Thermodynamics Equilibrium

Ernest O'Neal

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by Ernest O'Neal

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Application of Thermodynamics

Entropy is a function of a quantity of heat which shows the possibility of conversion of that heat into work.

For a thermodynamic system with a fixed number of particles, the first law of thermodynamics may be stated as:

$\delta Q = dU + \delta W$, or equivalently, $dU = \delta Q - \delta W,$

where δQ is the amount of energy added to the system by a heating process, δW is the amount of energy lost by the system due to work done by the system on its surroundings and dU is the increase in the internal energy of the system.

The δ's before the heat and work terms are used to indicate that they describe an increment of energy which is to be interpreted somewhat differently than the dU increment of internal energy.

Work and heat are processes which add or subtract energy, while the internal energy U is a particular form of energy associated with the system. Thus the term “heat energy” for δQ means “that amount of energy added as the result of heating” rather than referring to a particular form of energy.

Likewise, the term “work energy” for δW means “that amount of energy lost as the result of work”. The most significant result of this distinction is the fact that one can clearly state the amount of internal energy possessed by a thermodynamic system, but one cannot tell how much energy has flowed into or out of the system as a result of its being heated or cooled, nor as the result of work being performed on or by the system.

In simple terms, this means that energy cannot be created or destroyed, only converted from one form to another. For a simple compressible system, the work performed by the system may be written

$$\delta Q = P\,dV,$$

where P is the pressure and dV is a small change in the volume of the system, each of which are system variables. The heat energy may be written

$$\delta Q = T\,dS,$$

where T is the temperature and dS is a small change in the entropy of the system. Temperature and entropy are also system variables.

Mechanics

In mechanics, conservation of energy is usually stated as

$$E = T + V,$$

where T is kinetic and V potential energy.

Actually this is the particular case of the more general conservation law

$$\sum_{i=1}^{N} p_i \dot{q}_i - L = const \text{ and } p_i = \frac{\partial L}{\partial \dot{q}_i}$$

where L is the Lagrangian function. For this particular form to be valid, the following must be true:

- The system is scleronomous (neither kinetic nor potential energy are explicit functions of time)
- The kinetic energy is a quadratic form with regard to velocities.
- The potential energy doesn't depend on velocities.

Noether's Theorem

in many physical theories. It is understood as a consequence of Noether's theorem, which states every symmetry of a physical theory has an associated conserved quantity; if the theory's symmetry is time invariance then the conserved quantity is called "energy". In other words, if the theory is invariant under the continuous symmetry of time translation then its energy (which is canonical conjugate quantity to time) is conserved.

Conversely, theories which are not invariant under shifts in time (for example, systems with time dependent potential energy) do not exhibit conservation of energy — unless we consider them to exchange energy with another, external system so that the theory of the enlarged system becomes time invariant again.

Since any time-varying theory can be embedded within a time-invariant meta-theory energy conservation can always be recovered by a suitable re-definition of what energy is.

Thus conservation of energy is valid in all modern physical theories, such as special and general relativity and quantum theory (including QED).

Relativity

With the invention of special relativity by Albert Einstein, energy was proposed to be one component of an energy-momentum 4-vector. Each of the four components (one of energy and three of momentum) of this vector is separately conserved in any given inertial reference frame. Also conserved is the vector length (Minkowski norm), which is the rest mass.

The relativistic energy of a single massive particle contains a term related to its rest mass in addition to its kinetic energy of motion. In the limit of zero kinetic energy (or equivalently in the rest frame of the massive particle, or the center-of-momentum frame for objects or systems), the total energy of particle or object (including internal kinetic energy in systems) is related to its rest mass via the famous equation E = mc2.

Thus, the rule of conservation of energy in special relativity was shown to be a special case of a more general rule, alternatively called the conservation of mass and energy, the conservation of mass-energy, the conservation of energy-momentum, the conservation of invariant mass or now usually just referred to as conservation of energy.

In general relativity conservation of energy-momentum is expressed with the aids of a stress-energy-momentum pseudotensor.

Quantum Theory

In quantum mechanics, energy is defined as proportional to the time derivative of the wave function. Lack of commutation of the time derivative operator with the time operator itself mathematically results in an uncertainty principle for time and energy: the longer the period of time, the more precisely energy can be defined (energy and time become a conjugate Fourier pair). However, there is a deep contradiction between quantum theory's historical estimate of the vacuum energy density in the universe and the vacuum energy predicted by the cosmological constant.

The estimated energy density difference is of the order of 10^120 times. The consensus is developing that the quantum mechanical derived zero-point field energy density does not conserve the total energy of the universe, and does not comply with our understanding of the expansion of the universe. Intense effort is going on behind the scenes in physics to resolve this dilemma and to bring it into compliance with an expanding universe.

Mathematical Viewpoint

From a mathematical point of view, the energy conservation law is a consequence of the shift symmetry of time; energy conservation is implied by the empirical fact that the laws of physics do not change with time itself. Philosophically this can be stated as "nothing depends on time per se".

The Law of Conservation of Matter/Energy

The first law has been defined as follows: When a closed system is altered adiabatically, the total work associated with the change of state is the same for all possible processes between the two given equilibrium states.

A more succinct and comprehensible definition might be something like this: Matter/energy may be altered but not created (from nothingness) nor destroyed (reduced to nothingness). The First Law teaches that matter/energy cannot spring forth from nothing without cause, nor can it simply vanish.

The First Law, although not formally defined until the 19th century, helps make science possible. Science depends on the ability to identify cause-effect relationships. If matter/energy could spontaneously appear (and have effects on other matter/energy around it), scientists would never know whether a given observation was due to a rational cause, or to a spontaneous generation of matter or energy that was uncaused. Scientific conclusions would be on shaky ground. The Law of Causality is thus closely linked with the First Law of Thermodynamics.

