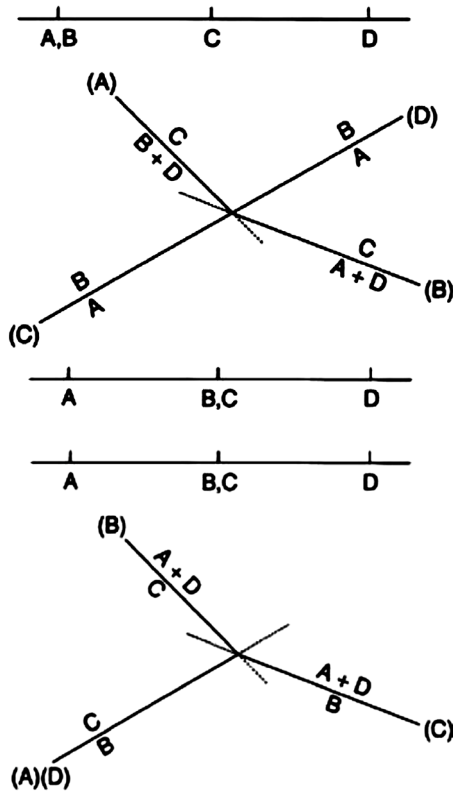
Figure 6: Two possible configurations of univariant curves about invariant points in binary systems, illustrating the effect of compositional degeneracy (polymorphism).

5.4 APPLICATIONS OF SCHREINEMAKERS' ANALYSIS TO TERNARY SYSTEMS

In a ternary system, the five phases that co-exist at the invariant point are co-planar in composition space (Figure 2a). In the general case, the system is defined by three components x, y and z, and contains phases A, B, C, D, E all with differing x/y or x/z. From the invariant point at which A + B + C + D + E co-exist, five univariant reactions, each involving four phases, will radiate.

In general, there are three possible (non-degenerate) compositional arrays of five phases (Figure 7). Each of these arrays generates a different arrangement of univariant reactions about the invariant point (Figure 7). In each case, only one of the enantiomorphic pairs is illustrated.
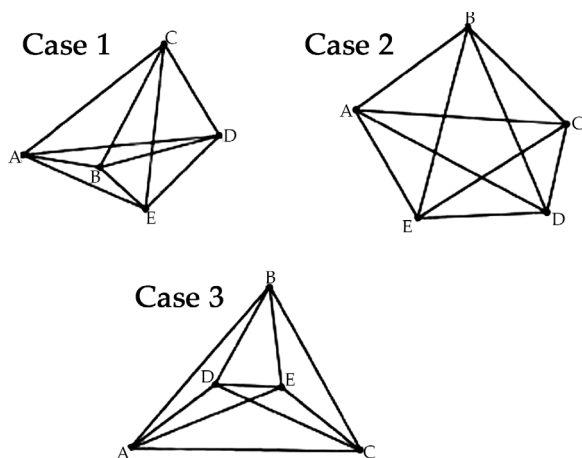
Figure 7: Ternary composition space, illustrating the three possible (non-degenerate) arrangements of five phases that co-exist at an invariant point.
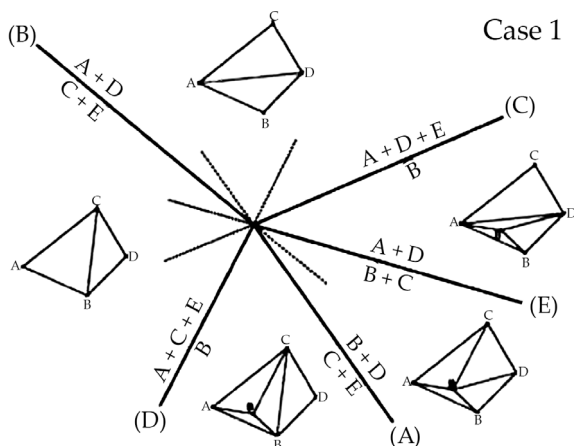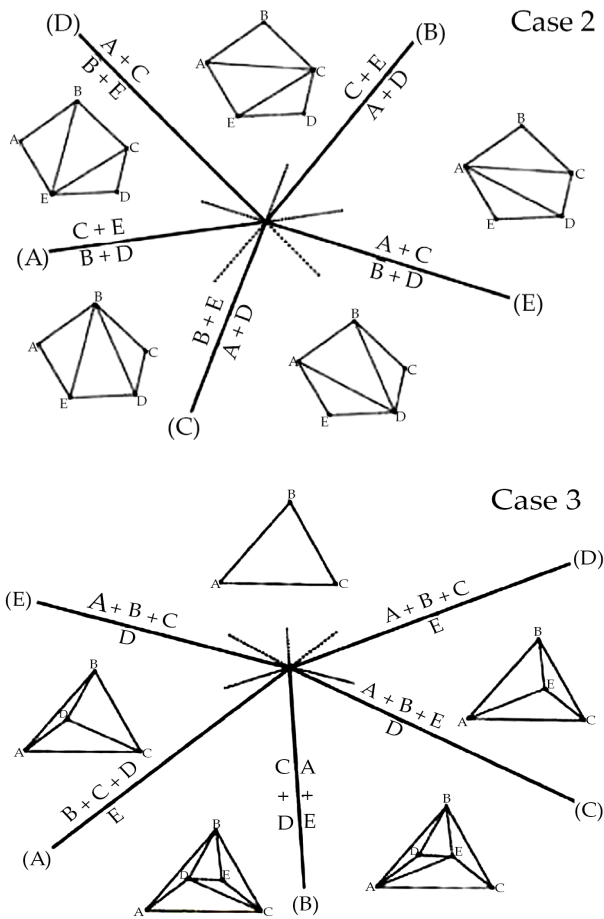
Figure 7: Arrangements of univariant curves about invariant points corresponding to the three different compositional situations in Figure P24. Only one of each enantiomorphic pair is illustrated for each case.

Degeneracy of two types is possible in ternary (and higher-order) systems. One type, polymorphism, is analogous to the case considered for the binary system (Figure 6). The other type is generated when the compositions of three (or more) of the phases involved in the invariant point are co-linear. This co-linearity means that these three phases are a binary subsystem within the ternary. Degeneracy of either type leads to coincidence of two, or more, of the univariant reactions, which then coincide, superimposing either stable portions (analogous to the binary case

illustrated in Figure 6b), or the stable portion of one overlapping the metastable portion of the other (Figure 6a). The 'cookbook' approach outlined above works equally well for degenerate situations as for non-degenerate ones, as long as the coincidence of some of the univariant curves is borne in mind. This coincidence is obvious immediately upon writing the reactions. For the example shown in Figure 8, the reactions are:
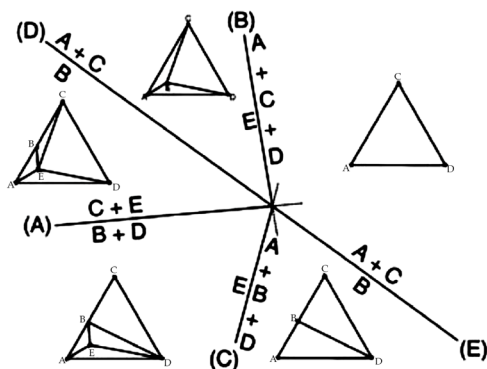
Figure 8: Example of the arrangement of univariant curves about an invariant point in a ternary system with a degeneracy wherein three phases are co-linear in composition spa

The study of phase equilibria is essential to much of petrology and geochemistry. The ability to analyze phase stabilities graphically provides a powerful tool in constraining natural systems. The recent progress in formulating internally consistent thermodynamic databases has not eliminated the need for the ability to analyze a phase diagram, differentiate between stable and metastable equilibria, and ensure that the phase diagram is thermodynamically valid.

5.5 FOUR-PHASE COEXISTENCE IN A SINGLE-COMPONENT SYSTEM

For different phases to coexist in equilibrium at constant temperature T and pressure P, the condition of equal chemical potential μ must be satisfied. This condition dictates that, for a

single-component system, the maximum number of phases that can coexist is three. Historically this is known as the Gibbs phase rule, and is one of the oldest and venerable rules of thermodynamics. Here we make use of the fact that, by varying model parameters, the Gibbs phase rule can be generalized so that four phases can coexist even in single-component systems. To systematically search for the quadruple point, we use a monoatomic system interacting with a Stillinger–Weber potential with variable tetrahedrality. Our study indicates that the quadruple point provides flexibility in controlling multiple equilibrium phases and may be realized in systems with tunable interactions, which are nowadays feasible in several soft matter systems such as patchy colloids.

Introduction

When different phases are in thermodynamic equilibrium with each other at constant temperature T and pressure P, the chemical potentials of the phases must be equal. The number of equality relationships determines the number of degrees of freedom F. This leads to the famous Gibbs phase rule1: F=C−N+2, where C is the number of chemically independent constituents of the system, and N is the number of phases. The rule should be valid, provided that the equilibrium between phases is not influenced by external fields and there is no spatial constraint on the phases. The latter condition is known to be violated for coherent solids2. This rule tells us that for a pure substance, it is only possible that three phases can exist together in equilibrium (N=3). For a one-component system, there are no degrees of freedom (F=0) when there are three phases (A, B and C), and the three-phase mixture can only exist at a single temperature and pressure, which is known as a triple point. The two equations $\mu A(T, P)=\mu B(T, P)=\mu C(T, P)$ are sufficient to uniquely determine the two thermodynamic variables, T and P. Four-phase coexistence should then be absent, as three chemical potential equations admit no solutions when there are only two independent variables T and P. Mathematically, however, this does not necessarily rule out the possibility that the set of equations may be solved in a special case. Here we seek such a possibility

in a systematic manner by tuning the interaction potential, or the Hamiltonian of the system. Extending the dimensionality of the system will allow us to investigate what are the conditions for the existence of a quadruple point.

The presence of a point where different phases coexist provides an interesting possibility of switching materials properties, including electric, magnetic, optical and mechanical properties, by a weak thermodynamic perturbation such as stressing or heating/cooling. The technological importance of a triple point has recently been shown for a popular candidate material for ultrafast optical and electrical switching applications, vanadium oxide (VO2): it has been revealed that the well-known metal-insulator transition in this material actually takes place exactly at the triple point. Large piezoelectricity near a morphotropic phase boundary is another important example of the importance of multi-phase coexistence. In these systems, structural transformations in lattice order are coupled with other orders such as dipole, spin, charge and orbital, which can be used for applications such as electromechanical or magnetoelectronic devices. Although the role of multi-phase coexistence in the ease of the transition is not so clear, the minimization of the volume change associated with a phase transition may be realized by combined nucleation of two phases with different signs of the volume change on the transition, which has been reported for a transition near a ferroelectric– anitiferroelectric–paraelectric triple point. So, the presence of a multiple point may provide a novel kinetic pathway of phase transition, for which the barrier for phase transformation is much lower than an ordinary phase transition between two phases. Thus, the fundamental understanding of multiple-phase coexistence is not only of scientific interest but also of technological importance.

To study the basics of multi-phase coexistence, we need a model system that shows rich polymorphism. In this context, it is well known that water exhibits a rich variety of crystal polymorphs (at least, 16 types of crystals). Motivated by this, here we study systems interacting with tetrahedral interactions (for example, covalent bonding and hydrogen bonding). Tetrahedral interactions are

the most important category of directional interactions found in nature, both in terms of abundance, and in terms of unique physical properties. They are ubiquitous in terrestrial and biological environments, and fundamental for technological applications. The disordered (liquid) phases of tetrahedral materials show unique thermodynamic properties, the most important being water's anomalies, like the density maximum, the isothermal compressibility and specific heat anomaly and so on. Ordered phases of tetrahedral materials are of fundamental importance in industrial application, as they include open crystalline structures, like the diamond cubic (dc) crystal, or the quartz crystal, with unique mechanical, optical and electronic properties. For example, in Si and Ge, the diamond cubic (dc) crystal is a semiconductor, whereas the liquid and body-centred cubic (BCC) crystal are metals. Furthermore, dc crystals of mesoscopic particles (like colloids) are also a promising candidate for photonic crystals. It is thus not surprising that tetrahedral interactions are one of the focus of nanotechnology, with the aim of producing new generation of materials with properties that can be finely controlled by design.

To understand the bulk behaviour of materials with tetrahedral interactions, several coarse-grained models have been introduced. Among them, probably the most important and successful model is the Stillinger–Weber (SW) potential, in which tetrahedrality is enforced with the use of three-body force terms. Originally devised as a potential for silicon, the model has found widespread applicability for several materials, especially group XIV elements, like germanium and carbon. The key parameter controlling the tetrahedrality of the model is the ratio between the strength of three-body interactions over two-body interactions, often referred to as λ. As tetrahedrality becomes less strong with increasing atomic number, the basic idea is that group XIV elements, apart from energy and length-scale differences, can be modelled by simply varying λ. Even more importantly, the modified SW potential has found general application as a coarse-grained model for molecular and supramolecular systems. The most important example is water, whose structural properties have been accurately reproduced with a parametrization of the SW potential (called

mW water) with a precision that is competitive (if not superior) to the best classical molecular models available to date.

Despite the importance and widespread applicability of the SW model, our knowledge of its phase diagram is still lacking. Determining the phase diagram is challenging because of the three-dimensional parameter space (temperature, pressure and λ), and the fact that all calculations are multiplied by a large number of crystalline structures with local tetrahedral symmetry that have to be tested for thermodynamic stability. The first study of the model as a function of λ was introduced in ref, where three crystalline structures were identified at zero pressure P: BCC, β-tin, and dc, respectively for low (λ⊚18), intermediate (18⊚λ⊚19) and high values (λ⊚19) of λ. Interestingly, the intermediate region showed increased glass-forming ability. The β-tin phase was believed to be the high-pressure phase for SW silicon (λ=21). So, according to the current view, starting from a perfectly tetrahedral diamond (dc) phase, the SW system would transform into β-tin by reducing the amount of global tetrahedrality, either by applying pressure or decreasing the value of λ. But this view was recently proven wrong when a new crystal of SW silicon was found, sc16, which replaces β-tin as the stable phase at high pressures. sc16 is a new crystal with a simple cubic unit cell and 16 atoms in the unit cell. This calls for a new understanding of the phase behaviour of the SW model, with new behaviour that should emerge in between the low P–λ region (where β-tin is stable) and the high P–λ region (where sc16 is stable).

5.6 MODIFIED STILLINGER–WEBER MODEL

To compute the phase diagram, we run Monte Carlo simulations in the isothermal–isobaric *NPT* ensemble. The SW potential can be written as the sum of a pairwise term U_2 and three-body interaction term U_3:

$$U = \sum_i \sum_{j>i} U_2(\mathbf{r}_{ij}) + \lambda \sum_i \sum_{j \neq i} \sum_{k>j} U_3(\mathbf{r}_{ij}, \mathbf{r}_{jk}).$$

(1)

Here U_2 models a steep repulsion at short distances and a short-range attraction, while U_3 is a directional repulsive interaction that promotes tetrahedral angles between triplets of particles (for the analytic expressions of these terms, see Methods). λ is a dimensionless parameter controlling the relative strength between pairwise and three-body term. Free energy calculations of all relevant crystalline structures are conducted with the Einstein crystal method, and both Gibbs–Duhem integration and Hamiltonian integration are employed to compute coexistence planes and triple lines. Critical points are estimated with grand canonical simulations and histogram reweighting techniques. A description of all methods can be found in Methods and from here we use internal units as explained there.

5.6.1 Phase behaviour of the modified SW model

We start from a liquid phase and four crystalline phases which are known to be stable for the SW model. The crystalline phases are body-centred cubic (BCC), β-tin, diamond cubic (dc) and sc16. BCC is known as a stable crystalline phase of the SW model at lower λ. β-tin crystal has a body-centred-tetragonal structure with two atoms per cell and is known as a stable crystalline phase for silicon at intermediate pressure. dc is known as a stable crystalline phase for group XIV elements. sc16 is a crystal which has recently been found to be stable at intermediate and high pressure. The sc16 crystal has a simple cubic unit cell with 16 atoms per cell. The space group of the sc16 crystal is Pa $Pa\bar{3}$.

First, we show the three-dimensional phase diagram of the SW model, for $\lambda \in [12.2:23.15]$, $T \in [0:1.12]$ and $P \in [0:1]$, in Fig. 10a. To aid the visualization, we also plot in Fig. 10b a projection of the coexistence surfaces on the (P, λ) plane. Each surface represents a coexistence surface between the liquid and the corresponding crystal. Thick lines are triple lines, where two crystalline phases and the liquid phase coexist. The order of the different crystals is as follows: BCC at low λ; β-tin at intermediate λ; dc and sc16, for low and high pressures, respectively, at high λ. The dot

in Fig. 10 highlights a quadruple point at the intersection of three triple lines. At the quadruple point dc, β-tin, sc16 and the liquid phase all coexist at the same T_{QP} and P_{QP}. The coordinates are approximately: λ_{QP}=20.08, T_{QP}=0.042 and P_{QP}=0.120. Incidentally, we note that λ_{QP} is very close to the value of λ for the SW model of Germanium (λ=20). We have checked our results with direct-coexistence simulations, in which each crystalline phase is placed in contact with the fluid phase and shown to be at coexistence.
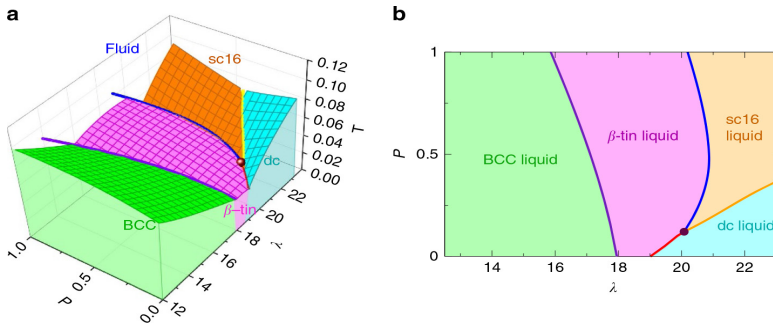
Figure 10: Phase diagrams of a system interacting with the SW potential. (a) The l–P–T phase diagram. The green, pink, turquoise and orange surfaces are liquid-BCC, liquid-b-tin, liquid-dc and liquid-sc16 coexistence surfaces. The purple, red, yellow and blue lines are liquid-BCC–b-tin, liquid-b-tin–dc, liquid-dc–sc16 and liquid-b-tin–sc16 coexisting lines. The brown point is a four-phase coexistence point for liquid, b-tin, dc and sc16. (b) The projection of the coexisting regions into l–P plane. The green, pink, turquoise and orange regions are the projection of BCC-liquid, b-tin-liquid, dc-liquid, sc16-liquid surfaces into l–P plane, respectively.

Our results confirm that the sc16 is indeed the stable crystalline phase at high (λ, P) and show that it shares a triple line with known β-tin phase down to the quadruple point, where the β-tin transforms directly into dc. We have further confirmed the stability and relevance of the sc16 crystalline phase by direct nucleation events, and showed that the fluid phase directly crystallizes in the sc16 phase at λ=21, P=0.5, and T=0.0395.