The First Law also demands, if we accept it, one of two possibilities about the nature of the universe. One is that it has always existed, changing form perhaps but never having come from nothingness, or returning to the same. The other possibility is that it did not come from nothingness, but from a transcendant (that is, outside the universe) creator who is not subject to the laws within the universe.

First, they have unconsciously granted to the Law of Causality the very property of self-existence (that is, an eternal, uncreated nature) that they are presuming God couldn't have. A being who created the universe and the laws within it, who pre-existed them, would not be slave to those laws. And since the Law of Causality is a statement about relationships between multiple entities, the law could not even exist until one entity began the act of creating another one (at which point it would implicitly come to exist).

Finally, most atheists who use this argument grant to the universe the exact property of self-existence that they deny God. They either deny the First Law of Thermodynamics and believe the universe came into existence from nothingness, or believe that it is itself self-existing.

However, this latter position violates the unity principle – that a valid law of science that is found to apply anywhere, applies everywhere and to everything in the universe, including the universe as a whole.

The only position that appears to be consistent with the First Law of Thermodynamics, the unity principle and causality is that the universe was created by a self-existent external agent not subject to the laws operational in the universe it created.

First Law of Thermodynamics

The first law of thermodynamics is the application of the conservation of energy principle to heat and thermodynamic processes:

The change in internal energy of a system is equal to the heat added to the system minus the work done by the system.

$$\underset{\text{Change in internal energy}}{\Delta U} = \underset{\text{Heat added to the system}}{Q} - \underset{\text{Work done by the system}}{W}$$

The first law makes use of the key concepts of internal energy, heat, and system work. It is used extensively in the discussion of heat engines.

It is typical for chemistry texts to write the first law as $\Delta U = Q + W$. It is the same law, of course - the thermodynamic expression of the conservation of energy principle. It is just that W is defined as the work done on the system instead of work done by the system.

In the context of physics, the common scenario is one of adding heat to a volume of gas and using the expansion of that gas to do work, as in the pushing down of a piston in an internal combustion engine. In the context of chemical reactions and process, it may be more common to deal with situations where work is done on the system rather than by it.

Enthalpy

Four quantities called "thermodynamic potentials" are useful in the chemical thermodynamics of reactions and non-cyclic processes. They are internal energy, the enthalpy, the Helmholtz free energy and the Gibbs free energy. Enthalpy is defined by

$$H = U + PV$$

where P and V are the pressure and volume, and U is internal energy. Enthalpy is then a precisely measurable state variable, since it is defined in terms of three other precisely definable state variables. It is somewhat parallel to the first law of thermodynamics for a constant pressure system

$$Q = \Delta U + P\Delta V \text{ since in this case } Q = \Delta H$$

It is a useful quantity for tracking chemical reactions. If as a result of an exothermic reaction some energy is released to a system, it has to show up in some measurable form in terms of the state variables. An increase in the enthalpy H = U + PV might be associated with an increase in internal energy which could be measured by calorimetry, or with work done by the system, or a combination of the two.

The internal energy U might be thought of as the energy required to create a system in the absence of changes in temperature or volume.

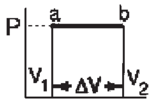
But if the process changes the volume, as in a chemical reaction which produces a gaseous product, then work must be done to produce the change in volume. For a constant pressure process the work you must do to produce a volume change ΔV is PΔV.

Then the term PV can be interpreted as the work you must do to "create room" for the system if you presume it started at zero volume.

System Work

When work is done by a thermodynamic system, it is ususlly a gas that is doing the work. The work done by a gas at constant pressure is:

$$W = P\Delta V$$

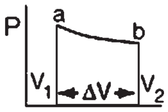


The line from a to b represents an expansion of a gas at constant pressure. The work done is the area under the curve.

For non-constant pressure, the work can be visualized as the area under the pressure-volume curve which represents the process taking place. The more general expression for work done is:

The integral expression gives the exact area under the curve which is equal to the work.

$$W = \int_{V_1}^{V_2} P\,dV$$



Work done by a system decreases the internal energy of the system, as indicated in the First Law of Thermodynamics. System work is a major focus in the discussion of heat engines.

Description

The first law of thermodynamics basically states that a thermodynamic system can store or hold energy and that this internal energy is conserved. Heat is a process by which energy is added to a system from a high-temperature source, or lost to a low-temperature sink. In addition, energy may be lost by the system when it does mechanical work on its surroundings, or conversely, it may gain energy as a result of work done on it by its surroundings. The first law states that this energy is conserved: The change in the internal energy is equal to the amount added by heating minus the amount lost by doing work on the environment. The first law can be stated mathematically as:

$$dU = dQ - \delta W$$

where dU is a small increase in the internal energy of the system, δQ is a small amount of heat added to the system, and δW is a small amount of work done by the system.

The δ's before the heat and work terms are used to indicate that they describe an increment of energy which is to be interpreted somewhat differently than the dU increment of internal energy. Work and heat are processes which add or subtract energy, while the internal energy U is a particular form of energy associated with the system. Thus the term "heat energy" for δQ means "that amount of energy added as the result of heating" rather than referring to a particular form of energy.