Unlike T and P, λ is not a thermodynamic variable but a parameter of the Hamiltonian (equation (1)). By choosing $\lambda=\lambda_{QP}$ we thus

have a system with a stable quadruple point in its phase diagram. To show this we compute the phase diagrams for $\lambda=\lambda_{QP}$ in the P–T and ρ–T planes, plotted respectively in Fig. 11a,b. The dc phase is stable at lower P and the β-tin phase at intermediate P. The stable region of the sc16 is instead split into two regions, at lower and higher P. Later, we discuss how the quadruple point emerges when $\lambda \rightarrow \lambda_{QP}$.
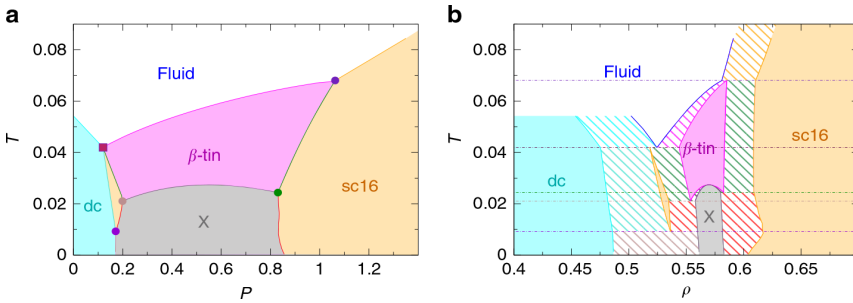
Figure 11: P–T and ρ–T **phase diagrams of the SW potential at** $\lambda\odot\lambda_{QP}$

In Fig. 11b, we show the densities of the different crystalline states. Diagonal lines represent coexistence regions between two different phases, while horizontal lines are plotted at the temperatures of the triple points and the quadruple point. dc is the phase with lowest density, lower than the fluid's density, as already could be inferred by the slope of the P, T coexistence line in Fig. 11a. The sc16 crystal can coexist with the fluid phase at two different densities: at the quadruple point with a density lower than the liquid's density, and at higher P with a density higher than the liquid's density. To summarize our study of the liquid–solid phase diagram, we report all thermodynamic values at triple and quadruple points in Table 1.

T	P	ρ_{dc}	$\rho_{\beta-tin}$	ρ_{sc16}	ρ_{liquid}	ρ_X
0.0093	0.171	0.486		0.536		0.560
0.0211	0.199		0.553	0.535		0.558
0.0244	0.831		0.583	0.609		0.580
0.0420	0.120	0.475	0.544	0.518	0.525	
0.0680	1.063		0.585	0.610	0.581	

T, P and ρ at triple and quadruple points for the system with λ=20.08, as shown also in Fig. 11.

Figure 11 shows also the presence of a new phase (denoted as X) that we found while computing the coexisting line between β-tin and sc16 at the λ_{QP}. The phase spontaneously forms from β-tin, with which it shares similar densities. As this is a low T phase that does not coexist with the liquid, and that lies well below the quadruple point, we have not focused on identifying it

Location of the gas–liquid phase transition

The phase diagrams obtained so far only include solid and liquid phases, so there is the possibility that the quadruple point is metastable with respect to liquid–gas phase separation. To exclude this possibility, we have computed the liquid–gas critical point and coexistence lines for $\lambda=\lambda_{QP}$. To obtain the critical point, we conducted grand canonical simulations to get the distribution function of the mixing order parameter M ($M=\rho+su$; ρ is density and u is internal energy per particle and s is mixing parameter), and use histogram reweighting to find the state point where this distribution matches the one from the Ising universality class. The results for the critical point is P_{CP}=0.004, T_{CP}=0.321. The gas–liquid phase diagram (the critical point and the coexistence line) is shown in Fig. 12, where it is clear that the liquid–gas critical point is located at pressures two orders of magnitude lower than P_{QP}. Therefore, the quadruple point is indeed a stable thermodynamic point of the model.
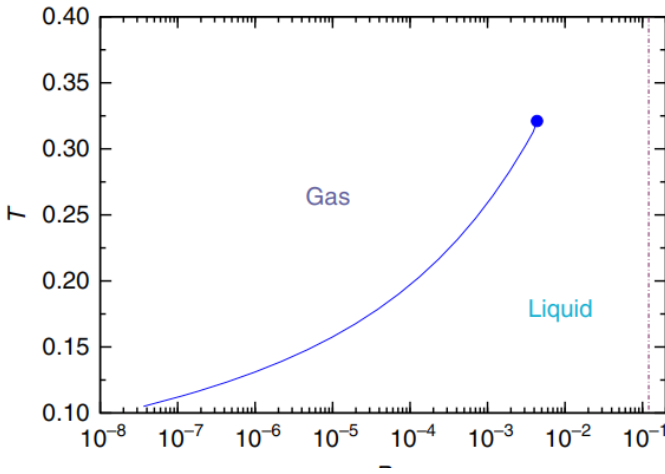
Figure 12: The liquid–gas phase diagram of the SW potential at $\lambda \odot \lambda_{QP \ A}$ circle point is a critical point. A broken brown line indicates the pressure of the quadruple point.

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6

IDEAL SOLUTIONS

INTRODUCTION

An ideal solution is a solution in which the gas phase exhibits thermodynamic properties analogous to those of a mixture of ideal gases. The enthalpy of mixing is zero as is the volume change on mixing by definition; the closer to zero the enthalpy of mixing is, the more "ideal" the behavior of the solution becomes. The vapor pressure of the solution obeys either Raoult's law or Henry's law (or both), and the activity coefficient of each component (which measures deviation from ideality) is equal to one.

The concept of an ideal solution is fundamental to chemical thermodynamics and its applications, such as the use of colligative properties. An ideal solution or ideal mixture is a solution in which the enthalpy of solution ($\Delta H_{solution} = 0$) is zero; with the closer to zero the enthalpy of solution, the more "ideal" the behavior of the

solution becomes. Since the enthalpy of mixing (solution) is zero, the change in Gibbs energy on mixing is determined solely by the entropy of mixing ($\Delta S_{solution}$).

6.1 SOLUTIONS

In normal life we rarely come across pure substances. Most of these are mixtures containing two or more pure substances. Their utility or importance in life depends on their composition.

For example, the properties of brass (mixture of copper and zinc) are quite different from those of German silver (mixture of copper, zinc and nickel) or bronze (mixture of copper and tin); 1 part per million (ppm) of fluoride ions in water prevents tooth decay, while 1.5 ppm causes the tooth to become mottled and high concentrations of fluoride ions can be poisonous (for example, sodium fluoride is used in rat poison); intravenous injections are always dissolved in water containing salts at particular ionic concentrations that match with blood plasma concentrations and so on.

6.1.1 Types of Solutions

Solutions are homogeneous mixtures of two or more than two components. By homogenous mixture we mean that its composition and properties are uniform throughout the mixture. Generally, the component that is present in the largest quantity is known as solvent.

Solvent determines the physical state in which solution exists. One or more components present in the solution other than solvent are called solutes. In this Unit we shall consider only binary solutions (i.e., consisting of two components). Here each component may be solid, liquid or in gaseous state and are summarized in Table 1.

Table 1: Types of Solutions

Type of Solution	Solute	Solvent	Common Examples
Gaseous Solutions	Gas	Gas	Mixture of oxygen and nitrogen gases
	Liquid	Gas	Chloroform mixed with nitrogen gas
	Solid	Gas	Camphor in nitrogen gas
Liquid Solutions	Gas	Liquid	Oxygen dissolved in water
	Liquid	Liquid	Ethanol dissolved in water
	Solid	Liquid	Glucose dissolved in water
Solid Solutions	Gas	Solid	Solution of hydrogen in palladium
	Liquid	Solid	Amalgam of mercury with sodium
	Solid	Solid	Copper dissolved in gold

6.1.2 Expressing Concentration of Solutions

Composition of a solution can be described by expressing its concentration. The latter can be expressed either qualitatively or quantitatively. For example, qualitatively we can say that the solution is dilute (i.e., relatively very small quantity of solute) or it is concentrated (i.e., relatively very large quantity of solute). But in real life these kinds of description can add to lot of confusion and thus the need for a quantitative description of the solution.

There are several ways by which we can describe the concentration of the solution quantitatively.

(i) *Mass percentage (w/w)*: The mass percentage of a component of a solution is defined as:

Mass % of a component

$$= \frac{\text{Mass of the component in the solution}}{\text{Total mass of the solution}} \times 100 \qquad (1)$$

For example, if a solution is described by 10% glucose in water by mass, it means that 10 g of glucose is dissolved in 90 g of water resulting in a 100 g solution. Concentration described by mass percentage is commonly used in industrial chemical applications. For example, commercial bleaching solution contains 3.62 mass percentage of sodium hypochlorite in water.

(ii)   *Volume percentage (V/V)*: The volume percentage is defined as:

$$\text{Volume \% of a component} = \frac{\text{Volume of the component}}{\text{Total volume of solution}} \times 100 \qquad (2)$$

For example, 10% ethanol solution in water means that 10 mL of ethanol is dissolved in water such that the total volume of the solution is 100 mL. Solutions containing liquids are commonly expressed in this unit. For example, a 35% (v/v) solution of ethylene glycol, an antifreeze, is used in cars for cooling the engine. At this concentration the antifreeze lowers the freezing point of water to 255.4K (–17.6°C).

(iii)   Mass by volume percentage (w/V): Another unit which is commonly used in medicine and pharmacy is mass by volume percentage. It is the mass of solute dissolved in 100 mL of the solution.

(iv)   *Parts per million*: When a solute is present in trace quantities, it is convenient to express concentration in parts per million (ppm) and is defined as:

$$\text{Parts per million} = \frac{\text{Number of parts of the component}}{\text{Total number of parts of all components of the solution}} \times 10^6 \qquad (3)$$

As in the case of percentage, concentration in parts per million can also be expressed as mass to mass, volume to volume and mass to volume. A litre of sea water (which weighs 1030 g) contains about 6×10^{-3} g of dissolved oxygen (O_2). Such a small concentration is also expressed as 5.8 g per 10^6 g (5.8 ppm) of sea water. The concentration of pollutants in water or atmosphere is often expressed in terms of $\mu g\ mL^{-1}$ or ppm.

(v)   *Mole fraction*: Commonly used symbol for mole fraction is x and subscript used on the right hand side of x denotes the component. It is defined as:

$$\text{Mole fraction of a component} = \frac{\text{Number of moles of the component}}{\text{Total number of moles of all the components}} \qquad (4)$$

For example, in a binary mixture, if the number of moles of A and B are n_A and n_B respectively, the mole fraction of A will be

$$x_A = \frac{n_A}{n_A + n_B}$$

(5)

For a solution containing i number of components, we have:

$$x_i = \frac{n_i}{n_1 + n_2 + \text{.......} + n_i} = \frac{n_i}{\sum n_i}$$

(6)

It can be shown that in a given solution sum of all the mole fractions is unity, i.e.

$$x_1 + x_2 + \text{.................} + x_i = 1$$

(7)

Mole fraction unit is very useful in relating some physical properties of solutions, say vapor pressure with the concentration of the solution and quite useful in describing the calculations involving gas mixtures.

(vi) *Molarity*: Molarity (M) is defined as number of moles of solute dissolved in one litre (or one cubic decimetre) of solution,

$$\text{Molarity} = \frac{\text{Moles of solute}}{\text{Volume of solution in litre}}$$

(8)

For example, 0.25 mol L^{-1} (or 0.25 M) solution of NaOH means that 0.25 mol of NaOH has been dissolved in one litre (or one cubic decimetre).

(viii) *Molality*: Molality (m) is defined as the number of moles of the solute per kilogram (kg) of the solvent and is expressed as:

$$\text{Molality (m)} = \frac{\text{Moles of solute}}{\text{Mass of solvent in kg}}$$

(9)

For example, 1.00 mol kg^{-1} (or 1.00 m) solution of KCl means that 1 mol (74.5 g) of KCl is dissolved in 1 kg of water.

Each method of expressing concentration of the solutions has its own merits and demerits. Mass %, ppm, mole fraction and molality are independent of temperature, whereas molarity is a function of temperature. This is because volume depends on temperature and the mass does not.

6.2 SOLUBILITY

Solubility of a substance is its maximum amount that can be dissolved in a specified amount of solvent at a specified temperature. It depends upon the nature of solute and solvent as well as temperature and pressure. Let us consider the effect of these factors in solution of a solid or a gas in a liquid.

6.2.1 Solubility of a Solid in a Liquid

Every solid does not dissolve in a given liquid. While sodium chloride and sugar dissolve readily in water, naphthalene and anthracene do not. On the other hand, naphthalene and anthracene dissolve readily in benzene but sodium chloride and sugar do not. It is observed that polar solutes dissolve in polar solvents and non polar solutes in nonpolar solvents. In general, a solute dissolves in a solvent if the intermolecular interactions are similar in the two or we may say like dissolves like.

When a solid solute is added to the solvent, some solute dissolves and its concentration increases in solution. This process is known as dissolution. Some solute particles in solution collide with the solid solute particles and get separated out of solution. This process is known as crystallization. A stage is reached when the two processes occur at the same rate. Under such conditions, number of solute particles going into solution will be equal to the solute particles separating out and a state of dynamic equilibrium is reached.

Solute + Solvent $\rightleftharpoons$ Solution   (10)

At this stage the concentration of solute in solution will remain constant under the given conditions, i.e., temperature and pressure. Similar process is followed when gases are dissolved in liquid solvents. Such a solution in which no more solute can be dissolved at the same temperature and pressure is called a saturated solution. An unsaturated solution is one in which more solute can be dissolved at the same temperature. The solution which is in dynamic equilibrium with undissolved solute is the saturated solution and contains the maximum amount of solute dissolved in a given amount of solvent. Thus, the concentration of solute in such a solution is its solubility.

Earlier we have observed that solubility of one substance into another depends on the nature of the substances. In addition to these variables, two other parameters, i.e., temperature and pressure also control this phenomenon.

Effect of Temperature

The solubility of a solid in a liquid is significantly affected by temperature changes. Consider the equilibrium represented by equation 10. This, being dynamic equilibrium, must follow Le Chateliers Principle. In general, if in a nearly saturated solution, the dissolution process is endothermic ($\Delta_{sol} H > 0$), the solubility should increase with rise in temperature and if it is exothermic ($\Delta_{sol} H < 0$) the solubility should decrease. These trends are also observed experimentally.

Effect of Pressure

Pressure does not have any significant effect on solubility of solids in liquids. It is so because solids and liquids are highly incompressible and practically remain unaffected by changes in pressure.

6.2.2 Solubility of a Gas in a Liquid

Many gases dissolve in water. Oxygen dissolves only to a small extent in water. It is this dissolved oxygen which sustains all aquatic life. On the other hand, hydrogen chloride gas (HCl) is highly soluble in water. Solubility of gases in liquids is greatly affected by pressure and temperature. The solubility of gases increase with increase of pressure. For solution of gases in a solvent, consider a system as shown in Fig. 1 (a). The lower part is solution and the upper part is gaseous system at pressure p and temperature T. Assume this system to be in a state of dynamic equilibrium, i.e., under these conditions rate of gaseous particles entering and leaving the solution phase is the same. Now increase the pressure over the solution phase by compressing the gas to a smaller volume [Fig. 1 (b)]. This will increase the number of gaseous particles per unit volume over the solution and also the rate at which the gaseous particles are striking the surface of solution to enter it. The solubility of the gas will increase until a new equilibrium is reached resulting in an increase in the pressure of a gas above the solution and thus its solubility increases.


(a)   (b)
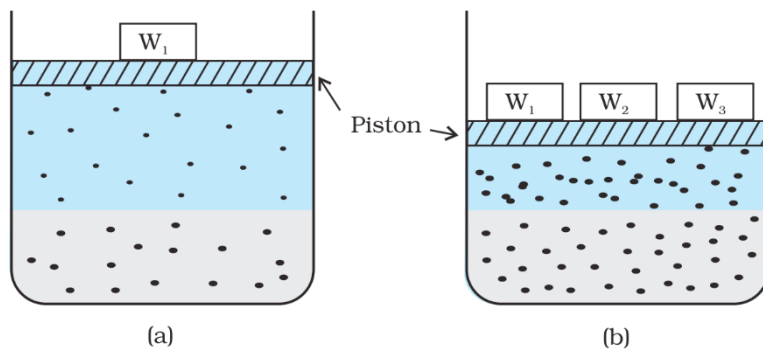
Figure 1. Effect of pressure on the solubility of a gas. The concentration of dissolved gas is proportional to the pressure on the gas above the solution.

Henry was the first to give a quantitative relation between pressure and solubility of a gas in a solvent which is known as Henry's law. The law states that at a constant temperature, the solubility of a gas in a liquid is directly proportional to the partial pressure of the gas present above the surface of liquid or solution. Dalton, a contemporary of Henry, also concluded independently that the solubility of a gas in a liquid solution is a function of partial pressure of the gas. If we use the mole fraction of a gas in the solution as a measure of its solubility, then it can be said that the mole fraction of gas in the solution is proportional to the partial pressure of the gas over the solution. The most commonly used form of Henry's law states that "the partial pressure of the gas in vapor phase (p) is proportional to the mole fraction of the gas (x) in the solution" and is expressed as:

$$p = K_H \, x \tag{11}$$

Here K_H is the Henry's law constant. If we draw a graph between partial pressure of the gas versus mole fraction of the gas in solution, then we should get a plot of the type as shown in Fig. 2.
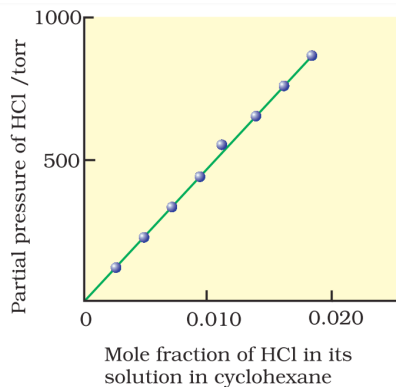
Figure 2. Experimental results for the solubility of HCl gas in cyclohexane at 293 K. The slope of the line is the Henry's Law constant, K_H.

Different gases have different K_H values at the same temperature (Table 2). This suggests that K_H is a function of the nature of the gas.

Table 2. Values of Henry's Law Constant for Some Selected Gases in Water

Gas	Temperature/K	K_H /kbar	Gas	Temperature/K	K_H/kbar
He	293	144.97	Argon	298	40.3
H_2	293	69.16	CO_2	298	1.67
N_2	293	76.48	Formaldehyde	298	1.83×10^{-5}
N_2	303	88.84			
O_2	293	34.86	Methane	298	0.413
O_2	303	46.82	Vinyl chloride	298	0.611

It is obvious from equation (11) that higher the value of K_H at a given pressure, the lower is the solubility of the gas in the liquid. It can be seen from Table 2 that K_H values for both N_2 and O_2 increase with increase of temperature indicating that the solubility of gases increases with decrease of temperature. It is due to this reason that aquatic species are more comfortable in cold waters rather than in warm waters.

Henry's law finds several applications in industry and explains some biological phenomena. Notable among these are:

- To increase the solubility of CO_2 in soft drinks and soda water, the bottle is sealed under high pressure.