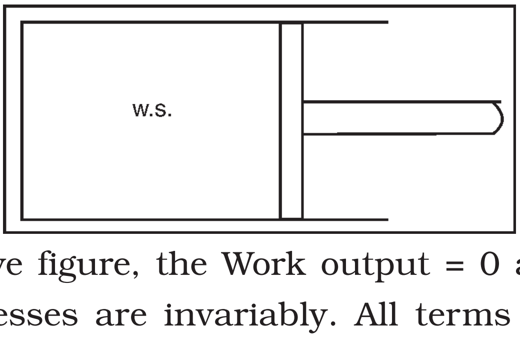
Likewise, the term "work energy" for δw means "that amount of energy lost as the result of work". The most significant result of this distinction is the fact that one can clearly state the amount of internal energy possessed by a thermodynamic system, but one cannot tell how much energy has flowed into or out of the system as a result of its being heated or cooled, nor as the result of work being performed on or by the system. The first explicit statement of the first law of thermodynamics was given by Rudolf Clausius in 1850: "There is a state function E, called 'energy', whose differential equals the work exchanged with the surroundings during an adiabatic process."

Note that the above formulation is favored by engineers and physicists. Chemists prefer a second form, in which the work term δw is defined as the work done on the system, and therefore insert a plus sign in the above equation before the work term. This article will use the first definition exclusively.

Application of First Law of Thermodynamics

Constant Volume

Consider a system as shown below



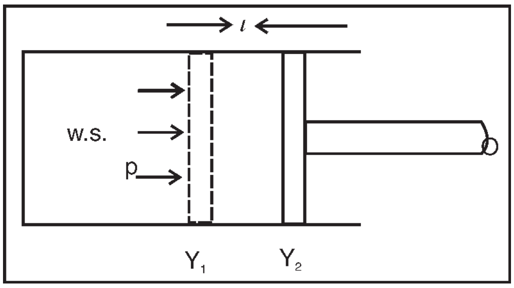
In the above figure, the Work output = 0 and Constant Volume Processes are invariably. All terms in the above equation are eliminated with the exception of:-

$$E_1 + Q_S = E_2$$

i.e. all the heat supplied goes to increasing the Internal Energy of the WS

Constant Pressure

Consider a system:



Non-Flow system

Force on the Piston = P A

Work Done = $P A \iota = P(V_2 - V_1)$

In the First Law equation, most terms are eliminated and left with:-

$$E_1 + Q_S = E_2 + W$$

$$\therefore\ QS = (E_2 - E_1) + P(V_2 - V_1) = (E_2 + P_2V_2) - (E_1 + P_1V_1)$$

$$= H_2 - H_1$$

i.e. The Heat Supplied = The Gain in ENTHALPY.

Adiabatic Process

An adiabatic process is one that occurs without the exchange of heat with the surroundings.

If the gas-piston system were insulated so that heat could not get in or out, any expansion or compression would occur adiabatically.

This is a Process during which there is NO heat transfer of heat between the WS and the surroundings.

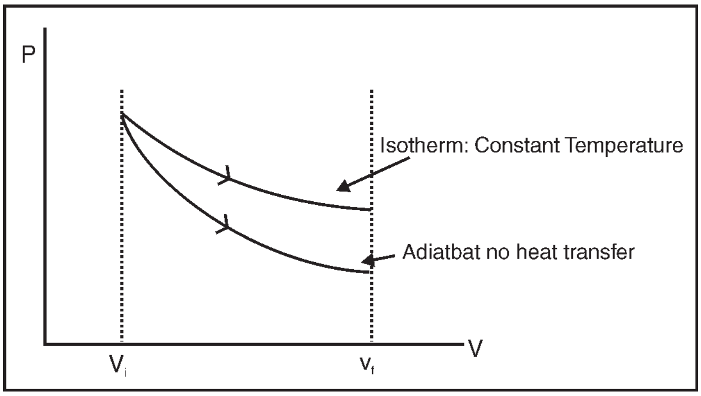
For Non Flow system:

$$E_1 = E_2 + W$$

Work Done = $(E_1 - E_2)$ i.e. Loss of Internal Energy

Therefore Work Done = Loss in Enthalpy.

Figure below shows P-V diagrams for these two processes.



This figure compares two processes that begin with the same state and involve expansion to the same volume.

For the isothermal process, the product of *P·V* remains constant since *T* remains constant.

Since the temperature decrease in an adiabatic process, therefore the pressure is also less.

Steady Flow Energy Equation

The steady flow energy equation relates to open systems working under steady conditions i.e in which conditions do not change with time.

The boundary encloses a system through which fluid flows at a constant rate, and heat transfer occurs and external work is done all under steady conditions.

The equation for steady flow is written per unit mass as

$$q - w = \Delta\left(h + \frac{1}{2}v^2 + gz\right)$$

q = heat transfer across boundary per unit mass

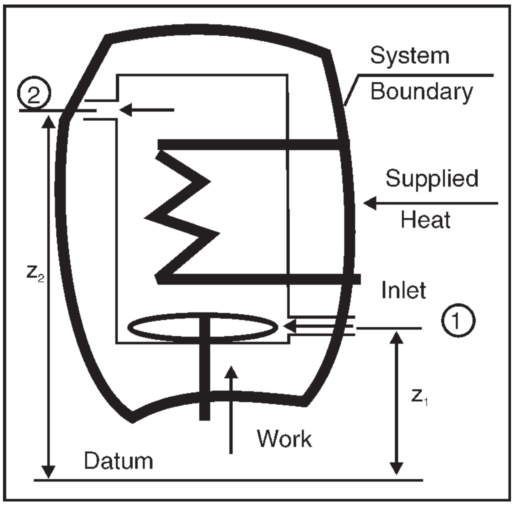
w = external work done by system per unit mass

z = fluid height

v = fluid velocity

h = fluid enthalpy (u (internal energy + pv (pressure. specific volume)