- Scuba divers must cope with high concentrations of dissolved gases while breathing air at high pressure underwater. Increased pressure increases the solubility of atmospheric gases in blood. When the divers come towards surface, the pressure gradually decreases. This releases the dissolved gases and leads to the formation of bubbles of nitrogen in the blood. This blocks capillaries and creates a medical condition known as bends, which are painful and dangerous to life. To avoid bends, as well as, the toxic effects of high concentrations of nitrogen in the blood, the tanks used by scuba divers are filled with air diluted with helium (11.7% helium, 56.2% nitrogen and 32.1% oxygen).

- At high altitudes the partial pressure of oxygen is less than that at the ground level. This leads to low concentrations of oxygen in the blood and tissues of people living at high

altitudes or climbers. Low blood oxygen causes climbers to become weak and unable to think clearly, symptoms of a condition known as anoxia.

Effect of Temperature

Solubility of gases in liquids decreases with rise in temperature. When dissolved, the gas molecules are present in liquid phase and the process of dissolution can be considered similar to condensation and heat is evolved in this process.

6.3 VAPOR PRESSURE OF LIQUID SOLUTIONS

Liquid solutions are formed when solvent is a liquid. The solute can be a gas, a liquid or a solid. In this Section, we shall discuss the solutions of liquids and solids in a liquid. Such solutions may contain one or more volatile components. Generally, the liquid solvent is volatile. The solute may or may not be volatile. We shall discuss the properties of only binary solutions, that is, the solutions containing two components, namely, the solutions of (i) liquids in liquids and (ii) solids in liquids.

6.3.1 Vapor Pressure of Liquid Solutions

Let us consider a binary solution of two volatile liquids and denote the two components as 1 and 2. When taken in a closed vessel, both the components would evaporate and eventually an equilibrium would be established between vapor phase and the liquid phase. Let the total vapor pressure at this stage be p_{total} and p_1 and p_2 be the partial vapor pressures of the two components 1 and 2 respectively. These partial pressures are related to the mole fractions x_1 and x_2 of the two components 1 and 2 respectively.

The French chemist, Francois Marte Raoult (1886) gave the quantitative relationship between them. The relationship is known as the Raoult's law which states that for a solution of

volatile liquids, the partial vapor pressure of each component of the solution is directly proportional to its mole fraction present in solution.

Thus, for component 1

$$p_1 \propto x_1$$

and

$$p_1 = p_1^0 \, x_1 \tag{12}$$

where p_1^0 is the vapor pressure of pure component 1 at the same temperature.

Similarly, for component 2

$$p_2 = p_2^0 \, x_2 \tag{13}$$

where p_2^0 represents the vapor pressure of the pure component 2. According to Dalton's law of partial pressures, the total pressure (p_{total}) over the solution phase in the container will be the sum of the partial pressures of the components of the solution and is given as:

$$p_{total} = p_1 + p_2 \tag{14}$$

Substituting the values of p1 and p_2, we get

$$p_{total} = x_1 \, p_1^0 + x_2 \, p_2^0$$
$$= (1 - x_2) \, p_1^0 + x_2 \, p_2^0 \tag{15}$$

$$= p_1^0 + (p_2^0 - p_1^0) \, x_2 \tag{16}$$

Following conclusions can be drawn from equation (16).
   (i)   Total vapor pressure over the solution can be related to the mole fraction of any one component.

(ii) Total vapor pressure over the solution varies linearly with the mole fraction of component 2.

(iii) Depending on the vapor pressures of the pure components 1 and 2, total vapor pressure over the solution decreases or increases with the increase of the mole fraction of component 1.

A plot of p_1 or p_2 versus the mole fractions x_1 and x_2 for a solution gives a linear plot as shown in Fig. 3. These lines (I and II) pass through the points for which x1 and x_2 are equal to unity. Similarly the plot (line III) of p_{total} versus x_2 is also linear (Fig. 3). The minimum value of p_{total} is p_1^0 and the maximum value is p_2^0, assuming that component 1 is less volatile than component 2, i.e., $p_1^0 < p_2^0$.
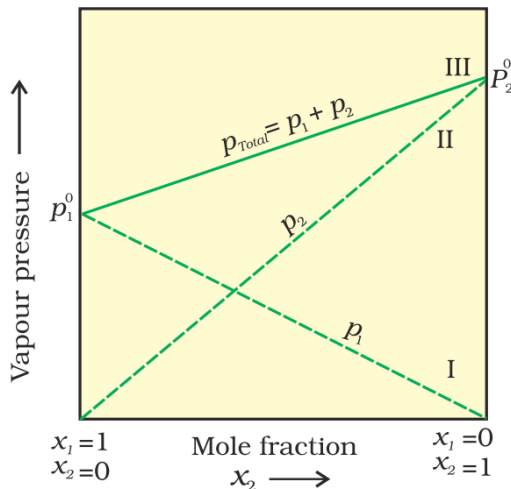
Figure 3. The plot of vapor pressure and mole fraction of an ideal solution at constant temperature. The dashed lines I and II represent the partial pressure of the components. (It can be seen from the plot that p_1 and p_2 are directly proportional to x_1 and x_2, respectively). The total vapor pressure is given by line marked III in the figure.

The composition of vapor phase in equilibrium with the solution is determined by the partial pressures of the components. If y_1 and y_2 are the mole fractions of the components 1 and 2 respectively in the vapor phase then, using Dalton's law of partial pressures:

$$p_1 = y_1 \, p_{total} \tag{17}$$

$$p_2 = y_2 \, p_{total} \tag{18}$$

In general

$$p_i = y_i \, p_{total} \tag{19}$$

6.4 RAOULT'S LAW

Raoult's law states that the vapor pressure of a solvent above a solution is *equal* to the vapor pressure of the pure solvent at the same temperature *scaled* by the mole fraction of the solvent present:

$$P_{solution} = \chi_{solvent} P^o_{solvent} \tag{20}$$

In the 1880s, French chemist François-Marie Raoult discovered that when a substance is dissolved in a solution, the vapor pressure of the solution will generally decrease. This observation depends on two variables:

1. the mole fraction of the amount of dissolved solute present and
2. the original vapor pressure (pure solvent).

At any given temperature for a particular solid or liquid, there is a pressure at which the vapor formed above the substance is in dynamic equilibrium with its liquid or solid form. This is the vapor pressure of the substance at that temperature. At equilibrium, the rate at which the solid or liquid evaporates is equal to the rate that the gas is condensing back to its original form. All solids and liquids have a vapor pressure, and this pressure is constant regardless of how much of the substance is present.

Raoult's Law only works for ideal solutions. "An ideal solution shows thermodynamic mixing characteristics identical to those of ideal gas mixtures [except] ideal solutions have intermolecular interactions equal to those of the pure components." Like many

other concepts explored in Chemistry, Raoult's Law only applies under ideal conditions in an ideal solution. However, it still works fairly well for the solvent in dilute solutions. In reality though, the decrease in vapor pressure will be greater than that calculated by Raoult's Law for extremely dilute solutions.
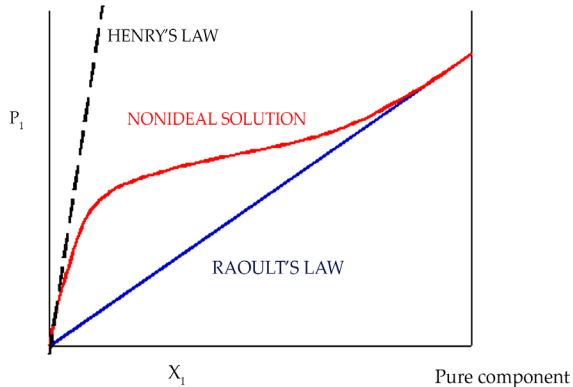

Figure 4. Positive non-ideal behavior of the vapor pressure of a solution follows Henry's Law at low concentrations and Raoult's Law at high concentrations (pure).

6.4.1 Why Raoult's Law works

If you look review the concepts of colligative properties, you will find that adding a solute lowers vapor pressure because the additional solute particles will fill the gaps between the solvent particles and take up space. This means less of the solvent will be on the surface and less will be able to break free to enter the gas phase, resulting in a lower vapor pressure. There are two ways of explaining why Raoult's Law works - a simple visual way, and a more sophisticated way based on entropy. Below is the simple approach.

Remember that saturated vapor pressure is what you get when a liquid is in a sealed container. An equilibrium is set up where the number of particles breaking away from the surface is exactly the same as the number sticking on to the surface again.
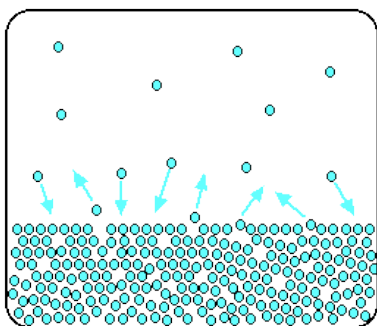
Figure 5. Dynamic equilibrium between volatile molecules in the liquid and gas phase.

Now suppose solute molecules were added so that the solvent molecules occupied only 50% of the surface of the solution.
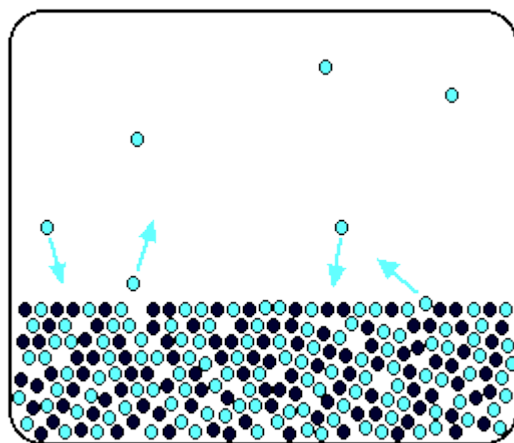
A certain fraction of the solvent molecules will have sufficient energy to escape from the surface (e.g., 1 in 1000 or 1 in a million). If you reduce the number of solvent molecules on the surface, you are going to reduce the number which can escape in any given time. But it will not make any difference to the ability of molecules in the vapor to stick to the surface again. If a solvent molecule in the vapor hits a bit of surface occupied by the solute particles, it may well stick. There are obviously attractions between solvent and solute otherwise you would not have a solution in the first

place.

The net effect of this is that when equilibrium is established, there will be *fewer* solvent molecules in the vapor phase - it is less likely that they are going to break away, but there is not any problem about them returning. However, if there are fewer particles in the vapor at equilibrium, the saturated vapor pressure is lower.

6.4.2 Limitations on Raoult's Law

In practice, there's no such thing as an ideal solution! However, features of one include:

- Ideal solutions satisfy Raoult's Law. The solution in the last diagram of Figure above would not actually obey Raoult's Law - it is far too concentrated, but was drawn so concentrated to emphasized the point.
- In an ideal solution, it takes exactly the same amount of energy for a solvent molecule to break away from the surface of the solution as it did in the pure solvent. The forces of attraction between solvent and solute are exactly the same as between the original solvent molecules - not a very likely event!

In an ideal solution, the forces between the solvent molecules. . .

. . .are exactly the same as those between solvent and solute.
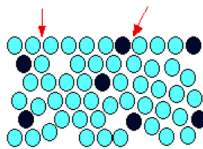
That means that it takes the same amount of energy for solvent molecules to break away from the surface in either case.

Suppose that in the pure solvent, 1 in 1000 molecules had enough energy to overcome the intermolecular forces and break away from the surface in any given time. In an ideal solution, that would still be exactly the same proportion. Fewer would, of course, break away because there are now fewer solvent molecules on the surface - but of those that are on the surface, the same proportion

still break away. If there were strong solvent-solute attractions, this proportion may be reduced to 1 in 2000, or 1 in 5000 or whatever.

In any real solution of, say, a salt in water, there are strong attractions between the water molecules and the ions. That would tend to slow down the loss of water molecules from the surface. However, if the solution is sufficiently dilute, there will be good-sized regions on the surface where you still have water molecules on their own. The solution will then approach ideal behavior.

6.4.3 The Nature of the Solute

There is another thing that you have to be careful of if you are going to do any calculations on Raoult's Law. You may have noticed in the little calculation about mole fraction that sugar was as a solute rather than salt. What matters is not actually the number of moles of substance that you put into the solution, but the **number** of moles of particles formed. For each mole of sodium chloride dissolved, you get 1 mole of sodium ions and 1 mole of chloride ions - in other words, you get twice the number of moles of particles as of original salt.

$$Na^+Cl^-_{(s)} \longrightarrow Na^+_{(aq)}Cl^-_{(aq)}$$

1 *moles of solid salt*   2 *moles of ions in solution*
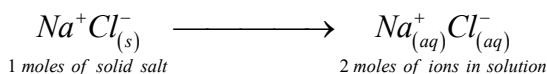
So, if you added 0.1 moles of sodium chloride, there would actually be 0.2 moles of particles in the solution - and that's the figure you would have to use in the mole fraction calculation. Unless you think carefully about it, Raoult's Law only works for solutes which **do not** change their nature when they dissolve. For example, they must not ionize or associate (e.g., if you put in substance A, it must not form A_2 in solution). If it does either of these things, you have to treat Raoult's law with great care.

### 6.4.4 Raoult's Law and Colligative Properties

The effect of Raoult's Law is that the saturated vapor pressure of a solution is going to be lower than that of the pure solvent

at any particular temperature. That has important effects on the phase diagram of the solvent. The next diagram shows the phase diagram for pure water in the region around its normal melting and boiling points. The 1 atmosphere line shows the conditions for measuring the normal melting and boiling points.
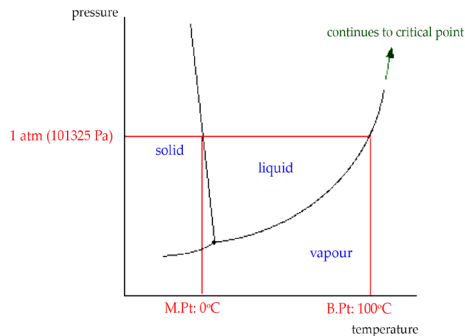
The line separating the liquid and vapor regions is the set of conditions where liquid and vapor are in equilibrium. It can be thought of as the effect of pressure on the boiling point of the water, but it is also the curve showing the effect of temperature on the saturated vapor pressure of the water.

If you draw the saturated vapor pressure curve for a solution of a non-volatile solute in water, it will always be lower than the curve for the pure water.
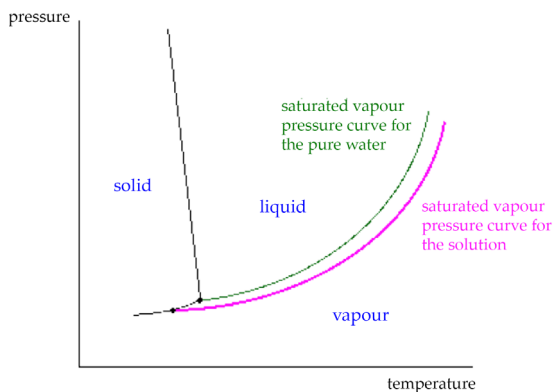

If you look closely at the last diagram, you will see that the point at which the liquid-vapor equilibrium curve meets the solid-vapor

curve has moved. That point is the triple point of the system - a unique set of temperature and pressure conditions at which it is possible to get solid, liquid and vapor all in equilibrium with each other at the same time. Since the triple point has solid-liquid equilibrium present (amongst other equilibria), it is also a melting point of the system - although not the normal melting point because the pressure is not one atmosphere.

The curves for the pure water and for the solution are often drawn parallel to each other. That has got to be wrong! Suppose you have a solution where the mole fraction of the water is 0.99 and the vapor pressure of the pure water at that temperature is 100 kPa. The vapor pressure of the solution will be 99 kPa - a fall of 1 kPa. At a lower temperature, where the vapor pressure of the pure water is 10 kPa, the fall will only be 0.1 kPa. For the curves to be parallel the falls would have to be the same over the whole temperature range. They aren't!

That must mean that the phase diagram needs a new melting point line (a solid-liquid equilibrium line) passing through the new triple point. That is shown in the next diagram.
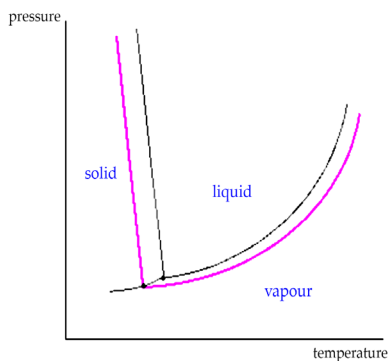
Now we are finally in a position to see what effect a non-volatile solute has on the melting and freezing points of the solution. Look at what happens when you draw in the 1 atmosphere pressure line which lets you measure the melting and boiling points. The diagram also includes the melting and boiling points of the pure water from the original phase diagram for pure water (black lines).
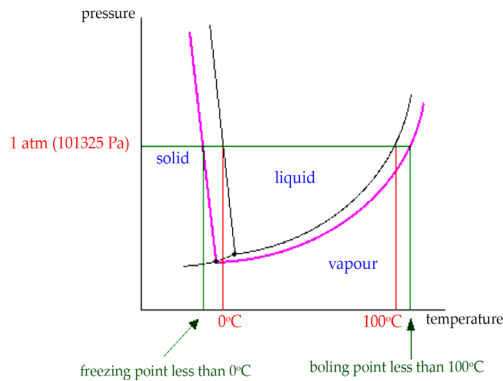
Because of the changes to the phase diagram, you can see that:

- the boiling point of the solvent in a solution is higher than that of the pure solvent;
- the freezing point (melting point) of the solvent in a solution is lower than that of the pure solvent.

We have looked at this with water as the solvent, but using a different solvent would make no difference to the argument or the conclusions. The only difference is in the slope of the solid-liquid equilibrium lines. For most solvents, these slope forwards whereas the water line slopes backwards. You could prove to yourself that that does not affect what we have been looking at by re-drawing all these diagrams with the slope of that particular line changed. You will find it makes no difference whatsoever.

6.4.5 How to Calculate the Vapor Pressure of a Solution

We can calculate the vapor pressure of the solution in two ways, depending on the volatility of the solute. If the solute is volatile, it will exert its own vapor pressure and this amount is a significant contribution to the overall vapor pressure of the solution, and thus needs to be included in the calculations. On the other hand, if it is nonvolatile, the solute will not produce vapor pressure in solution at that temperature.

Nonvolatile Solutes

These calculations are fairly straightforward if you are comfortable with stoichiometric conversions. Because the solute is nonvolatile, you need only determine the change in vapor pressure for the solvent. Using the equation for Raoult's Law, you will need to find the mole fraction of the solvent and the vapor pressure of the pure solvent is typically given.

Example 1: Kool-Aid

1.5 moles of cherry Kool-Aid are added to a pitcher containing 2 liters of water on a nice day at 25°C. The vapor pressure of water alone is 23.8 mm Hg at 25°C. What is the new vapor pressure of Kool-Aid?

Solution

$$P_{H_2O} = 23.8 \ mm \ Hg$$

To solve for the mole fraction, you must first convert the 2 L of water into moles:

1 L = 1000 mL = 1000 g

Knowing this, you can convert the mass of water (2000 g) into moles:

2000 g / 18.02 g (molar mass of water) = 110.9 moles H_2O

Solve for the mole fraction, χ_{H_2O}:

$\chi_{H_2O} = moles \ H_2O \ / \ total \ moles$

$= 110.9 \ moles \ / \ 110.9 + 1.5 \ moles \ = \ 0.979$

Finally, apply Raoult's Law

$$P_{Kool-Aid} = \chi_{H_2O} P_{H_2O} = (0.979)(23.8 \ mm \ Hg) \ = \ 23.3 \ mm \ Hg$$

Example 2A: Non-electrolyte

Calculate the vapor pressure of a solution made by dissolving 50.0 g glucose, $C_6H_{12}O_6$, in 500 g of water. The vapor pressure of pure water is 47.1 torr at 37°C

Solution

To use Raoult's Law (Equation 20), we need to calculate the mole fraction of water (the solvent) in this sugar-water solution.

$$X_{solvent} = \frac{\text{moles of water}}{\text{moles of solute} + \text{moles of solvent}}$$

$$X_{solvent} = \frac{n_{water}}{n_{glucose} + n_{water}}$$

The molar mass of glucose if 180.2 g/mol and of water is 18 g/mol. So

$$n_{water} = \frac{500g}{18g/mol} = 27.7mol$$

and

$$n_{glucose} = \frac{50g}{180.2g/mol} = 0.277mol$$

and

$$X_{solvent} = \frac{27.7mol}{0.277mol + 27.7mol} = 0.99$$

Note that this still relatively dilute.

$$P_{solution} = 0.99 \times 47.1 = 46.63torr$$

not much of a change at all.

Example 2B: Electrolyte

Calculate the vapor pressure of a solution made by dissolving 50.0 g $CaCl_2$, $C_6H_{12}O_6$, in 500 g of water. The vapor pressure of pure water is 47.1 torr at 37°C

Solution

To use Raoult's Law (Equation 20), we need to calculate the mole fraction of water (the solvent) in this salt-water solution.

$$X_{solvent} = \frac{\text{moles of water}}{\text{moles of solute} + \text{moles of solvent}}$$

$$X_{solvent} = \frac{n_{water}}{n_{solutes} + n_{water}}$$

The molar mass of $CaCl_2$ if 111 g/mol and of water is 18 g/mol. So

$$n_{water} = \frac{500g}{18g/mol} = 27.7mol$$

and

$$n_{solutes} = \frac{50g}{111g/mol} = 0.45mol$$

but this is really:

- $n_{Ca^+} = 0.45mol$

- $n_{Cl^-} = 0.9mol$

and

$$X_{solvent} = \frac{27.7mol}{0.45mol + 0.9mol + 27.7mol} = 0.953$$

Note that this still relatively dilute.

$P_{solution} = 0.953 \times 47.1 = 44.88 torr$

A bigger change that the glucose example above.

Volatile Solutes

The only difference between volatile and nonvolatile solutes, is that the partial pressure exerted by the vapor pressure of the volatile solute and the vapor pressure of the solvent must be accounted for. The sum of the two will give you the total vapor pressure of the solution.

Example 3

What are the partial pressures of benzene and toluene in a solution in which the mole fraction of benzene is 0.6? What is the total vapor pressure? The vapor pressure of pure benzene is 95.1 mm Hg and the vapor pressure of pure toluene 28.4 mm Hg at 25°C.

Solution

If $\chi_{benzene} = 0.6$, than $\chi_{toluene} = 0.4$ because $1 - 0.6 = 0.4$.

Now that we know the mole fractions and vapor pressures, this problem is a cinch.

$P_{benzene} = x_{benzene} P_{benzene} = (0.6)(95.1 \text{ mm Hg}) = 57.1 \text{ mm Hg}$

$P_{toluene} = x_{toluene} P_{toluene} = (0.4)(28.4 \text{ mm Hg}) = 11.4 \text{ mm Hg}$

The total vapor pressure is simply the sum of the partial pressures:

$P_{total} = P_{benzene} + P_{tuolene} = 57.1 \text{ mm Hg} + 11.4 \text{ mm Hg} = 68.5 \text{ mm Hg}$

6.5 HENRY'S LAW

Henry's law is one of the gas laws formulated by William Henry in 1803 and states: "At a constant temperature, the amount of a given gas that dissolves in a given type and volume of liquid is directly proportional to the partial pressure of that gas in equilibrium with that liquid." An equivalent way of stating the law is that the solubility of a gas in a liquid is directly proportional to the partial pressure of the gas above the liquid:

$C = kP_{gas}$

where

- C is the solubility of a gas at a fixed temperature in a particular solvent (in units of M or mL gas/L)
- k is Henry's law constant (often in units of M/atm)
- P_{gas} is the partial pressure of the gas (often in units of atm)

Example 1

What is Henry's constant for neon dissolved in water given: $C_{Ne} = 23.5 mL / L$ solution and STP (22,414 mL/mole gas) and pressure (1 atm)?

Solution

Now we can rearrange our equation from above to solve for the constant:

$C = kP_{Ne}$

To use C we must convert 23.5 mL/L solution to Molarity. Since Ne is a gas, we can use our standard molar volume. Thus giving us:

$$\frac{23.5 \text{ mL/L soln}}{1 \text{ mole Ne/22,414 mL}} = 0.00105M.$$

Now we have solved for the solubility of Ne in the solution. C= 0.00105M and we know the pressure at STP is 1 atm, so we can now use our rearranged equation:

$$k = \frac{C}{P_{Ne}}$$

Where C= 0.00105M, P_{Ne} = 1 atm, thus giving us k=0.00105 M/atm

Example 2

Compute the molar solubility in water that is saturated with air.

Solution

This time, we need to use constant (k) that we just calculated and our P_{Ne} in air.

$$\begin{aligned}
C &= kP_{gas} \\
&= (0.00105\, M\,/\,atm)(0.0341\, atm) \\
&= 3.58 \times 10^{-5}\, M
\end{aligned}$$

6.5.1 Applicability of Henry's Law

- Henry's law only works if the molecules are at equilibrium.
- Henry's law does not work for gases at high pressures (e.g., $N_{2(g)}$ at high pressure becomes very soluble and harmful when in the blood supply).
- Henry's law does not work if there is a chemical reaction between the solute and solvent (e.g., $HCl_{(g)}$ reacts with water by a dissociation reaction to generate H_3O^+ and Cl^- ions).

6.6 IDEAL AND NON-IDEAL SOLUTIONS

Liquid-liquid solutions can be classified into ideal and non-ideal solutions on the basis of Raoult's law.

6.6.1 Ideal Solutions

The solutions which obey Raoult's law over the entire range of concentration are known as ideal solutions. The ideal solutions have two other important properties. The enthalpy of mixing of the pure components to form the solution is zero and the volume of mixing is also zero, i.e.,

$$\Delta_{mix}H = 0, \qquad \Delta_{mix}V = 0 \qquad (21)$$

It means that no heat is absorbed or evolved when the components are mixed. Also, the volume of solution would be equal to the sum of volumes of the two components. At molecular level, ideal behavior of the solutions can be explained by considering two components A and B. In pure components, the intermolecular attractive interactions will be of types A-A and B-B, whereas in the binary solutions in addition to these two interactions, A-B type of interactions will also be present. If the intermolecular attractive forces between the A-A and B-B are nearly equal to those between A-B, this leads to the formation of ideal solution. A perfectly ideal solution is rare but some solutions are nearly ideal in behavior. Solution of n-hexane and n-heptane, bromoethane and chloroethane, benzene and toluene, etc. fall into this category.

6.6.2 Non-ideal Solutions

When a solution does not obey Raoult's law over the entire range of concentration, then it is called non-ideal solution. The vapor pressure of such a solution is either higher or lower than that predicted by Raoult's law. If it is higher, the solution exhibits positive deviation and if it is lower, it exhibits negative deviation

from Raoult's law. The plots of vapor pressure as a function of mole fractions for such solutions are shown in Fig. 6.
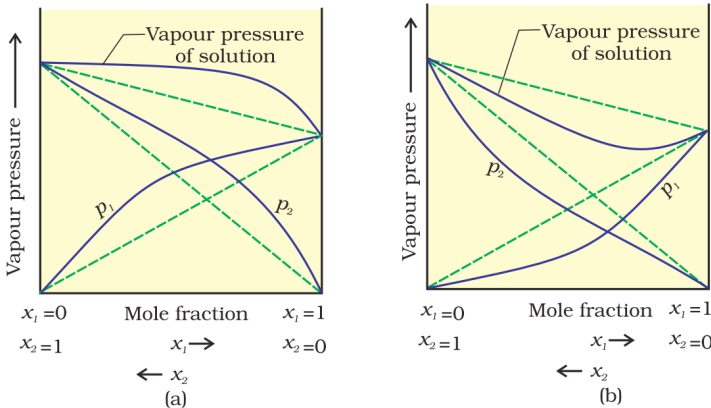
Figure 6. The vapor pressures of two component systems as a function of composition (a) a solution that shows positive deviation from Raoult's law and (b) a solution that shows negative deviation from Raoult's law.

The cause for these deviations lie in the nature of interactions at the molecular level. In case of positive deviation from Raoult's law, A-B interactions are weaker than those between A-A or B-B, i.e., in this case the intermolecular attractive forces between the solute-solvent molecules are weaker than those between the solute-solute and solvent-solvent molecules. This means that in such solutions, molecules of A (or B) will find it easier to escape than in pure state. This will increase the vapor pressure and result in positive deviation. Mixtures of ethanol and acetone behave in this manner. In pure ethanol, molecules are hydrogen bonded. On adding acetone, its molecules get in between the host molecules and break some of the hydrogen bonds between them. Due to weakening of interactions, the solution shows positive deviation from Raoult's law [Fig. 6 (a)]. In a solution formed by adding carbon disulphide to acetone, the dipolar interactions between solute-solvent molecules are weaker than the respective interactions among the solute-solute and solvent-solvent molecules. This solution also shows positive deviation.

In case of negative deviations from Raoult's law, the intermolecular attractive forces between A-A and B-B are weaker than those between A-B and leads to decrease in vapor pressure resulting in negative deviations. An example of this type is a mixture of phenol and aniline. In this case the intermolecular hydrogen bonding between phenolic proton and lone pair on nitrogen atom of aniline is stronger than the respective intermolecular hydrogen bonding between similar molecules. Similarly, a mixture of chloroform and acetone forms a solution with negative deviation from Raoult's law. This is because chloroform molecule is able to form hydrogen bond with acetone molecule as shown.
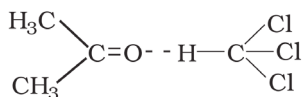
This decreases the escaping tendency of molecules for each component and consequently the vapor pressure decreases resulting in negative deviation from Raoult's law [Fig. 6. (b)].

Some liquids on mixing, form azeotropes which are binary mixtures having the same composition in liquid and vapor phase and boil at a constant temperature. In such cases, it is not possible to separate the components by fractional distillation. There are two types of azeotropes called minimum boiling azeotrope and maximum boiling azeotrope. The solutions which show a large positive deviation from Raoult's law form minimum boiling azeotrope at a specific composition.

For example, ethanol-water mixture (obtained by fermentation of sugars) on fractional distillation gives a solution containing approximately 95% by volume of ethanol. Once this composition, known as azeotrope composition, has been achieved, the liquid and vapor have the same composition, and no further separation occurs.

The solutions that show large negative deviation from Raoult's law form maximum boiling azeotrope at a specific composition. Nitric acid and water is an example of this class of azeotrope. This azeotrope has the approximate composition, 68% nitric acid and 32% water by mass, with a boiling point of 393.5 K.

6.7 COLLIGATIVE PROPERTIES AND DETERMINATION OF MOLAR MASS

The vapor pressure of solution decreases when a non-volatile solute is added to a volatile solvent. There are many properties of solutions which are connected with this decrease of vapor pressure. These are: (1) relative lowering of vapor pressure of the solvent (2) depression of freezing point of the solvent (3) elevation of boiling point of the solvent and (4) osmotic pressure of the solution. All these properties depend on the number of solute particles irrespective of their nature relative to the total number of particles present in the solution. Such properties are called colligative properties (colligative: from Latin: co means together, ligare means to bind). In the following Sections we will discuss these properties one by one.

6.7.1 Relative Lowering of Vapor Pressure

The vapor pressure of a solvent in solution is less than that of the pure solvent. Raoult established that the lowering of vapor pressure depends only on the concentration of the solute particles and it is independent of their identity. The equation given a relation between vapor pressure of the solution, mole fraction and vapor pressure of the solvent, i.e.,

$$p_1 = x_1 \, p_1^{\,0} \tag{22}$$

The reduction in the vapor pressure of solvent (Δp_1) is given as:

$$\Delta p_1 = p_1^{\,0} - p_1 = p_1^{\,0} - p_1^{\,0} x_1$$
$$= p_1^{\,0} (1 - x_1) \tag{23}$$

Knowing that $x_2 = 1 - x_1$, equation (23) reduces to

$$\Delta p_1 = x_2 \, p_1^{\,0} \tag{24}$$

In a solution containing several non-volatile solutes, the lowering

of the vapor pressure depends on the sum of the mole fraction of different solutes.

Equation (24) can be written as

$$\frac{\Delta p_1}{p_1^0} = \frac{p_1^0 - p_1}{p_1^0} = x_2 \tag{25}$$

The expression on the left hand side of the equation as mentioned earlier is called relative lowering of vapor pressure and is equal to the mole fraction of the solute. The above equation can be written as:

$$\frac{p_1^0 - p_1}{p_1^0} = \frac{n_2}{n_1 + n_2} \quad \left(\text{since } x_2 = \frac{n_2}{n_1 + n_2} \right) \tag{26}$$

Here n_1 and n_2 are the number of moles of solvent and solute respectively present in the solution. For dilute solutions $n_2 << n_1$, hence neglecting n_2 in the denominator we have

$$\frac{p_1^0 - p_1}{p_1^0} = \frac{n_2}{n_1} \tag{27}$$

or

$$\frac{p_1^0 - p_1}{p_1^0} = \frac{w_2 \times M_1}{M_2 \times w_1} \tag{28}$$

Here w_1 and w_2 are the masses and M_1 and M_2 are the molar masses of the solvent and solute respectively.

From this equation (28), knowing all other quantities, the molar mass of solute (M_2) can be calculated.

6.7.2 Elevation of the Boiling-Point

The vapor pressure of a liquid increases with increase of temperature. It boils at the temperature at which its vapor pressure

is equal to the atmospheric pressure. For example, water boils at 373.15 K (100° C) because at this temperature the vapor pressure of water is 1.013 bar (1 atmosphere). Vapor pressure of the solvent decreases in the presence of non-volatile solute. Fig. 7 depicts the variation of vapor pressure of the pure solvent and solution as a function of temperature. For example, the vapor pressure of an aqueous solution of sucrose is less than 1.013 bar at 373.15 K. In order to make this solution boil, its vapor pressure must be increased to 1.013 bar by raising the temperature above the boiling temperature of the pure solvent (water). Thus, the boiling point of a solution is always higher than that of the boiling point of the pure solvent in which the solution is prepared as shown in Fig. 7. Similar to lowering of vapor pressure, the elevation of boiling point also depends on the number of solute molecules rather than their nature. A solution of 1 mol of sucrose in 1000 g of water boils at 373.52 K at one atmospheric pressure.
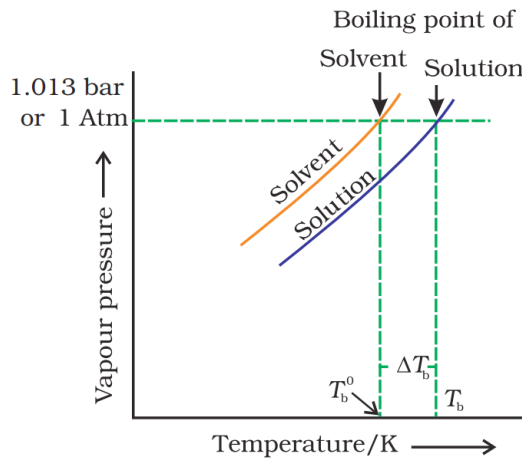
Figure 7. The vapor pressure curve for solution lies below the curve for pure water. The diagram shows that ΔT_b denotes the elevation of boiling point of a solvent in solution.

Let T_b^0 be the boiling point of pure solvent and T_b be the boiling point of solution. The increase in the boiling point $\Delta T_b = T_b - T_b^0$ is known as elevation of boiling point.

Experiments have shown that for dilute solutions the elevation of boiling point (ΔT_b) is directly proportional to the molal concentration of the solute in a solution. Thus

$$\Delta T_b \propto m \tag{29}$$

or

$$\Delta T_b = K_b\, m \tag{30}$$

Here m (molality) is the number of moles of solute dissolved in 1 kg of solvent and the constant of proportionality, K_b is called Boiling Point Elevation Constant or Molal Elevation Constant (Ebullioscopic Constant). The unit of K_b is K kg mol^{-1}. Values of K_b for some common solvents are given in Table 3. If w_2 gram of solute of molar mass M_2 is dissolved in w_1 gram of solvent, then molality, m of the solution is given by the expression:

$$m \;=\; \frac{w_2/M_2}{w_1/1000} \;=\; \frac{1000 \times w_2}{M_2 \times w_1} \tag{31}$$

Substituting the value of molality in equation (30) we get

$$\Delta T_b \;=\; \frac{K_b \times 1000 \times w_2}{M_2 \times w_1} \tag{32}$$

$$M_2 \;=\; \frac{1000 \times w_2 \times K_b}{\Delta T_b \times w_1} \tag{33}$$

Thus, in order to determine M_2, molar mass of the solute, known mass of solute in a known mass of the solvent is taken and ΔT_b is determined experimentally for a known solvent whose K_b value is known.

6.7.3 Depression of the Freezing-Point

The lowering of vapor pressure of a solution causes a lowering of the freezing point compared to that of the pure solvent (Fig.

8). We know that at the freezing point of a substance, the solid phase is in dynamic equilibrium with the liquid phase. Thus, the freezing point of a substance may be defined as the temperature at which the vapor pressure of the substance in its liquid phase is equal to its vapor pressure in the solid phase. A solution will freeze when its vapor pressure equals the vapor pressure of the pure solid solvent as is clear from Fig. 8. According to Raoult's law, when a non-volatile solid is added to the solvent its vapor pressure decreases and now it would become equal to that of solid solvent at lower temperature. Thus, the freezing point of the solvent decreases.
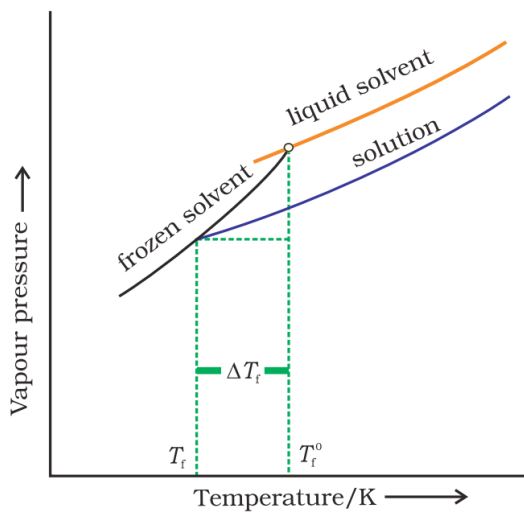
Figure 8. Diagram showing ΔT_f, depression of the freezing point of a solvent in a solution.