Consider a system as shown in figure below:



By applying first law of thermodynamics to above system, we can write equation as:

$$dQ/dt + dW/dt = m[\Delta h + \Delta C^2/2 + \Delta Zg]$$

Where,

dQ/dt= Supplied heat to the system per unit time,

dW/dt= Input work to the system per unit time,

m= Mass flow rate,

$\Delta h = h2 - h1$

h= Specific enthalpy,

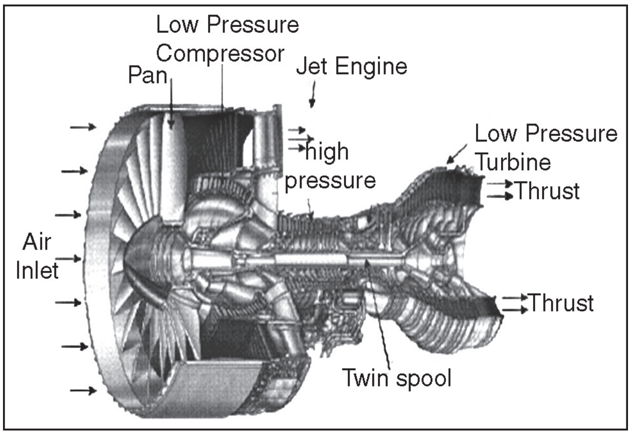
$\Delta C^2/2$= Difference in kinetic energy between outlet and inlet,

Z= Height measured from some reference datum,

1, 2 = refer to inlet and outlet, respectively.

Steady Flow Energy Equation of Gas Turbine

Consider an example of a turbine as shown in figure 4.3 below. The engine is designed to produce about 84,000 lbs of thrust at takeoff.



The fan and low pressure compressor are driven by the low pressure turbine.

The high pressure compressor is driven by the high pressure turbine.

f = total pressure ratio across the fan Å 1.4

c = total pressure ratio across the fan + compressor Å 45

Tin let = 300K

Heat transfer from the gas streams is negligible so we write the First Law equation as:

$$Q - W_S = m(h_{T2} - h_{T1})$$

Now we see that:

$$\begin{aligned} -W_S &= m_f \Delta h_{Tf} + m_c \Delta h_{Tc} \\ &= m_f c_p \Delta T_{Tf} + m_c c_p \Delta T_{Tc} \end{aligned}$$

In above equations we obtain the temperature change by assuming that the compression process is quasi-static and adiabatic.

So

$$\frac{T_2}{T_1} = \left(\frac{P_2}{P_1}\right)^{\frac{\gamma-1}{\gamma}}$$

then

$$\left(\frac{T_{T_2}}{T_{T_1}}\right)_{fan} = (\pi_f)^{\frac{\gamma-1}{\gamma}} = 1.1 \Rightarrow \Delta T_{T_{fan}} = 30K$$

$$\left(\frac{T_{T_2}}{T_{T_1}}\right)_{core} = (\pi_{core})^{\frac{\gamma-1}{\gamma}} = 3.0 \Rightarrow \Delta T_{T_{core}} = 600K$$

$$-W_S = 610\frac{Kg}{s}\cdot 30K\cdot 1008\frac{J}{KgK} + 120\frac{Kg}{s}\cdot 600K\cdot 1008\frac{J}{KgK}$$

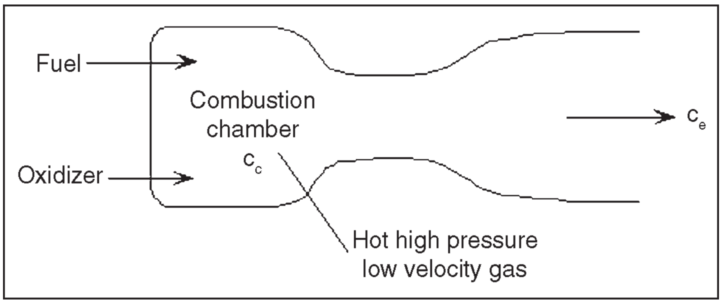
= 91 x 106 Joules/sec

W_s = -91 Megawatts (Negative sign implies work doneon the fluid)

Note that 1 Hp = 745 watts

Steady Flow Energy Equation of Nozzle

Consider a rocket with a chamber and nozzle. In this the liquid propellants moves inside the chamber, which converts the chemical energy into thermal energy.



Once the rocket is operating we see that all the flow processes are steady, hence we can use the steady flow energy equation.

We assume that the gas behaves as an ideal gas, and there will be no external work.

Then we can write the First Law as

$$q_{1-2} - W_{S1-2} = h_{T2} - h_{T1}$$

which becomes $h_{T2} = h_{T1}$

or

$$C_pT_c + \frac{C_c^2}{2} = C_pT_e + \frac{C_e^2}{2}$$

therefore

$$C_e = \sqrt{2C_p(T_c - T_e)}$$

If we assume quasi-static, adiabatic expansion then

$$\frac{T_e}{T_c} = \left(\frac{P_e}{P_c}\right)^{\frac{\gamma-1}{\gamma}}$$

so

$$C_e = \sqrt{2C_p T_c \left[1 - \left(\frac{P_e}{P_c}\right)^{\frac{\gamma-1}{\gamma}}\right]}$$