Let T_f^0 be the freezing point of pure solvent and T_f be its freezing point when non-volatile solute is dissolved in it. The decrease in freezing point.

$\Delta T_f = T_f^0 - T_f$ is known as depression in freezing point.

Similar to elevation of boiling point, depression of freezing point (ΔT_f) for dilute solution (ideal solution) is directly proportional to

molality, m of the solution. Thus,

$$\Delta T_f \quad \propto \quad m$$

or

$$\Delta T_f = K_f \, m$$

$$(34)$$

The proportionality constant, K_f, which depends on the nature of the solvent is known as Freezing Point Depression Constant or Molal Depression Constant or Cryoscopic Constant. The unit of K_f is K kg mol^{-1}. Values of K_f for some common solvents are listed in Table 3.

Table 3: Molal Boiling Point Elevation and Freezing Point Depression Constants for Some Solvents

Solvent	b. p./K	K_b/K kg mol^{-1}	f. p./K	K_f/K kg mol^{-1}
Water	373.15	0.52	273.0	1.86
Ethanol	351.5	1.20	155.7	1.99
Cyclohexane	353.74	2.79	279.55	20.00
Benzene	353.3	2.53	278.6	5.12
Chloroform	334.4	3.63	209.6	4.79
Carbon tetrachloride	350.0	5.03	250.5	31.8
Carbon disulphide	319.4	2.34	164.2	3.83
Diethyl ether	307.8	2.02	156.9	1.79
Acetic acid	391.1	2.93	290.0	3.90

If w_2 gram of the solute having molar mass as M_2, present in w_1 gram of solvent, produces the depression in freezing point ΔT_f of the solvent then molality of the solute is given by the equation.

$$m = \frac{w_2 / M_2}{w_1 / 1000}$$

Substituting this value of molality in equation (34) we get:

$$\Delta T_f = \frac{K_f \times w_2 / M_2}{w_1 / 1000}$$

$$\Delta T_f = \frac{K_f \times w_2 \times 1000}{M_2 \times w_1}$$

$$(35)$$

$$M_2 = \frac{K_f \times w_2 \times 1000}{\Delta T_f \times w_1}$$

(36)

Thus for determining the molar mass of the solute we should know the quantities w_1, w_2, ΔT_f, along with the molal freezing point depression constant.

The values of K_f and K_b, which depend upon the nature of the solvent, can be ascertained from the following relations.

$$K_f = \frac{R \times M_1 \times T_f^2}{1000 \times \Delta_{fus}H}$$

(37)

$$K_b = \frac{R \times M_1 \times T_b^2}{1000 \times \Delta_{vap}H}$$

(38)

Here the symbols R and M_1 stand for the gas constant and molar mass of the solvent, respectively and T_f and T_b denote the freezing point and the boiling point of the pure solvent respectively in kelvin. Further, $\Delta_{fus}H$ and $\Delta_{vap}pH$ represent the enthalpies for the fusion and vaporization of the solvent, respectively.

6.7.4 The Osmotic Pressure of an Ideal Solution

There are many phenomena which we observe in nature or at home. For example, raw mangoes shrivel when pickled in brine (salt water); wilted flowers revive when placed in fresh water, blood cells collapse when suspended in saline water, etc. If we look into these processes we find one thing common in all, that is, all these substances are bound by membranes. These membranes can be of animal or vegetable origin and these occur naturally such as pig's bladder or parchment or can be synthetic such as cellophane. These membranes appear to be continuous sheets or films, yet they contain a network of submicroscopic holes or pores. Small solvent molecules, like water, can pass through these holes but the passage of bigger molecules like solute is hindered. Membranes having this kind of properties are known as semipermeable membranes (SPM).

Assume that only solvent molecules can pass through these semipermeable membranes. If this membrane is placed between the solvent and solution as shown in Fig. 9, the solvent molecules will flow through the membrane from pure solvent to the solution. This process of flow of the solvent is called osmosis.
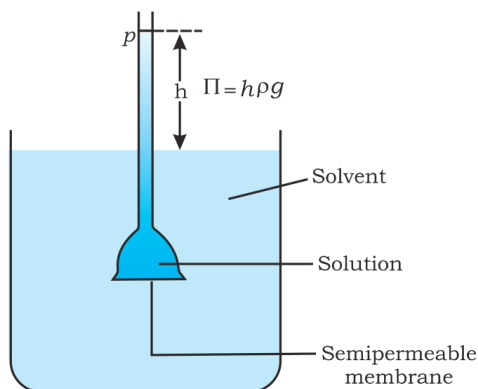
Figure 9. Level of solution rises in the thistle funnel due to osmosis of solvent.

The flow will continue till the equilibrium is attained. The flow of the solvent from its side to solution side across a semipermeable membrane can be stopped if some extra pressure is applied on the solution. This pressure that just stops the flow of solvent is called osmotic pressure of the solution. The flow of solvent from dilute solution to the concentrated solution across a semipermeable membrane is due to osmosis. The important point to be kept in mind is that solvent molecules always flow from lower concentration to higher concentration of solution. The osmotic pressure has been found to depend on the concentration of the solution.

The osmotic pressure of a solution is the excess pressure that must be applied to a solution to prevent osmosis, i.e., to stop the passage of solvent molecules through a semipermeable membrane into the solution. This is illustrated in Fig. 10. Osmotic pressure is a colligative property as it depends on the number of solute molecules and not on their identity. For dilute solutions, it has

been found experimentally that osmotic pressure is proportional to the molarity, C of the solution at a given temperature T. Thus:

$$\Pi = C\,R\,T \tag{39}$$

Here Π is the osmotic pressure and R is the gas constant.

$$\Pi = (n_2\,/V)\,R\,T \tag{40}$$

Here V is volume of a solution in litres containing n_2 moles of solute. If w_2 grams of solute, of molar mass, M_2 is present in the solution, then $n_2 = w_2\,/\,M_2$ and we can write,

$$\Pi\,V = \frac{w_2\,R\,T}{M_2} \tag{41}$$

or

$$M_2 = \frac{w_2\,R\,T}{\Pi\,V} \tag{42}$$

Thus, knowing the quantities w_2, T, Π and V we can calculate the molar mass of the solute.
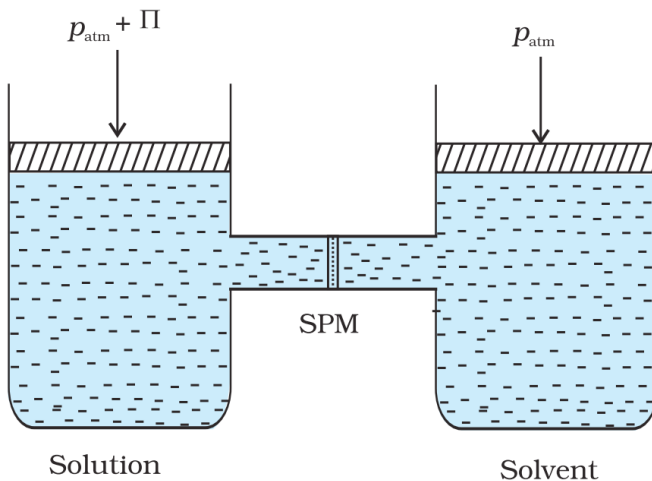
Figure 10. The excess pressure equal to the osmotic pressure must be applied on the solution side to prevent osmosis.

Measurement of osmotic pressure provides another method of determining molar masses of solutes. This method is widely used to determine molar masses of proteins, polymers and other macromolecules. The osmotic pressure method has the advantage over other methods as pressure measurement is around the room temperature and the molarity of the solution is used instead of molality. As compared to other colligative properties, its magnitude is large even for very dilute solutions. The technique of osmotic pressure for determination of molar mass of solutes is particularly useful for biomolecules as they are generally not stable at higher temperatures and polymers have poor solubility.

Two solutions having same osmotic pressure at a given temperature are called isotonic solutions. When such solutions are separated by semipermeable membrane no osmosis occurs between them. For example, the osmotic pressure associated with the fluid inside the blood cell is equivalent to that of 0.9% (mass/ volume) sodium chloride solution, called normal saline solution and it is safe to inject intravenously. On the other hand, if we place the cells in a solution containing more than 0.9% (mass/volume) sodium chloride, water will flow out of the cells and they would shrink. Such a solution is called hypertonic. If the salt concentration is less than 0.9% (mass/volume), the solution is said to be hypotonic. In this case, water will flow into the cells if placed in this solution and they would swell.

The phenomena mentioned in the beginning of this section can be explained on the basis of osmosis. A raw mango placed in concentrated salt solution loses water via osmosis and shrivel into pickle. Wilted flowers revive when placed in fresh water. A carrot that has become limp because of water loss into the atmosphere can be placed into the water making it firm once again. Water will move into its cells through osmosis. When placed in water containing less than 0.9% (mass/ volume) salt, blood cells swell due to flow of water in them by osmosis. People taking a lot of salt or salty food experience water retention in tissue cells and intercellular spaces because of osmosis. The resulting puffiness or swelling is called edema. Water movement from soil into plant

roots and subsequently into upper portion of the plant is partly due to osmosis. The preservation of meat by salting and of fruits by adding sugar protects against bacterial action. Through the process of osmosis, a bacterium on salted meat or candid fruit loses water, shrivels and dies.

6.7.5 Reverse Osmosis and Water Purification

The direction of osmosis can be reversed if a pressure larger than the osmotic pressure is applied to the solution side. That is, now the pure solvent flows out of the solution through the semi permeable membrane. This phenomenon is called reverse osmosis and is of great practical utility. Reverse osmosis is used in desalination of sea water. A schematic set up for the process is shown in Fig. 11.
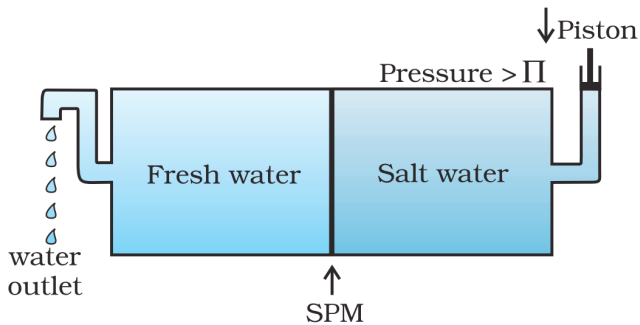
Figure 11. Reverse osmosis occurs when a pressure larger than the osmotic pressure is applied to the solution.

When pressure more than osmotic pressure is applied, pure water is squeezed out of the sea water through the membrane. A variety of polymer membranes are available for this purpose.

The pressure required for the reverse osmosis is quite high. A workable porous membrane is a film of cellulose acetate placed over a suitable support. Cellulose acetate is permeable to water but impermeable to impurities and ions present in sea water. These days many countries use desalination plants to meet their potable water requirements.

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7

REACTION EQUILIBRIUM IN SOLUTIONS: ELECTROLYTE

INTRODUCTION

Electrolyte, in chemistry and physics, substance that conducts electric current as a result of a dissociation into positively and negatively charged particles called ions, which migrate toward and ordinarily are discharged at the negative and positive terminals (cathode and anode) of an electric circuit, respectively. The most familiar electrolytes are acids, bases, and salts, which ionize when dissolved in such solvents as water or alcohol. Many salts, such as sodium chloride, behave as electrolytes when melted in the absence of any solvent; and some, such as silver iodide, are electrolytes even in the solid state.

The equilibrium properties of electrolyte solutions can be studied experimentally by electrochemical measurements, freezing-point depressions, solubility determinations, osmotic pressures,

or measurements of vapour pressure. Most electrolytes, such as salts, are nonvolatile at ordinary temperature, and, in that event, the vapour pressure exerted by the solution is the same as the partial pressure of the solvent. The activity coefficient of the solvent can, therefore, be found from total-pressure measurements, and, using the Gibbs-Duhem equation, it is then possible to calculate the activity coefficient of the electrolyte solute. This activity coefficient is designated by $\gamma_\pm$ to indicate that it is a mean activity coefficient for the positive and negative ions. Since it is impossible to isolate positive ions and negative ions into separate containers, it is not possible to determine individual activity coefficients for the positive ions and for the negative ions. The mean activity coefficient $\gamma_\pm$ is so defined that it approaches a value of unity at very low molality where the ions are so far apart that they exert negligible influence on one another. A German chemist, relates $\gamma_\pm$ to the ionic strength, which is the sum of the products of the concentration of each ion (in moles per litre) and the square of its charge; the equation predicts that $\gamma_\pm$ decreases with rising ionic strength in agreement with experiment at very low ionic strength; at higher ionic strength, however, $\gamma_\pm$ rises, and in some cases $\gamma_\pm$ is greater than 1. The derivation of the Debye-Hückel theory clearly shows that it is limited to low concentrations. Many attempts have been made to extend the Debye-Hückel equation to higher electrolyte concentrations. One of the more successful attempts is based on the idea that the ions are solvated, which means that every ion is surrounded by a tight-fitting shell of solvent molecules.

The concept of solvation is often used to explain properties of aqueous solutions; one well-known property is the salting-out effect, in which the solubility of a nonelectrolyte in water is decreased when electrolyte is added. For example, the solubility of ethyl ether in water at 25° C is 0.91 mole percent, but, in an aqueous solution containing 15 weight percent sodium chloride, it is only 0.13 mole percent. This decrease in solubility can be explained by postulating that some of the water molecules cannot participate in the dissolution of the ether because they are tightly held (solvated) by sodium and chloride ions.

Electrolyte solutions have long been of interest in industry since many common inorganic chemicals are directly obtained, or else separated, by crystallization from aqueous solution. Further, many important chemical and metallurgical products (e.g., aluminum) are obtained or refined by electrochemical processes that occur in liquid solution. In recent years there has been renewed interest in electrolyte solutions because of their relevance to fuel cells as a possible source of power for automobiles.

The properties of electrolyte solutions also have large importance in physiology. Many molecules that occur in biological systems bear electric charges; a large molecule that has a positive electric charge at one end and a negative charge at the other is called a zwitterion. Very large molecules, such as those of proteins, may have numerous positive and negative charges; such molecules are called polyelectrolytes. In solution, the conformation (i.e., the three-dimensional structure) of a large, charged molecule is strongly dependent on the ionic strength of the dissolving medium; for example, depending on the nature and concentration of salts present in the solvent, a polyelectrolyte molecule may coagulate into a ball, it may stretch out like a rod, or it may form a coil or helix. The conformation, in turn, is closely related to the molecule's physiological function.
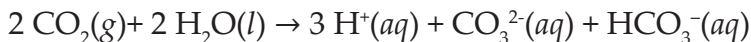
7.1 ELECTROLYTE SOLUTION

An electrolyte is any salt or ionizable molecule that, when dissolved in solution, will give that solution the ability to conduct electricity. This is because when a salt dissolves, its dissociated ions can move freely in solution, allowing a charge to flow.

Electrolyte solutions are normally formed when a salt is placed into a solvent such as water. For example, when table salt, $NaCl$, is placed in water, the salt (a solid) dissolves into its component ions, according to the dissociation reaction:

$NaCl(s) \rightarrow Na^+(aq) + Cl^-(aq)$

It is also possible for substances to react with water to yield ions

in solution. For example, carbon dioxide gas, CO_2, will dissolve in water to produce a solution that contains hydrogen ions, carbonate, and hydrogen carbonate ions:

$$2\ CO_2(g) + 2\ H_2O(l) \rightarrow 3\ H^+(aq) + CO_3^{2-}(aq) + HCO_3^-(aq)$$

The resulting solution will conduct electricity because it contains ions. It is important to keep in mind, however, that CO_2 is *not* an electrolyte, because CO_2 itself does not dissociate into ions. Only compounds that dissociate into their component ions in solution qualify as electrolytes.

Strong and Weak Electrolytes

As mentioned above, when an ionizable solute dissociates, the resulting solution can conduct electricity. Therefore, compounds that readily form ions in solution are known as strong electrolytes. (By this reasoning, all strong acids and strong bases are strong electrolytes.)

By contrast, if a compound dissociates to a small extent, the solution will be a weak conductor of electricity; a compound that only dissociates weakly, therefore, is known as a weak electrolyte.

A strong electrolyte will completely dissociate into its component ions in solution; a weak electrolyte, on the other hand, will remain mostly undissociated in solution. An example of a weak electrolyte is acetic acid, which is also a weak acid.

Nonelectrolyte Solutions

Nonelectrolytes are compounds that do not ionize at all in solution. As a result, solutions containing nonelectrolytes will not conduct electricity. Typically, nonelectrolytes are primarily held together by covalent rather than ionic bonds. A common example of a nonelectrolyte is glucose, or $C_6H_{12}O_6$. Glucose (sugar) readily dissolves in water, but because it does not dissociate into ions in solution, it is considered a nonelectrolyte; solutions containing glucose do not, therefore, conduct electricity.

7.1.1 Water's Solvent Properties

Water, which not only dissolves many compounds but also dissolves more substances than any other liquid, is considered the universal solvent. A polar molecule with partially-positive and negative charges, it readily dissolves ions and polar molecules. Water is therefore referred to as a solvent: a substance capable of dissolving other polar molecules and ionic compounds. The charges associated with these molecules form hydrogen bonds with water, surrounding the particle with water molecules. This is referred to as a sphere of hydration, or a hydration shell, and serves to keep the particles separated or dispersed in the water.

When ionic compounds are added to water, individual ions interact with the polar regions of the water molecules during the dissociation process, disrupting their ionic bonds. Dissociation occurs when atoms or groups of atoms break off from molecules and form ions. Consider table salt (NaCl, or sodium chloride): when NaCl crystals are added to water, the molecules of NaCl dissociate into Na^+ and Cl^- ions, and spheres of hydration form around the ions. The positively-charged sodium ion is surrounded by the partially-negative charge of the water molecule's oxygen; the negatively-charged chloride ion is surrounded by the partially-positive charge of the hydrogen in the water molecule.
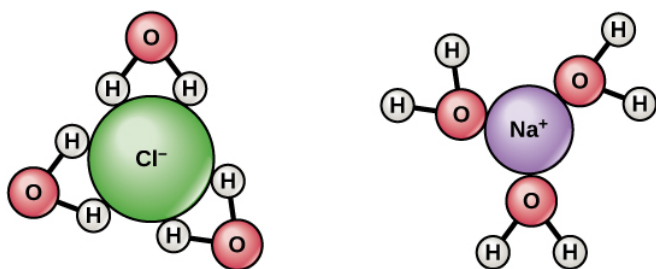
Since many biomolecules are either polar or charged, water readily dissolves these hydrophilic compounds. Water is a poor solvent, however, for hydrophobic molecules such as lipids. Nonpolar molecules experience hydrophobic interactions in water: the water changes its hydrogen bonding patterns around the hydrophobic molecules to produce a cage-like structure called a clathrate. This change in the hydrogen-bonding pattern of the water solvent causes the system's overall entropy to greatly decrease, as the molecules become more ordered than in liquid water. Thermodynamically, such a large decrease in entropy is not spontaneous, and the hydrophobic molecule will not dissolve.

7.1.2 Electrolytic Properties

When electrodes are placed in an electrolyte solution and a voltage is applied, the electrolyte will conduct electricity. Lone electrons cannot usually pass through the electrolyte; instead, a chemical reaction occurs at the cathode that consumes electrons from the anode. Another reaction occurs at the anode, producing electrons that are eventually transferred to the cathode. As a result, a negative charge cloud develops in the electrolyte around the cathode, and a positive charge develops around the anode. The ions in the electrolyte neutralize these charges, enabling the electrons to keep flowing and the reactions to continue.

For example, in a solution of ordinary table salt (sodium chloride, NaCl) in water, the cathode reaction will be:

$$2H_2O + 2e^- \rightarrow 2OH^- + H_2$$
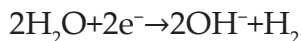
and hydrogen gas will bubble up. The anode reaction is:

$2NaCl \rightarrow 2Na^+ + Cl2 + 2e^-$

and chlorine gas will be liberated. The positively-charged sodium ions Na^+ will react toward the cathode, neutralizing the negative charge of OH^- there; the negatively-charged hydroxide ions OH^- will react toward the anode, neutralizing the positive charge of Na^+ there. Without the ions from the electrolyte, the charges around the electrode slow continued electron flow; diffusion of H^+ and OH^- through water to the other electrode takes longer than movement of the much more prevalent salt ions.

In other systems, the electrode reactions can involve electrode metal as well as electrolyte ions. In batteries for example, two materials with different electron affinities are used as electrodes: outside the battery, electrons flow from one electrode to the other; inside, the circuit is closed by the electrolyte's ions. Here, the electrode reactions convert chemical energy to electrical energy.

Oxidation and Reduction at the Electrodes

Oxidation of ions or neutral molecules occurs at the anode, and the reduction of ions or neutral molecules occurs at the cathode. Two mnemonics for remembering that reduction happens at the cathode and oxidation at the anode are: "Red Cat" (reduction – cathode) and "An Ox" (anode – oxidation). The mnemonic "LeO said GeR" is useful for remembering "lose an electron in oxidation" and "gain an electron in reduction."

It is possible to oxidize ferrous ions to ferric ions at the anode. For example:

$Fe^{2+}(aq) \rightarrow Fe^{3+}(aq) + e^-$
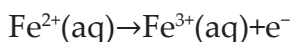
Neutral molecules can also react at either electrode. For example, p-Benzoquinone can be reduced to hydroquinone at the cathode:

$+2e^- + 2H^+ \rightarrow$
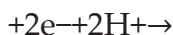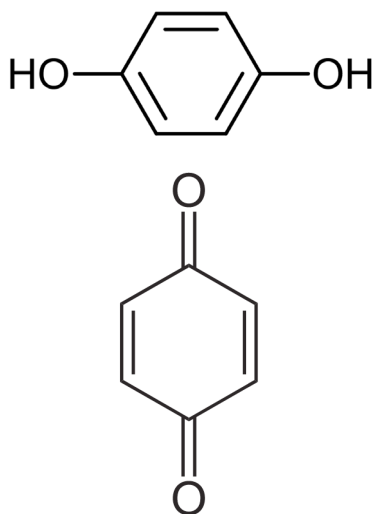
7.1.3 Electrolytes in Body Fluids

Our body fluids are solutions of electrolytes and many other things. The combination of blood and the circulatory system is the river of life, because it coordinates all the life functions. When the heart stops pumping in a heart attack, the life ends quickly. Getting the heart restarted as soon as one can is crucial in order to maintain life.

The primary electrolytes required in the body fluid are cations (of calcium, potassium, sodium, and magnesium) and anions (of chloride, carbonates, aminoacetates, phosphates, and iodide). These are nutritionally called macrominerals.

Electrolyte balance is crucial to many body functions. Here's some extreme examples of what can happen with an imbalance of electrolytes: elevated potassium levels may result in cardiac arrhythmias; decreased extracellular potassium produces paralysis; excessive extracellular sodium causes fluid retention; and decreased plasma calcium and magnesium can produce muscle spasms of the extremities.

When a patient is dehydrated, a carefully prepared (commercially available) electrolyte solution is required to maintain health and well being. In terms of child health, oral electrolyte is need when a child is dehydrated due to diarrhea. The use of oral electrolyte maintenance solutions, which is responsible for saving millions of lives worldwide over the last 25 years, is one of the most important medical advances in protecting the health of children in the century, explains Juilus G.K. Goepp, MD, assistant director of the Pediatric Emergency Department of the Children's Center at Johns Hopkins Hospital. If a parent provides an oral electrolyte maintenance solution at the very start of the illness, dehydration can be prevented. The functionality of electrolyte solutions is related to their properties, and interest in electrolyte solutions goes far beyond chemistry.

7.1.4 Electrolytes and Batteries

Solutions of electrolytes are always required in batteries, even in dry cells. The simplest battery consists of two electrodes. The figure here illustrates a copper-zinc battery. The left hand is a zinc electrode. The zinc atoms have a tendency to become ions, leaving the electrons behind.

$$Zn_{(s)} \rightarrow Zn^{2+}_{(aq)} + 2e^-$$
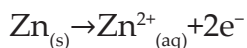
As the zinc ions going into the solution, anions move from the copper cell to the zinc cell to compensate for the charge, and at the same time, electrons go from the Z_n electrode to the C_u electrode to neutralize the copper ions.

$$Cu^{2+}_{(aq)} + 2e^- \rightarrow Cu_{(s)}$$
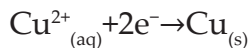
In dry cells, the solution is replaced by a paste so that the solution will not leak out of the package. In this cell, the Z_n and C_u electrode has a voltage of 1.10 V, if the concentrations of the ions are as indicated.

$$Zn = Zn^{2+} + 2\,e^-$$

7.1.5 Chemical Reactions of Electrolytes

When solutions of electrolytes are combined, the cations and anions will meet each other. When the ions are indifferent of each other, there is no reaction. However, some cations and anions may form a molecule or solid, and thus the cations and anions change partners. These are called metathesis reactons, which include:

Solid formation (or precipitation) reactions: the cations and anions form a less soluble solid, resulting in the appearance of a precipitate.

Neutralization reactions: H^+ of an acid and OH^- of a base combine to give the neutral water molecule.

Gas formation reactions: When neutral gaseous molecules are formed in a reaction, they leave the solution forming a gas.

Redox reactions are also possible between the various ions. In fact, the battery operations involve redox reactions.

7.1.6 Activity Coefficients of Electrolyte Solutions

To begin the discussion of nonideality in electrolyte solutions, we first define the activity coefficients. Let's say we have an electrolyte which when one mole of it is dissolved in an aqueous solution, v_+ moles of positive ions with charge z_+ and v_- moles of negative ions with charge z_- are produced. An example is Na_2SO_4, for which

v+ = 2, z_+ = +1, v_- = 1, and z− = −2. If n moles of this electrolyte is dissolved, the solute's contribution to the Gibbs free energy of the entire solution is:

$$G - G_s = n\mu = n(\nu_+\mu_+ + \nu_-\mu_-), \tag{1}$$

where μ_+ and μ_- are the chemical potentials of the positive and negative ions separately, and G_s is the free enrgy due to the solvent.

Because the effects of the positive and negative ions are difficult to separate, we often define the mean ionic chemical potential $\mu_\pm$ as:

$$\mu = \nu\mu_\pm = \nu_+\mu_+ + \nu_-\mu_- \tag{2}$$

where ν is the total number of ions produced by one mole of solute:

$$\nu = \nu_+ + \nu_-. \tag{3}$$

In this way, the chemical potential of the solute (from both the positive and negative ions) becomes:

$$\mu = \mu^\circ + RT \ln a = \nu(\mu_\pm^\circ + RT \ln a_\pm), \tag{4}$$

where $a_\pm$ is the mean ionic activity of the solute, which is related to the activity a by a = a $\nu_\pm$. On the other hand, if we were able to write the chemical potential separately for the positive and the negative ions, we would have:

$$\mu = \nu_+(\mu_+^\circ + RT \ln a_+) + \nu_-(\mu_-^\circ + RT \ln a_-), \tag{5}$$

where a_+ and a_- are their activities separately, we see that the mean ionic activity is just the geometric mean of the two separate ionic activities:

$$a_\pm^\nu = a_+^{\nu_+} \cdot a_-^{\nu_-}. \tag{6}$$

To quantify the concentration of electrolyte solutions, it is often convenient to use the molality instead of mole fraction. The molality m of a solute is defined as the number of moles of the solute n per kilogram of solvent. Because the solvent has a certain molar mass, the molality of solute i is simply related to its mole fraction x_i by:

$$m_i = \frac{1000 x_i}{x_s M_s},$$

(7)

where xs and Ms are the mole fraction and the molar mass (in g/mol) of the solvent (the factor 1000 is needed because the molar mass is usually represented in units of grams per mole). The nice feature about using the molality to describe solute concentration instead of the mole fraction or the molarity is that the molality of one solute is independent of all other solutes. In contrast to the molarity, the molality is also independent of temperature or the mixing volume. In the dilute limit, all three concentration measures are proportional to each other. The activity of a solute in an electrolyte solution is often written as the activity coefficient γ multiplied by its molality m, so that Eqs.(4) and (5) become:

$$
\begin{aligned}
\mu &= \mu^\circ + RT \ln \gamma m = \nu(\mu_\pm^\circ + RT \ln \gamma_\pm m_\pm) \\
&= \nu_+(\mu_+^\circ + RT \ln \gamma_+ m_+) + \nu_-(\mu_-^\circ + RT \ln \gamma_- m_-),
\end{aligned}
$$

(8)

which requires that the mean ionic activity coefficient $\gamma_\pm$ and the mean ionic molality $m_\pm$ be related to the corresponding properties of the separate ions as:

$$\gamma_\pm^\nu m_\pm^\nu = \gamma_+^{\nu_+} \gamma_-^{\nu_-} m_+^{\nu_+} m_-^{\nu_-},$$

(9)

or separating the activity coefficient from the molality:

$$
\begin{aligned}
\gamma_\pm^\nu &= \gamma_+^{\nu_+} \gamma_-^{\nu_-},
\end{aligned}
$$

(10)

$$
\begin{aligned}
m_\pm^\nu &= m_+^{\nu_+} m_-^{\nu_-}.
\end{aligned}
$$

(11)

Using the molality of the positive and negative ions

$$m_+ = \nu_+ m \qquad m_- = \nu_- m,$$

(12)

we can obtain the necessary relationship between the mean ionic molality and the molality of the solute as

$$m_\pm = (\nu_+^{\nu_+} \nu_-^{\nu_-})^{1/\nu} m.$$

(13)

With this relationship, we can calculate m± from the molality of the solute. The corresponding expression for the chemical potential is:

$$\mu = \mu^\circ + \nu RT \ln \gamma_\pm m_\pm. \qquad (14)$$

7.1.7 Equilibria in Electrolyte Solutions

As we know, to first order the correction to the chemical potential for a compound i that is not pure is given by the term $RT \ln x_i$. Since the molality mi is proportional to xi , we can replace x_i by mi by switching to a standard state where $m_i = 1$ instead of $x_i = 1$. The activity coefficient can then be thought of as the second order correction to the chemical potential due to concentration:

$$\mu = \mu^\circ + RT \ln m_i + RT \ln \gamma_i. \qquad (15)$$

For an ideal solution $\gamma_i \to 1$.

To illustrate how the inclusion of the activity coefficient influences equilibria in electolyte solutions, consider first the effect of the solute on the freezing point of the solution.

We saw how freezing point depression is related to the solute's mole fraction. For a nonideal solution, the mole fraction should be replaced by the activity $a_i = \gamma_i m_i$, so for a dilute solution with only one solute:

$$T_f' - T_f = \left(\frac{RT_f^2 M_s}{1000\Delta H_{fus}^\circ} \right) \gamma m, \qquad (17)$$

where we have used the definition of the molality in Eq.(7) and approximated the mole fraction of the solvent by 1. The freezing point depression of an electrolyte solution therefore provides an estimate of the activity coefficient near the freezing temperature. The mean ionic activity coefficients for several electrolyte solutions are shown in Fig. 1 as a function of the square root of the molality. One thing is immediately clear – in this molality range (1 molal or less), the activity coefficients are all less than unity and the larger the charges of the dissolved ions, the small it becomes. A second thing that may not be as obvious is that solutions with ions of the same charge composition (e.g. +1:-1 electrolytes like HCl and KCl) seem to have the same activity coefficient in the dilute limit.

Interestingly, solutions of a +1:-2 electrolyte like $Ca(NO_3)_2$ and a +2:-1 electrolyte like H_2SO_4 also seem to have the same activity coefficients in the dilute limit. Therefore, it appears that it is not the sign of the ionic charges that is important for determining the mean activity coefficient, but rather the absolute values of the charges of the ions and their density in the solution. Other colligative properties, such as the osmotic pressure, can also be used to determine the activity coefficients of electrolyte solutions, but the freezing point depression is by far the easiest and most accurate though it only provides activity data near the freezing temperature. Other than colligative properties, equilibrium constants in electrolyte solutions can also be used to determine their activity coefficients.

As a second example of how the activity coefficient of electrolyte solutions may modify their equilibria, consider the dissociation equilibrium of a weak acid HA:
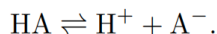
$$HA \rightleftharpoons H^+ + A^-.$$

The equilibrium constant for this reaction is

$$K = \frac{a_{H^+} a_{A^-}}{a_{HA}}.$$

$$(18)$$
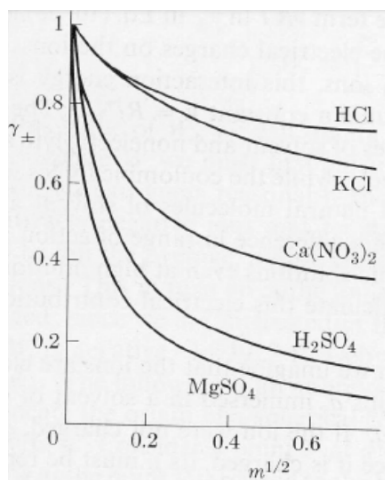
Figure 1: The mean ionic activity coefficients for several electrolyte solutions.

Since

$$a_{H+} = \gamma_+ m_{H+}, \qquad a_{A-} = \gamma_- m_{A-}, \qquad a_{HA} = \gamma_{HA} m_{HA}, \qquad (19)$$

expressing the molalities in terms of the extent of reaction ξ and the initial molality m:

$$m_{H+} = m_{A-} = \xi m, \qquad m_{HA} = (1 - \xi)m, \qquad (20)$$

we obtain the following equation for the equilibrium constant:

$$K = \frac{\gamma_\pm^2 \xi^2 m}{\gamma_{HA}(1 - \xi)}, \qquad (21)$$

where we have used the mean activity coefficient $\gamma_\pm = \gamma_+ \gamma_-$. If the acid is weak ($\xi \ll 1$) and assuming that $\gamma_{HA} \approx 1$, we can estimate the extent of reaction by the approximation:

$$\xi = \left(\frac{K}{m}\right)^{1/2} \frac{1}{\gamma_\pm}. \qquad (22)$$

As we have seen in Fig. 1, deviation from ideality produces an activity coefficient less than unity. Therefore, the extent of dissociation is larger than expected. For example for chloroacetic acid, $K = 1.4 \times 10^{-3}$. The extent of dissociation in a 1 molal solution assuming an ideal value of $\gamma_\pm = 1$ is 3.7%. Based on this, the effective ionic molality of this solution is approximately 0.04 m. We can use Fig. 1 to estimate $\gamma_\pm$ for a +1:-1 electrolyte, which for m = 0.04 is about 0.8. Using this value for $\gamma_\pm$, we obtain a dissociation of 4.6%, which is about 25% larger than the ideal value.

By measuring the equilibrium constants of various reactions in electrolyte solutions, their activity coefficients can be determined under a variety of conditions.

7.2 THERMODYNAMIC MODELS FOR ELECTROLYTE SOLUTIONS

In order to properly model electrolyte systems, all different types of interactions: ion-ion, iondipole, dipole-dipole, molecule-molecule should be taken into account. The potential energy caused by ion-

ion interactions is proportional to the inverse separation distance, $1/r$. Electrostatic ion-ion interactions therefore have an effect over a relatively long distance and are called long range interactions. The potential energy caused by molecule-molecule interactions is proportional to the sixth power of the inverse separation distance, $1/r^6$. These interactions are therefore called short-range interactions. The potential energy of ion-dipole interactions is proportional to $1/r^2$ and the potential energy of dipole-dipole interactions is proportional to $1/r^3$. These interactions could be called intermediate range interactions.

7.2.1 Electrostatic Interactions

Debye-Hückel theory

The first really successful model for the electrostatic interactions between ions in aqueous electrolyte systems was developed in 1923 by P. Debye and E. Hückel.

Debye and Hückel described the thermodynamics of ideal solutions of charged ions. As mentioned above, the electrostatic interactions between charged ions only represent the long range interactions in such solutions and not the short range interactions. The interactions between ions and water are not described by the Debye-Hückel model, which has led people to describe this model as a "dielectric continuum model". In this model, the solvent only plays a role due to its relative permittivity (dielectric constant) and its density. The DebyeHückel model can therefore not stand alone as a model for electrolyte solutions. It only represents some of the electrostatic interactions and should be combined with a term for short and intermediate range interactions in order to fully describe the properties of concentrated electrolyte solutions.

In the Debye-Hückel theory, the electrostatic force that a positive ion exerts on a negative through the solvent medium is expressed through Coulombs law:

$$F = -\frac{1}{4\pi\varepsilon_0\varepsilon_r}\frac{e^2}{r^2}$$

(23)

e is the electronic charge = $1.60206\cdot10^{-19}$ C

ε_0 is the permittivity in vacuum = $8.8542\cdot10^{-12}$ C^2 J^{-1} m^{-1}

ε_r is the dielectric constant (relative permittivity) of the solvent (unitless). The value of the relative permittivity of water is 78.4 at 298.15K

r is the distance between the ions (meter).

Poisson's equation gives a relationship between the charge density (ϱ_i Cm^{-3}) around ion i and the electrical potential (ψ_i J/C) for a sphere with radius r around ion i:

$$\frac{1}{r^2}\frac{d}{dr}\left(r^2\frac{d\psi_i}{dr}\right) = -\frac{\rho_i}{\varepsilon_0\varepsilon_r}$$

(24)

Due to the charges, the ions are not distributed evenly or randomly in the solution. Near a cation, anions tend to be in excess, near an anion, cations tend to be in excess. An ion j has an electrical potential energy of z_j $e\psi_i$ if it is in the distance r from the ion i. Debye and Hückel assumed the distribution of the ions in the solution to be a Boltzmann distribution. This assumption gives another relation between the charge density and the electrical potential:

$$\rho_i = eN_A \sum_{all\ ions} \frac{n_j z_j}{nV} e^{-\frac{z_j e\psi_i}{kT}}$$

(25)

n_j is the mol number of component j, z_j is the charge of component j, NA is Avogadro's number = $6.023\cdot10^{23}$ mol^{-1}, k is the Boltzmanns constant = $1.381\cdot10^{-23}$ JK^{-1}, and T is the temperature in Kelvin, V is the molar volume of the solution.