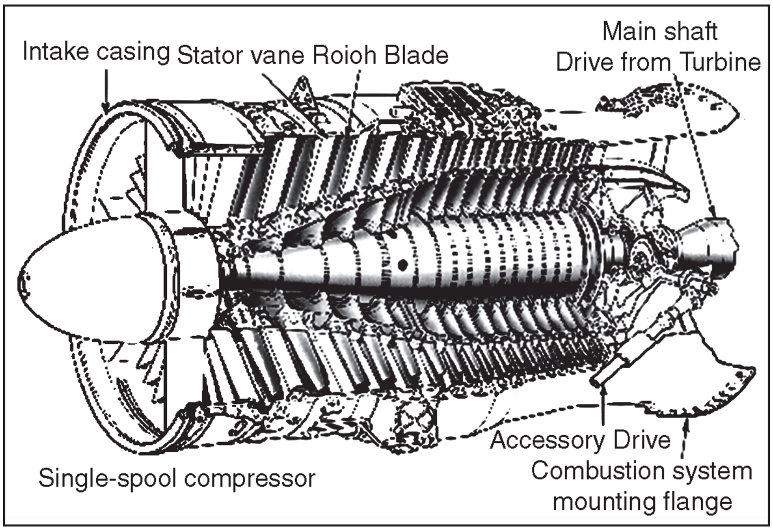
Where Tc and pc are conditions in the combustion chamber and pe is the external static pressure.

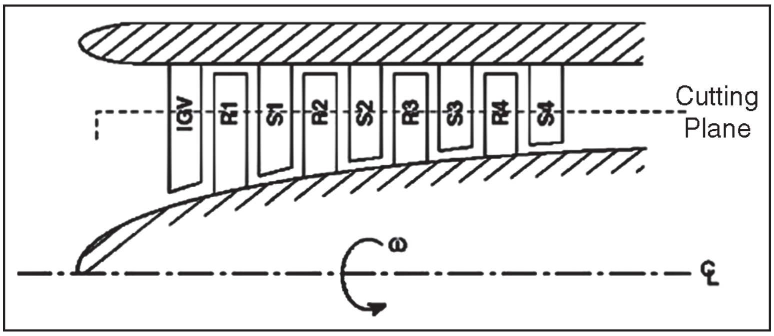
Steady Flow Energy Equation of Compressors

An axial compressor is typically made up of many alternating rows of rotating and blades called as rotors and stators respectively as shown in Figures.

The first row is typically called as the inlet guide vanes or IGV.

Each successive rotor-stator pair is called a compressor stage.



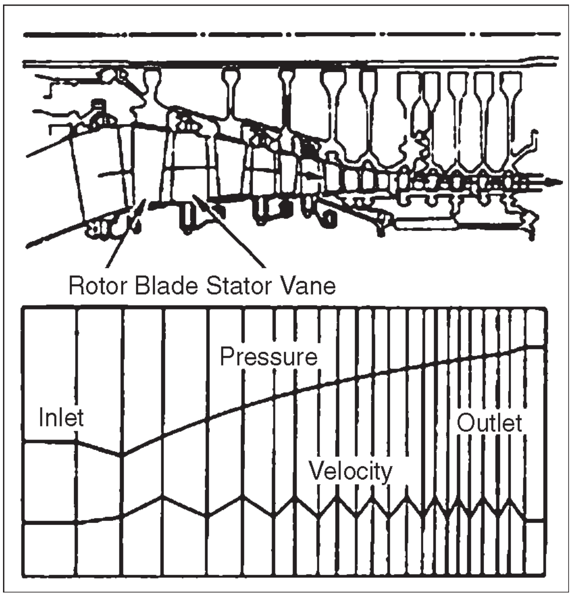


Considering Bernoulli Equation, where P_T is the stagnation pressure, p is the static pressure and velocity (u is radial, v is tangential, w is axial).

$$P_T = p + \frac{1}{2}p(u^2 + v^2 + w^2)$$

In this the rotor increases the energy and angular momentum by adding to the kinetic energy as $1/2rv^2$.

We see that a compressor look like as shown in Figure



Note that the IGV adds no energy to the flow. It is designed to add swirl in the direction of motion to lower the Mach number of the flow.

Heat Source

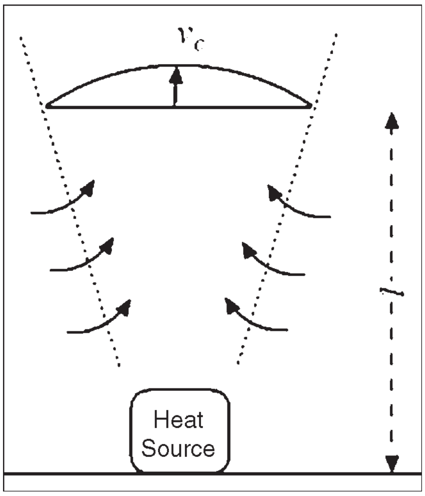
A heat source is anything that can heat up a spacecraft. Heat sources can be external or internal.

External Heat

External heat sources include:

- The Sun
- Reflected sunlight from planets and moons
- Heating by friction when traveling through an atmosphere or gas clouds, and
- Released heat from planets.

Heat source such as engine, stove or melting pot, will generate a vertical air flow.



Air Velocity

The air velocity is the center of the air flow which is at a distance above the floor and can be written as

$v_c = c_1 (1000 P / l)^{1/3}$

where

v_c = *air velocity in the center of the air flow (m/s)*

c_1 = *constant characterizing the actual application, typical values between 1 to 2.*

P = *heating power from the source (W)*

l = *distance above the floor and the heat source (m)*

Air Flow Volume

The air flow in a distance above the floor can be calculated as

$Q = c_2 P^{1/3} l^{5/3}$

where

Q = *air flow volume* (m^3/s)

c_2 = *constant characterizing the actual application, typical values between 0.05 to 0.15*

Heat Sink

Heat sinks are cooling mechanisms used to draw out thermal energy from a variety of electronic components.