Debye and Hückel combined the Poisson equation and the Boltzmann equation thereby eliminating the charge density. The

resulting Poisson-Boltzmann equation was solved for the electrical potential ψ_i.

Debye and Hückel finally arrived at an excess Helmholtz function for an ideal solution of charged ions. It sounds like a contradiction to have an excess Helmholtz function for an ideal solution of charged ions. Ideal solutions do not have excess terms. But as mentioned before, this excess Helmholtz function only takes the non-ideality caused by the electrostatic interactions into account and does not deal with the traditional non-ideality, caused by short range forces. The molar excess Helmholtz function for the electrostatic interactions can be expressed by the equation:

$$\frac{A^E}{RT} = -\frac{1}{3}\sum x_i z_i^2 s\kappa\chi(\kappa a_i)$$

(26)

The term s is defined by:

$$s = \frac{e^2}{4\pi\varepsilon_0\varepsilon_r kT}$$

(27)

The distance of closest approach to the ion i was given the symbol a_i, (a for "annäherungsabstand"). The distance of closest approach is a parameter for the radius of ion i, not its diameter. It is expected that a_i is larger than the radius of the ion, because the ions are thought to be surrounded by water that gives the ions a larger radius than the bare ion. The product ka_i is dimensionless and κ is therefore a reciprocal length. $1/\kappa$ is a characteristic length called the screening length. The screening length provides a good first estimate of the distance beyond which Coulomb interactions can be essentially ignored, as well as the size of the region near a point charge where opposite-charge counter-ions can be found. The expression for κ is:

$$\kappa = \left(\frac{e^2 N_A}{\varepsilon_0\varepsilon_r kT}\frac{\sum n_i z_i^2}{nV}\right)^{1/2}$$

(28)

The function χ is given by:

$$\chi(x) = \frac{3}{x^3}\left(\frac{3}{2} + \ln(1+x) - 2(1+x) + \frac{1}{2}(1+x)^2\right)$$

(29)

Debye-Hückel Extended Law

The so-called extended Debye-Hückel law represents a simplification of the original DebyeHückel equation. The relation between Gibbs energy and Helmholtz energy is G = A + PV. No PV term was added to the Helmholtz function. The PV term was considered insignificant and was therefore discarded. Chemical potentials were derived from the energy function by molar differentiation at constant temperature and pressure, rather than molar differentiation at constant temperature and volume. Equation (30) shows how the chemical potential is derived from the different energy functions.

$$\mu_i \equiv \left[\frac{\partial G}{\partial n_i}\right]_{T,P,n_j} = \left[\frac{\partial H}{\partial n_i}\right]_{S,P,n_j} = \left[\frac{\partial A}{\partial n_i}\right]_{T,V,n_j} = \left[\frac{\partial U}{\partial n_i}\right]_{S,V,n_j}$$

(30)

A Gibbs energy function was created from the Helmholtz function in equation (26) by replacing the molarity concentration unit with molality and simplifying the expression for κ in equation (28). The density of an electrolyte solution with the molar volume V and the total volume nV can be written as:

$$d_{solution} = \frac{n_w M_w + \sum_{ions} n_i M_i}{nV}$$

(31)

This expression is converted to an expression for nV, which is inserted into equation (28):

$$\kappa = \left(\frac{e^2 N_A d_{solution}}{\varepsilon_0 \varepsilon_r kT} \frac{\sum n_i z_i^2}{n_w M_w + \sum_{ions} n_i M_i}\right)^{1/2}$$

(32)

Next, the approximation is made that the volume and the mass of the ions is zero. This approximation represents a small error for dilute solutions and a more serious error for concentrated solutions. By making this approximation, the density of the solution becomes equal to the density of pure water, d0 kg/m³. To make the expressions simpler, the ionic strength, a concept first introduced by Lewis and Randall in 1921 is introduced:

$$I = 0.5 \sum_i m_i Z_i^2$$

(33)

The expression for κ can now be written:

$$\kappa \approx \left(\frac{e^2 N_A d_0}{\varepsilon_0 \varepsilon_r kT} \frac{\sum n_i z_i^2}{n_w M_w} \right)^{1/2} = \left(\frac{2e^2 N_A d_0}{\varepsilon_0 \varepsilon_r kT} \frac{1}{2} \sum m_i z_i^2 \right)^{1/2} = \left(\frac{2e^2 N_A d_0}{\varepsilon_0 \varepsilon_r kT} \right)^{1/2} I^{1/2}$$

(34)

With this approximation, the product sκ from equation (26) can be written as:

$$s\kappa \approx \frac{e^2}{4\pi \varepsilon_0 \varepsilon_r kT} \left(\frac{2e^2 N_A d_0}{\varepsilon_0 \varepsilon_r kT} \right)^{1/2} I^{1/2} = 2\left(2\pi N_A d_0 \right)^{1/2} \left(\frac{e^2}{4\pi \varepsilon_0 \varepsilon_r kT} \right)^{3/2} I^{1/2}$$

(35)

This approximated value of sκ is expressed as $2AI^{\frac{1}{2}}$ where A is the Debye-Hückel parameter:

$$A = \left(2\pi N_A d_0 \right)^{1/2} \left(\frac{e^2}{4\pi \varepsilon_0 \varepsilon_r kT} \right)^{3/2}$$

(36)

The value of the Debye-Hückel parameter A is 1.1717 $(kg/mol)^{\frac{1}{2}}$ at 25°C.

The term κa_i from equation (26) was replaced by $BaI^{\frac{1}{2}}$ where a is a common ion size parameter replacing the individual distance of closest approach, a_i. The ion size parameter a is often in the range 3.5-6.2·10⁻¹⁰ m. B is derived from the approximated value of κ in equation (33)

$$B = \left(\frac{2e^2 N_A d_0}{\varepsilon_0 \varepsilon_r kT} \right)^{1/2}$$

(37)

The molar Gibbs excess function arrived at by the simplification is:

$$\frac{G^E_{Extended\ Debye-Hückel}}{RT} = -x_w M_w \frac{4}{3} AI^{3/2} \chi\left(BaI^{1/2}\right)$$

$$= -x_w M_w \frac{4A}{(Ba)^3}\left[\ln\left(1+BaI^{1/2}\right)-BaI^{1/2}+\frac{(Ba)^2 I}{2}\right]$$

(38)

x_w is the mole fraction of water, Mw kg mol^{-1} is the molar mass of water. The function $\chi(x)$ is given in equation (29).

The extended Debye-Hückel law usually gives good results for activity coefficients up to an ionic strength of about 0.1 molal. Above this concentration, short range interactions apparently give a significant contribution to the deviation from ideality. The activity coefficients are derived from the total Gibbs excess function by molar differentiation:

$$\left[\frac{\partial\left(nG^E_{Extended\ Debye-Hückel}/RT\right)}{\partial n_i}\right]_{T,P,n_j,j\neq i} = \ln\gamma^*_i = -Z_i^2 \frac{A\sqrt{I}}{1+Ba\sqrt{I}}$$

(39)

The activity coefficients calculated with the extended Debye-Hückel equation are the rational activity coefficients and not the molal activity coefficients.

The Hückel Equation

In 1925 it was found by E. Hückel that the addition of an extra parameter, C to the extended Debye-Hückel law made it possible to calculate activity coefficients up to higher concentrations with good accuracy. With the C parameter, a term proportional to the ionic strength was added to the logarithm of the rational, unsymmetrical activity coefficient:

$$\ln\gamma^*_\pm = -|Z_C Z_A|\frac{A\sqrt{I}}{1+Ba\sqrt{I}}+CI$$

(40)

E. Hückel justified the addition of the C parameter by showing that according to theory, a term proportional to the ionic strength

would take the variation of the dielectric constant with the composition into account.

The performances of the Debye-Hückel limiting law, the Debye-Hückel extended law, and the Hückel equation are illustrated in Figure 2 and Figure 3. In these figures, the calculated activity coefficients of aqueous hydrochloric acid solutions are plotted together with experimental values from a number of sources. For the preparation of Figure 2 and Figure 3, a value of 1.5 (kg/mol)$^{1/2}$ was used for Ba in equations (40). The best value of the C parameter in equation (40) was determined to be C = 0.321 kg/mol.

Figure 3 shows that the C parameter in the Hückel equation expands the concentration range in which the Debye-Hückel theory can be applied considerably. The C parameter is a function of temperature and of the ions in the solution.

In dilute solutions the activity coefficients of electrolytes decrease with increasing concentration, see Figure 2. For very dilute solutions the slope of the activity coefficient curve versus concentration will be minus infinity. For most electrolytes the activity coefficients will pass through a minimum and increase again at high concentrations reaching values which may be much higher than unity. Some systems however, show a behavior where the activity coefficient continues to drop for increasing concentration.
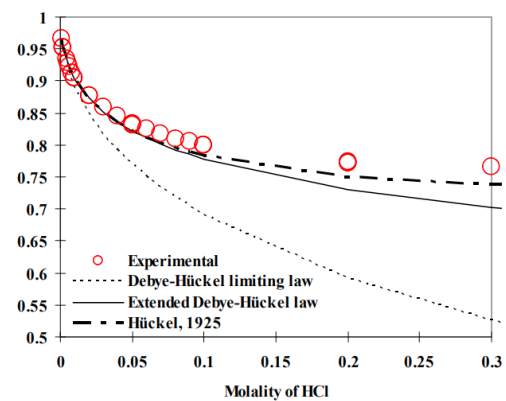
Figure 2: The rational mean ionic activity coefficient of aqueous HCl at concentrations up to 0.3 molal, experimental and calculated values.
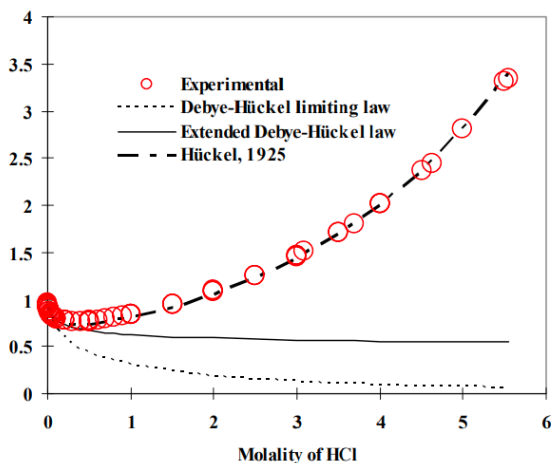
Figure 3: The rational mean ionic activity coefficient of aqueous HCl at concentrations up to 6 molal, experimental and calculated values.

The Born Equation

While the Debye-Hückel theory deals with the interaction between charged ions, Born derived an equation for the interaction between an ion and the surrounding solvent. Around an electrical charge there is an electrostatic field. Polar molecules are affected by such fields and redirect themselves to have as low energy as possible in the field. The positive part of a polar molecule is attracted to a negative charge and vice versa for the negative part. A orientation polarization is taking place.

A solvent consisting of polar molecules is polarizable and is also referred to as a dielectric medium. Highly polarizable solvents have high relative permittivities (dielectric constants). As expressed by Coulomb's law in equation (23), electrostatic interactions are lowered by solvents with a high relative permittivity. Salts do not dissociate spontaneously in a vacuum because the electrostatic interactions between the ions are too strong. In water, the electrostatic interactions between ions are lowered by a factor ε_r = 78.4 at 25 °C. The water molecules are shielding the ions from each other and allowing them to be separate. The relative permittivity

of a solvent is defined as the ratio between the permittivity of the solvent and the permittivity of vacuum:

$$\varepsilon_r \equiv \frac{\varepsilon}{\varepsilon_0}$$

(41)

The relative permittivity was called the dielectric constant and it was referred to as D. The relative permittivity of a medium can be measured by exposing the medium to a perturbing external electromagnetic field of small field strength. The medium is placed between the plates (conductors) of a capacitor. The response of the medium to this field is measured, and from this response, the relative permittivity of the medium can be deduced.

When ions are dissolved in a dielectric medium, the solvent molecules are polarized by the electrical charges. This ion-solvent interaction is called solvation. For the special case of water as solvent, the term hydration is used instead. Here, hydration is not the formation of ion-hydrates of a specific stoichiometric composition, but the redirection of the polar water molecules around the charged ions. The energy change associated with solvation is the solvation energy or in the special case of water, the hydration energy.

Consider a spherical ion with charge Z_i and radius r_i in a medium with the permittivity $\varepsilon_0\varepsilon_r$. Born calculated the solvation energy of this ion by integrating the energy of the electrical field from the surface of the spherical ion to infinity. Born found the electrostatic contribution to the Helmholtz energy of the ion to be:

$$A = \frac{Z_i^2 e^2}{8\pi\varepsilon_0\varepsilon_r r_i}$$

(42)

The expression was derived for a single ion in a solvent with the relative permittivity ε_r. When more ions are present, the electrostatic fields generated by the ions influence each other,

and these electrostatic interactions influence the ion-solvent interactions.

Equation (42) shows that the Helmholtz energy is lower in a medium of high relative permittivity, ε_r. The solvation energy is therefore negative if the ion is transferred from vacuum to a solvent.

By multiplying the energy in equation (42) with Avogadro's number, the Helmholtz energy of one mol of ions with charge Z_i is calculated. It is often of interest to know the change in Helmholtz energy when one mole of an ion is moved from a medium with one permittivity to a medium with another permittivity. This is the Helmholtz energy of transfer. If one mole of ions is moved from vacuum to a medium of relative permittivity ε_r, the energy change can be calculated as:

$$\Delta_{solv} A = \frac{Z_i^2 e^2 N_A}{8\pi\varepsilon_0\varepsilon_r r_i} - \frac{Z_i^2 e^2 N_A}{8\pi\varepsilon_0 r_i} = \frac{Z_i^2 e^2 N_A}{8\pi\varepsilon_0 r_i}\left(\frac{1}{\varepsilon_r} - 1\right)$$

(43)

It has been found that equation (6.26) gives very accurate results compared to experimental values of the solvation energy. An effective radius corresponding to the radius of the spherical cavity in the solvent created by an ion should be used in equation (43) rather than the ionic radius of the ion. According to Rashin and Honig, the radius of the cavity produced by the same ion is different in different solvents. When the Helmholtz energy of transfer between two solvents is calculated it is therefore necessary to use two different radii for the same ion. Besides, Rashin and Honig found that the cavity radius of anions in water can be calculated by adding 7% to their ionic radius, while the cavity radius of cations can be calculated by adding 7 % to their covalent radius.

The covalent radius is half the distance between two identical atoms bonded together by a single covalent bond. The covalent radius of a metal cation is usually larger than the ionic radius

but smaller than the atomic radius of the corresponding metal. The atomic radius of sodium is 190 pm, while the covalent radius of sodium is 154 pm and the ionic radius of the sodium ion is 102 pm. The argument for using the covalent radius of the metal rather than the ionic radius of the cation is that the covalent radius corresponds to the radius of the empty orbital around the cation. This empty orbital is assumed to form a part of the cavity.

For the transfer of one mole of ion i from a medium with relative permittivity $\varepsilon_{r,1}$ to a medium with relative permittivity $\varepsilon_{r,2}$, the Helmholtz energy of transfer is according to Rashin and Honig

$$\Delta_{transfer} A = \frac{Z_i^2 e^2 N_A}{8\pi\varepsilon_0 r_{i,2}}\left(\frac{1}{\varepsilon_{r,2}}-1\right) - \frac{Z_i^2 e^2 N_A}{8\pi\varepsilon_0 r_{i,1}}\left(\frac{1}{\varepsilon_{r,1}}-1\right)$$

$$= \frac{Z_i^2 e^2 N_A}{8\pi\varepsilon_0}\left(\frac{1}{r_{i,2}\varepsilon_{r,2}} - \frac{1}{r_{i,2}} - \frac{1}{r_{i,1}\varepsilon_{r,1}} + \frac{1}{r_{i,1}}\right)$$

(44)

The radii of the solvent cavities are marked with subscript 1 and 2 for the two solvents. The Born term in equation (43) is often used with equations of state for electrolyte solutions. In this case, the Born term contributes to the activity coefficients because of the variation of the relative permittivity with pressure. The Born term is also used for calculating the Gibbs energy of transfer. This is the difference in standard state chemical potential for a solute in two solvents with different relative permittivities. It is usually assumed that the Helmholtz energy difference calculated with equation (43) is identical to the corresponding difference in Gibbs energy.

The Helmholtz energy calculated from equation (44) is the difference in Helmholtz energy of a charged particle in a dielectric medium compared to the Helmholtz energy of an uncharged particle of the same size, in the same medium. The equation thus represents the contribution to the excess Helmholtz energy from the interaction between a single ion and a number of solvent molecules.

7.2.2 Empirical Models for Intermediate/Short Range Interactions

The theory presented by Debye and Hückel was only meant to take the electrostatic interactions between spherical ions into account. The equations presented for the mean spherical approximation are also limited to the electrostatic interactions between spherical ions. These equations therefore have to be combined with models or equations that describe other types of interactions such as ion-dipole and dipoledipole interactions and short range interactions in order to be used for real solutions.

The Meissner Correlation

The basis for their method was the observation that curves of the reduced activity coefficient, Γ, versus the ionic strength, I, for different salts form a family of curves that did not cross each other. This only applies to curves of the reduced activity coefficient, not to curves of mean ionic activity coefficients. One of the graphs is reproduced in Figure 3. It was pointed out one year later by Bromley that Meissner had painted an idealized picture of electrolyte behavior and that some of the curves for common salts actually do cross each other.

The reduced activity coefficient, Γ, for a salt S was defined via the following equation:

$$\Gamma \equiv \left(\gamma_\pm^m \right)^{\frac{1}{|Z_C Z_A|}} \quad \text{or} \quad \gamma_\pm^m = \Gamma^{|Z_C Z_A|} \tag{45}$$

Initially, the method of Meissner and Tester was a graphical method for determining activity coefficients in binary solutions using graphs like the one shown in Figure 3 valid up to two molal or valid up to 20 molal. Meissner and Kusik showed how activity coefficients for multi component solutions could be calculated from the activity coefficients from binary solutions. In a solution of the three ions, 1, 2 and 3, which could represent Na^+, Cl^-, and

K^+ the reduced activity coefficient of electrolyte 12 (one-two) in the solution is given as a function of the reduced activity coefficients of the binary solutions of electrolyte 12 and 32 by:

$$\ln \Gamma_{12} = \ln \Gamma_{12}^0 + \tfrac{1}{2} X_3 \ln \frac{\Gamma_{32}^0}{\Gamma_{12}^0}$$

(46)

The reduced activity coefficients of binary solutions are indicated with superscript 0. The fraction X_3 is given by:

$$X_3 = \frac{m_3 Z_3^2}{m_1 Z_1^2 + m_3 Z_3^2}$$

(47)

Similar methods were given for the calculation of reduced activity coefficients in solutions containing four or more ions.