Heat Sink prevent components from overheating. The most common heat sink applications are for computer CPU's, microprocessor chips and circuit boards.

The materials used to construct a heat sink are aluminum and copper, because of its high conductivity. Gold plating is also heat sinks, as it is used to increase the transfer of thermal energy.

Depending on design, a fan can be used to make heat sink airflow that benefits the cooling process.

The Second Law of Thermodynamics

In plain English the Second Law states that entropy always increases or remains constant in a closed system. (As a practical matter, for any non-trivial system entropy tends to increase due to irreversible processes.) The entropy of an entire closed system can never decrease within that system. Since the universe can be modeled as a closed system the universe is considered to be entropic – that is, running down. The change in entropy (delta S) is equal to the heat transfer (delta Q) divided by the temperature (T).

delta S = (delta Q) / T

Second Law of Thermodynamics(heat engine): It is impossible to extract an amount of heat Q H from a hot reservoir and use it all to do work W . Some amount of heat Q C must be exhausted to a cold reservoir. This precludes a perfect heat engine.

Second Law of Thermodynamics(refrigerator): It is not possible for heat to flow from a colder body to a warmer body without any work having been done to accomplish this flow. Energy will not flow spontaneously from a low temperature object to a higher temperature object. This precludes a perfect refrigerator

The Third Law of Thermodynamics

The Third Law of Thermodynamics is the lesser known of the three major thermodynamic laws. Together, these laws help form the foundations of modern science. The laws of thermodynamics are absolute physical laws – everything in the observable universe is subject to them. Like time or gravity, nothing in the universe is exempt from these laws. In its simplest form, the Third Law of Thermodynamics relates the entropy (randomness) of matter to its absolute temperature.

The Third Law of Thermodynamics refers to a state known as “absolute zero.” This is the bottom point on the Kelvin temperature scale. The Kelvin scale is absolute, meaning 0° Kelvin is mathematically the lowest possible temperature in the universe. This corresponds to about -273.15° Celsius, or -459.7 Fahrenheit .

In actuality, no object or system can have a temperature of zero Kelvin, because of the Second Law of Thermodynamics. The Second Law, in part, implies that heat can never spontaneously move from a colder body to a hotter body. So, as a system approaches absolute zero, it will eventually have to draw energy from whatever systems are nearby. If it draws energy, it can never obtain absolute zero. So, this state is not physically possible, but is a mathematical limit of the universe.

In its shortest form, the Third Law of Thermodynamics says: "The entropy of a pure perfect crystal is zero (0) at zero Kelvin (0° K)."

Entropy is a property of matter and energy discussed by the Second Law of Thermodynamics. The Third Law of Thermodynamics means that as the temperature of a system approaches absolute zero, its entropy approaches a constant (for pure perfect crystals, this constant is zero). A pure perfect crystal is one in which every molecule is identical, and the molecular alignment is perfectly even throughout the substance. For non-pure crystals, or those with less-than perfect alignment, there will be some energy associated with the imperfections, so the entropy cannot become zero.

The Third Law of Thermodynamics can be visualized by thinking about water. Water in gas form has molecules that can move around very freely. Water vapor has very high entropy (randomness). As the gas cools, it becomes liquid. The liquid water molecules can still move around, but not as freely. They have lost some entropy. When the water cools further, it becomes solid ice. The solid water molecules can no longer move freely, but can only vibrate within the ice crystals. The entropy is now very low. As the water is cooled more, closer and closer to absolute zero, the vibration of the molecules diminishes. If the solid water reached absolute zero, all molecular motion would stop completely. At this point, the water would have no entropy (randomness) at all.

Temperature

Temperature is the property of a body or region of space that determines whether or not there will be a net flow of heat into it or out of it from a neighboring body or region and in which direction the heat will flow. If there is no heat flow the bodies or regions are said to be in thermal equilibrium and at the same temperature.

If there is a flow of heat, the direction of the flow is from the body or region of higher temperature. Broadly, there are two methods of quantifying this property. The empirical method is to take two or more reproducible temperature-dependent events and assign fixed points on a scale of values to these events. For example, the Celsius temperature scale uses the freezing point and boiling point of water as the two fixed points, assigns the values 0 and 100 to them, respectively, and divides the scale between them into 100 degrees.

This method is serviceable for many practical purposes but lacking a theoretical basis it is awkward to use in many scientific contexts. In the 19th century, Lord Kelvin proposed a thermodynamic method to specify temperature, based on the measurement of the quantity of heat flowing between bodies at different temperatures. This concept relies on an absolute scale of temperature with an absolute zero of temperature, at which no body can give up heat. He also used Sadi Carnot's concept of an ideal frictionless perfectly efficient heat engine. This Carnot engine takes in a quantity of heat q1 at a temperature T1, and exhausts heat q2 at T2, so that T1/T2 = q1/q2.

If T2 has a value fixed by definition, a Carnot engine can be run between this fixed temperature and any unknown temperature T1, enabling T1 to be calculated by measuring the values of q1 and q2. This concept remains the basis for defining thermodynamic temperature, quite independently of the nature of the working substance.

The unit in which thermodynamic temperature is expressed is the kelvin. In practice, thermodynamic temperatures cannot be measured directly; they are usually inferred from measurements with a gas thermometer containing a nearly ideal gas.

This is possible because another aspect of thermodynamic temperature is its relationship to the internal energy of a given amount of substance. This can be shown most simply in the case of an ideal monatomic gas, in which the internal energy per mole (U) is equal to the total kinetic energy of translation of the atoms in one mole of the gas (a monatomic gas has no rotational or vibrational energy). According to the kinetic theory, the thermodynamic temperature of such a gas is given by T = 2U/3R, where R is the universal gas constant.

2

Kinetics and Equilibrium

The connection between the equilibrium constant for a reaction and the rate constants of the elementary steps by which it occurs is an important one. We begin by stating the relationship. We will then demonstrate, for a specific case, that it is true.

The equilibrium constant for a net reaction is the ratio of the product of the forward rate constants for all steps in the mechanism to the product of the reverse rate constants for all steps in the mechanism:

$K_{eq} = k_1 k_2 k_3 \ldots / k_{-1}\, k_{-2}\, k_{-3} \ldots$

We now show for a specific net reaction and a specific (proposed) mechanism that this statement is true. Consider again the reaction of NO_2 and F_2 to produce NO_2F, reaction:

$$2NO_2 + F_2 \Leftrightarrow 2NO_2F$$

We have written the reaction with the double arrow because we are now interested in the forward and reverse rates at equilibrium. At equilibrium, the overall forward rate and overall reverse rate must be equal:

$\text{rate}_f = \text{rate}_r$

This must be true regardless of the detailed pathway by which the reaction occurs. All available experimental evidence indicates that the mechanism is the two-step process:

$$NO_2 + F_2 \Leftrightarrow NO_2F + F \ [k_1,\ k_{-1}]$$
$$NO_2 + F \rightarrow NO_2F \ [k_2,\ k_{-2}]$$

When the overall reaction is in equilibrium, so must each elementary step be.

Consequently, we have used double arrows in the elementary steps as well. The equality of the forward and reverse rates of the individual steps is expressed mathematically as follows.

$k_1[NO_2]_e[F_2]_e = k_{-1}[NO_2F]_e[F]_e$

$k_2[NO_2]_e\,[F]_e = k_{-2}[NO_2F]_e$

Eliminating the concentration of the intermediate, F.

$[NO_2F]_e^{\,2}/[NO_2]_e[F_2]_e = k_1k_2/k_{-2}\ k_{-2} = K_{eq}$

The statement made at the outset is thus seen to be true for this specific case: the equilibrium constant is the ratio of the product of forward rate constants to the product of reverse rate constants. For the general overall reaction occuring by an *n*-step mechanism,

$K_{eq} = k_1k_2 \ldots\ k_n/k_{-1}\ k_{-2} \ldots\ k_{-n}$

Objection is frequently made to the method of derivation that we have just used, because the mechanism for is not known with certainty; it is and will remain a hypothesis, however well based in experiment.

If it is found that the two step mechanism is indeed NOT correct, then the relationship is invalid. This is certainly true. However, even if the mechanism above is incorrect, Reaction must occur by some mechanism. At equilibrium each step in the mechanism must be balanced in rate, enabling us to eliminate concentrations of any and all intermediates just as we did above, to arrive at a modified version. The validity of the general relationship is independent of the details of mechanism.

Thus the intuitively-expected connection between k and K does indeed exist. In fact, there are many examples in which the equilibrium constant for a reaction has been obtained from kinetics studies. This process can never be reversed however; it is not possible to obtain k by performing equilibrium studies. Before leaving this matter, we make one more very important point.

There is a tendency to believe that reactions with large equilibrium constants are fast, whereas those with small equilibrium constants are slow. However, neither of these beliefs is true.

A large value for K_{eq} means that the product of forward rate constants is much larger than the product of reverse rate constants. It does not follow, however, that the forward rate constants are LARGE. It means only that they are larger than the reverse rate constants.

$k_1 \, k_2 \ldots \, k_n >> k_{-1} \, k_{-2} \ldots \, k_{-n}$ does not mean that

$k_1, \, k_2, \, \ldots, \, k_n$ are large in the absolute sense.

A large K_{eq} can result from the ratio of a slow forward rate to an even slower reverse rate.

Catalysis

A number of chemical reactions that ordinarily occur slowly can be induced to occur more rapidly by the addition of a suitable substance called a catalyst. We will define a catalyst as a substance that speeds up a reaction without itself being consumed or chemically changed in the overall reaction process. This definition is in practice rather restrictive, because eventually, all real catalysts become deactivated by "poisoning" or via irreversible structural changes; thus they cannot function indefinitely.

For our purposes, here, however, this definition will serve. The reactant molecule that is affected by the catalyst is called the substrate. The process by which a catalyst effects its action is called catalysis. Catalysis is one of the most intensely studied areas in science because it is of tremendous biological and industrial importance. We begin our exploration of catalysts by discussing how they work.

The Mode of Catalyst Function

A catalyst functions either by entering into a slow step of the uncatalyzed reaction mechanism, or by creating an entirely new mechanism for the reaction. In either case, it is thought that the catalyzed pathway has a lower activation energy than the uncatalyzed path. We can illustrate catalytic action generically in terms of the following reaction scheme, where A, B, D, and F are reactants and products in the overall reaction, and C is a catalyst for the reaction.

$$A + B \rightarrow D + F \text{ [overall]}$$

Uncatalyzed mechanism:

$A + B \rightarrow AB$ [slow]

$AB \rightarrow D + F$

Catalyzed mechanism:

$A + C \rightarrow CA$ [fast]

$CA + B \rightarrow CAB$ [less slow than first step of uncatalyzed mechanism]

$CAB \rightarrow \mathrm{D} + CF$ [fast]

$CF \rightarrow C + F$ [fast]

The effect of the catalyst on the activation energy of the slow step of the reaction is shown schematically. The catalyst affects only E_a; it does not affect the energy of either the reactants or products of the reaction. The intermediate, *CAB*, in which both reactants are bound to the catalyst, is of particular interest. A possible (and fairly common) structural motif for this intermediate.