Kusik and Meissner presented in 1978 a set of equations for computer application of the method for calculating the reduced activity coefficients for binary solutions.

The value of the reduced activity coefficient Γ is calculated as:

$$\Gamma = \left[1 + B(1 + 0.1 \cdot I)^q - B \right] \Gamma^*$$

(48)

In this equation,

$$B = 0.75 - 0.065q$$

(49)

$$\log_{10} \Gamma^* = - \frac{0.5107 \sqrt{I}}{1 + C \sqrt{I}}$$

(50)

$$C = 1 + 0.055q \exp\left(- 0.023 \cdot I^3\right)$$

(51)

The parameter q, Meissner's parameter, is dependent on the type of salt and of temperature. Each of the curves in Figure 3 corresponds to a different value of the q parameter.

If one experimental value of the activity coefficient is known, it is possible to identify which curve the electrolyte belongs to, and what q parameter is associated with the curve. Using the q parameter,

the value of the activity coefficient at other concentrations and temperatures can then be predicted. Kusik and Meissner presented values of the q parameter for about 120 salts.
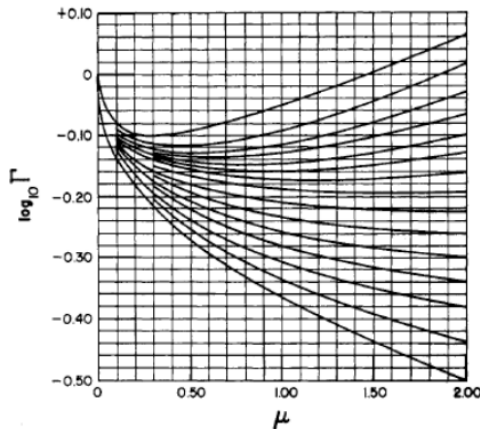
Figure 3: The logarithm of the reduced activity coefficient Γ versus ionic strength μ over the ionic strength range from 1 to 2 molal.

The q parameter is temperature dependent according to:

$$q_t = q + (aq + b) \cdot (t - 25) \qquad (52)$$

The temperature t is in °C. The parameter a has the value -0.0079, b has the value -0.0029 for sulfates (except sulfuric acid!). For most other electrolytes a is about -0.005 while b has the value 0.0085.

The Meissner method includes a graphical method for calculating water activities and a method for calculating mean ionic activity coefficients in multi-ion solutions. The reader is referred to the paper by Kusik and Meissner (1978). In spite of the resemblance between one of the terms in the Meissner correlation and the extended Debye-Hückel law, the Meissner correlation is an empirical model.

7.2.3 Intermediate/Short Range Interactions from Local Composition Models

Local composition models are models based on the local composition concept introduced by Grant M. Wilson in 1964. It is assumed that the composition on a molecular level is different from the bulk composition. Depending on sizes, shapes, and interaction energies, molecules are preferentially surrounded by other molecules that give them a lower energy level. The Debye-Hückel theory can be considered to be a local composition theory for electrostatic interactions.

The Extended UNIQUAC Model

The UNIQUAC model by adding a Debye-Hückel term allowing this Extended UNIQUAC model to be used for electrolyte solutions. The model has since been modified and it has proven itself applicable for calculations of vapor-liquid-liquid-solid equilibria and of thermal properties in aqueous solutions containing electrolytes and non-electrolytes.

The extended UNIQUAC model consists of three terms: a combinatorial or entropic term, a residual or enthalpic term and an electrostatic term

$$G^{ex} = G^{ex}_{Combinatorial} + G^{ex}_{Residual} + G^{ex}_{Extended\,Debye-Hückel} \qquad (56)$$

The combinatorial and the residual terms are identical to the terms used in the traditional UNIQUAC equation. The electrostatic term corresponds to the extended DebyeHückel law.

The combinatorial, entropic term is independent of temperature and only depends on the relative sizes of the species:

$$\frac{G^{ex}_{Combinatorial}}{RT} = \sum_i x_i \ln\left(\frac{\phi_i}{x_i}\right) - \frac{z}{2}\sum_i q_i x_i \ln\left(\frac{\phi_i}{\theta_i}\right) \qquad (57)$$

$z = 10$ is the co-ordination number. x_i is the mole fraction, φ_i is the volume fraction, and θ_i is the surface area fraction of component i:

$$\phi_i = \frac{x_i r_i}{\sum_l x_l r_l}; \quad \theta_i = \frac{x_i q_i}{\sum_l x_l q_l}$$

(58)

The two model parameters ri and qi are the volume and surface area parameters for component i. In the classical application of the UNIQUAC model, these parameters are calculated from the properties of non electrolyte molecules. In the Extended UNIQUAC application to multi component electrolyte solutions, this approach gave unsatisfactory results. The volume and surface area parameters were instead considered to be adjustable parameters. The values of these two parameters are determined by fitting to experimental data. Especially thermal property data such as heat of dilution and heat capacity data are efficient for determining the value of the surface area parameter q, because the UNIQUAC contribution to the excess enthalpy and excess heat capacity is proportional to the parameter q.

The residual, enthalpic term is dependent on temperature through the parameter ψ_{kl}:

$$\frac{G_{Residual}^{ex}}{RT} = -\sum_i x_i q_i \ln\left(\sum_k \theta_k \psi_{kl}\right)$$

(59)

the parameter ψ_{kl} is given by:

$$\psi_{kl} = \exp\left(-\frac{u_{kl} - u_{ll}}{T}\right)$$

(60)

u_{kl} and u_{ll} are interaction energy parameters. The interaction energy parameters are considered symmetrical and temperature dependent in this model

$$u_{kl} = u_{kl}^0 + u_{kl}^T (T - 298.15)$$

(61)

The interaction parameters u_{kl}^0 and u_{kl}^T are model parameters that are fitted to experimental data.

By partial molar differentiation of the combinatorial and the residual UNIQUAC terms, the combinatorial and the residual parts of the rational, symmetrical activity coefficients are obtained:

$$\ln \gamma_i^C = \ln\left(\frac{\phi_i}{x_i}\right) + 1 - \frac{\phi_i}{x_i} - \frac{z}{2} q_i \left[\ln\left(\frac{\phi_i}{\theta_i}\right) + 1 - \frac{\phi_i}{\theta_i} \right]$$

(62)

$$\ln \gamma_i^R = q_i \left[1 - \ln\left(\sum_k \theta_k \psi_{ki}\right) - \sum_k \frac{\theta_k \psi_{ik}}{\sum_l \theta_l \psi_{lk}} \right]$$

The infinite dilution terms are obtained by setting $x_w = 1$ in equation (62).

$$\ln \gamma_i^{C\infty} = \ln \frac{r_i}{r_w} + 1 - \frac{r_i}{r_w} - \frac{z}{2} q_i \left[\ln \frac{r_i q_w}{r_w q_i} + 1 - \frac{r_i q_w}{r_w q_i} \right]$$

$$\ln \gamma_i^{R\infty} = q_i [1 - \ln \psi_{wi} - \psi_{iw}]$$

(63)

The combinatorial and the residual terms of the UNIQUAC excess Gibbs energy function are based on the rational, symmetrical activity coefficient convention. The Debye-Hückel electrostatic term however is expressed in terms of the rational, symmetrical convention for water, and the rational, unsymmetrical convention for ions.

The electrostatic contributions to the water activity coefficients and the ionic activity coefficients are obtained by partial molar differentiation of the extended Debye-Hückel law excess Gibbs energy term (37). The term used for water is slightly modified compared to equation (41) so that the parameter $b = 1.5$ (kg/mol)½ is used instead of the Ba term:

$$\ln \gamma_w^{DH} = \frac{2}{3} M_w A I^{3/2} \sigma\left(b I^{\frac{1}{2}}\right)$$

$$\sigma(x) = \frac{3}{x^3}\left\{ 1 + x - \frac{1}{1+x} - 2\ln(1+x) \right\}$$

(64)

Also the term used for ions is slightly modified compared to equation (42) so that the parameter b replaces Ba:

$$\ln\gamma_i^{*DH} = -Z_i^2 \frac{A\sqrt{I}}{1+b\sqrt{I}}$$

(65)

Based on table values of the density d_0 of pure water, and the relative permittivity of water, ε_r, the Debye-Hückel parameter A in equation (35) used in equation (64) and (65) can be approximated in the temperature range 273.15 K < T < 383.15 K by

$$A = [1.131+1.335\cdot10^{-3}(T-273.15)+1.164\cdot10^{-5}\cdot(T-273.15)^2](kg/mol)^{\frac{1}{2}}$$

(66)

The activity coefficient for water is calculated in the Extended UNIQUAC model by summation of the three terms:

$$\ln\gamma_w = \ln\gamma_w^C + \ln\gamma_w^R + \ln\gamma_w^{DH}$$

(67)

The activity coefficient for ion i is obtained as the rational, unsymmetrical activity coefficient according to the definition of rational unsymmetrical activity coefficient by adding the three contributions:

$$\ln\gamma_i^* = \ln\frac{\gamma_i^C}{\gamma_i^{C\infty}} + \ln\frac{\gamma_i^R}{\gamma_i^{R\infty}} + \ln\gamma_i^{*DH}$$

$$= \ln\gamma_i^C - \ln\gamma_i^{C\infty} + \ln\gamma_i^R - \ln\gamma_i^{R\infty} + \ln\gamma_i^{*DH}$$

(68)

The rational, unsymmetrical activity coefficient for ions calculated with the Extended UNIQUAC model can be converted to a molal activity coefficient. This is relevant for comparison with experimental data.

Parameters for water and for the following ions can be found in Thomsen (1997): H^+, Na^+, K^+, NH_4^+, C_1^-, SO_4^{2-}, HSO_4^-, NO_3^-, OH^-, CO_3^{2-}, HCO_3^-, $S_2O_8^{2-}$.

Parameters and model modifications for gas solubility at pressures up to 100 bar in aqueous electrolyte systems. Also phase equilibria for systems containing non-electrolytes are described by the model, including liquid-liquid equilibria. Besides, parameters

have been determined for systems containing heavy metal ions. The model has been applied by A.V. Garcia to include the pressure dependence of the solubility of salts. Two parameters for the pressure dependence of the solubility product of each salt.

A significant advantage of the Extended UNIQUAC model compared to models like the Bromley model or the Pitzer model is that temperature dependence is built into the model. This enables the model to also describe thermodynamic properties that are temperature derivatives of the excess Gibbs function, such as heat of mixing and heat capacity.

The Electrolyte NRTL Model

The electrolyte NRTL model combines the Pitzer-Debye-Hückel term with the NRTL local composition model. The local composition concept is modified for ions and the model parameters are salt specific. The Extended UNIQUAC model is also a combination of a Debye-Hückel term and a local composition model. At first glance, the two models therefore seem to be similar. Some of the differences between the two models are listed in Table 1.

Table 1: Differences between the electrolyte NRTL model and the Extended UNIQUAC model.

Property	Model	
	Electrolyte NRTL model	Extended UNIQUAC model
Local composition term:	Modified NRTL	Standard UNIQUAC
Electrostatic term:	Pitzer-Debye-Hückel	Extended Debye-Hückel
Parameters:	Salt specific	Ion specific
Gibbs excess function	$G^E = H^E$	$G^E = H^E - TS^E$

The electrolyte NRTL model uses a local composition concept adapted to electrolyte solutions. The expressions for the activity coefficients are considerably more complicated and require more time for programming than those from the Extended UNIQUAC model. The use of a Pitzer-Debye-Hückel term instead of the Extended Debye-Hückel term does not make much difference.

The NRTL local composition model only has an enthalpic term, it uses no volume and surface area fractions and has no entropic term.

The use of salt specific parameters rather than ion specific parameters requires that a suitable mixing rule is applied. Otherwise calculations of solution properties would depend on how the composition of the solution is defined. A solution of equal amounts of CaCl2 and MgNO3 could as well be defined as a solution of $Ca(NO_3)_2$ and $MgCl_2$. The electrolyte NRTL model is widely used as it is the model implemented in the commercial simulator ASPEN

7.3 VAPOR PRESSURE OF ELECTROLYTE SOLUTIONS

The vapor pressure of an electrolytic solution is dependent on the ratio of solute to solvent molecules in a solution. Vapor pressure is the pressure exerted by a vapor in equilibrium with its condensed phase, either liquid or solid, at a particular temperature. Basically, it is a measure of how much the solvent molecules tend to escape from a liquid or solid phase into the atmosphere. Vapor pressure of a liquid is a colligative property. To better visualize the effect of solute on the vapor pressure of a solution, consider a pure solvent. This pure solvent has a certain vapor pressure associated with it. Subjected to temperatures below the solvent's boiling point, the molecules going into the gaseous phase are mostly situated on the top layer of the solution. Now consider a solution composed of both solvent and solute. Some solute molecules will occupy space near the surface of the liquid, decreasing the number of solvent molecules that can be there. Therefore, fewer molecules are changing from the liquid phase into the gas phase, and the vapor pressure of the solvent decreases. In an electrolyte solution, the number of dissolved particles is larger because the solute breaks apart into ions. The greater the number of ions, the larger the impact on colligative properties will be. A simple example of an electrolyte solution is sodium chloride in water. In the presence of

water, solid sodium chloride dissociates as it is dissolved, forming an electrolyte solution:

$$NaCl_{(s)} \rightarrow Na^+_{(aq)} + Cl^-_{(aq)}$$

Nonelectrolyte solutions are those in which the solute does not dissociate into ions when dissolved; sugar does not dissociate, for example. The number of moles of dissolved particles is greater for electrolyte solutions, so there will be a greater impact on colligative properties.
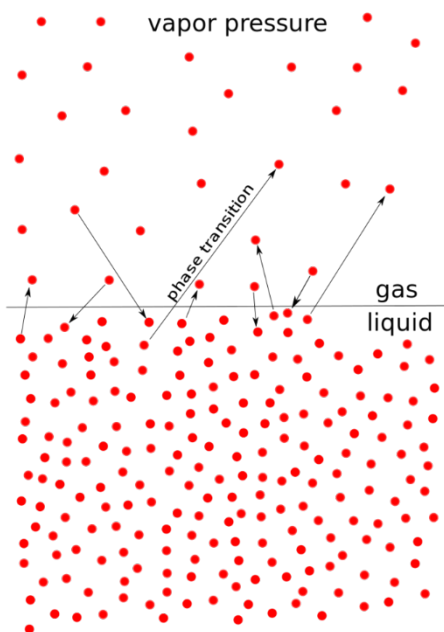
7.3.1 Medical Solutions: Colligative Properties

Medical solutions must be tailored to restore and maintain a proper homeostatic environment.

The Human Solution

At normal physiological conditions, organisms regulate their internal environments and maintain stable, constant conditions

despite influences from the outside environment. Internally, many mechanisms allow for a constant environment, but often, when a person becomes sick or incapacitated, the homeostatic environment becomes disrupted. To assist in the treatment and recovery process, medical scientists and doctors often introduce electrolytic solutions into the body. The solutions must be of proper osmolality and concentrations, otherwise irreversible damage can be caused. These electrolytic solutions share the same colligative properties as chemical solutions.

Saline Solutions

Medical solutions are important for treating dehydration and for cleaning and treating wounds. One class of medical solutions is known as saline solutions. These solutions are composed of water and sodium chloride. Saline solutions are typically used for rinsing contact lenses, nasal irrigation, and cleaning new piercings. Saline solutions can vary in their concentrations.

Typically, saline is found at a 0.90% w/v of NaCl in water. Referred to as "normal saline," this type of electrolytic solution is used frequently in intravenous drips for patients who have lost a lot of water and are at risk for dehydration. Normal saline is also used to treat decreased blood volume. The saline solution is expected to restore the salinity levels in the blood. Most commonly, saline is used in intravenous (IV) therapy, which provides water and electrolytes to a patient. Normal saline has low osmolality, which can introduce problems, so IV solutions generally have glucose added to maintain a safe osmolality.

Electrolytes in Solutions

As mentioned before, humans maintain a homeostatic internal environment. The electrolyte-water ratio that regulates many of the body's functions is part of this. Plasma osmolarity is the measure of the body's electrolyte-water balance. Its name is derived from osmosis, which is the net movement of solvent molecules through a partially permeable membrane; the molecules travel from a

region of higher solute concentration to a region with lower solute concentration. There are two common measurements used to determine the amount of electrolyte in a solution.

Osmolality is affected by changes in water content, whereas osmolarity is affected by temperature and pressure. These two values are slightly different; osmolarity is slightly less than osmolality because it does not take into account the weight of the solutes. The normal range of osmolality in human blood plasma is 270-310 milli-osmoles/kg.

Cell membranes are permeable to water, so the osmolality of the extracellular fluid (ECF) is approximately equal to that of the intracellular fluid (ICF). Any shift in the osmolality of the ECF will directly impact the ICF and can cause problems with normal cell functions and water volume. Therefore, the introduction of saline that is too hypotonic will cause water to fill the cells too rapidly, potentially causing the cells to burst. Conversely, the introduction of saline that is too hypertonic will cause water to leave the cells, making them shrivel. There are medical solutions with a range of concentrations to ensure the cell maintains an isotonic environment.

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Chemical Equilibrium

Chemical equilibrium refers to the state of a system in which the concentration of the reactant and the concentration of the products do not change with time and the system does not display any further change in properties. The definition of chemical equilibrium is the point at which the concentrations of reactants and products do not change with time. It appears as though the reaction has stopped but in fact the rates of the forward and reverse reactions are equal so reactants and products are being created at the same rate. When equilibrium reactions are disrupted, such as the binding of oxygen by hemoglobin, as in carbon monoxide poisoning, it can be life threatening. Conversely, controlling an equilibrium reaction is important in chemical manufacturing, like in the synthesis of ammonia.

This book is designed for learners with background in material and energy balances, chemical reactions, calculus, numerical methods, and basic thermodynamics. You will understand the principles of chemical equilibrium thermodynamics to solve multiphase equilibria and chemical reaction equilibria. This book contains seven chapters. Chapter 1: First and Second Law of Thermodynamics; chapter 2: Introduction to Equilibrium; chapter 3: Equilibria of Reactions Involving Gases; chapter 4: Phase Rule; chapter 5: Phase Equilibria in Single Component Systems; chapter 6: Ideal Solutions; chapter 7: Reaction Equilibrium in Solutions: Electrolyte. The equilibrium properties of electrolyte solutions can be studied experimentally by electrochemical measurements, freezing-point depressions, solubility determinations, osmotic pressures, or measurements of vapor pressure. Most electrolytes, such as salts, are nonvolatile at ordinary temperature, and, in that event, the vapor pressure exerted by the solution is the same as the partial pressure of the solvent. The activity coefficient of the solvent can, therefore, be found from total-pressure measurements, and, using the Gibbs-Duhem equation, it is then possible to calculate the activity coefficient of the electrolyte solute.

Simon Boman is a professor at the Faculty of sciences in the department of Chemistry. His current research interests include organic and physical chemistry, biology, and pharmacy. His principal axis of research are Organometallic Catalysis, Green Chemistry, CO2 chemistry and Synthesis of chelating macrocyles for the complexation of metals.