Notice that, although *A* and *B* are bound to different sites on the catalyst, *C*, they are in proximity and can effectively interact. Binding of *A* and *B* to *C* causes shifts in electron density that may facilitate bond breaking within *A* and/or *B* and bond formation between *A* and *B* or fragments of them. Thus the catalyst provides an organizing centre for *A* and *B*, facilitating their interaction. In this manner the catalyst can overcome the orientation factor discussed earlier.

As soon as the molecule of catalyst is regenerated in the last step of the 4-step mechanism, it may bind another molecule of *A* and proceed once again through the sequence, converting *A* and *B* to D and *F*. This sequence is repeated a large number of times, so that generally only a small amount of catalyst is required to convert a substantial quantity of reactant to product.

Chemists call the process by which the catalyst cycles through the reaction over and over again a catalytic loop. The unbound form of the catalyst, *C*, is placed at the 12 oclock position of the loop, and the various forms in which the catalyst is found are placed more or less evenly around the remainder of the loop. Arrows show the direction of reaction around the loop, with reactants brought in from outside the loop, and products ejected out of the loop.

This is a very effective visual presentation of catalyst action. The number of times that a molecule of catalyst cycles through the loop per unit time is called the turnover number of the catalyst. An effective measure of turnover number is moles product produced per mole catalyst present per time.

Let's look at a specific example of the effect of a catalyst on a simple reaction, from which we can draw some general conclusions.

Example: The reaction of ethanol (ethyl alcohol) with bromide ion to produce ethyl bromide and hydroxide ion.

$$C_2H_5OH + Br^- \rightarrow C_2H_5Br + OH^-$$

The reaction is quite slow in neutral or basic solution, but occurs quite rapidly in acidic solution because it is catalyzed by the hydronium ion, H_3O^+. Discuss the mechanisms for the uncatalyzed and catalyzed processes.

Solution: The uncatalyzed reaction is thought to occur in a single elementary step, in which bromide ion attacks the hydroxyl carbon atom of ethanol while the hydroxide group simultaneously departs:

$Br^- + C_2H_5OH \rightarrow$ activated complex $\rightarrow C_2H_5Br + OH^-$

Rate = $k_{obs}[C_2H_5OH][Br^-]$

This mechanism is proposed based on the experimental rate law, which is overall second order. The observed rate law for the catalyzed process is

Rate = $k_{obs}[Br^-][C_2H_5OH][H_3O^+]$

The following three-step mechanism is consistent with this rate law if k_{obs} is identified with k_2K_1:

$C_2H_5OH + H_3O^+ \rightarrow C_2H_5OH_2^+ + H_2O$ [fast, K_1]

$C_2H_5OH_2^+ + Br^- \rightarrow C_2H_5Br + H_2O$ [slow k_2]

$2H_2O \rightarrow H_3O^+ + OH^-$

The reaction coordinate diagrams for the uncatalyzed and catalyzed pathways. Several general statements about catalysis are evident from this example.

- Because the catalyst does not appear in the overall equation for the reaction, it does not affect the equilibrium; it affects only the kinetics. The catalyst speeds up not only the forward reaction, but also the reverse, by the same factor. The position of equilibrium remains the same.
- the activation barrier is lower in the catalyzed mechanism. Even though the catalyzed path involves more steps, the overall reaction occurs more rapidly.
- The concentration of the catalyst appears in the rate law, even though the catalyst does not appear as a reactant or product in the overall equation.
- Although a catalyst and an intermediate share the property of not appearing in the overall equation, they

are different types of things. First, the catalyst appears in the rate law; an intermediate cannot. Second, the catalyst appears first as a reactant, then is generated later as a product. An intermediate appears first as a product, then later as a reactant.

Examples of Catalysis

We will now briefly discuss several examples of catalysis that are actually used on a mammoth scale in the chemical industry. Each of these processes, in its own way, has a major impact on the quality of our lives.

The Polymerization of Ethylene

Ethylene is a very simple molecule with formula C_2H_4. It is a gas, obtained as a byproduct during the catalytic cracking of petroleum. Under certain conditions, ethylene molecules can be made to join together end-to-end to form very long chain-like molecules of polyethylene, so called because it consists of many (poly) ethylenes. The process is represented.

$TiCl_3$

$$2n\ CH_2 = CH_2 \rightarrow -(CH_2CH_2CH_2CH_2)_n^-$$

Even at high temperature and pressure of ethylene, this process occurs negligibly slowly. In the presence of a small amount of a modified form of $TiCl_3$ (called tickle-3 in the plastics industry), however, it occurs rapidly at only moderately high temperature and pressure. The process is referred to as Ziegler-Natta catalysis after its two coinventors, who jointly received the Nobel Prize in Chemistry in 1963. Since the discovery of this process in the 1950's, the entire plastics industry has developed and grown to huge proportions.

To this day, the mechanism of Ziegler-Natta catalysis is not fully understood. Mechanistic studies are difficult for several reasons, one of which is that the process is heterogeneous; that is, the catalyst ($TiCl_3$) and substrate (ethylene) are in different phases. The catalytic process takes place on the surface of crystals of $TiCl_3$, which rapidly become covered with and blocked from view by the resulting polyethylene. Much effort is ongoing in the US chemical industry to develop more efficient and easily handled Ziegler-Natta catalysts.

The Production of Sulfuric Acid.

Year after year, sulfuric acid ranks first on the list of the top ten chemical substances produced in the United States: billions of pounds are produced annually. Sulfuric acid is synthesized by the so-called Contact Process, which involves the four sequential steps below:

$S + O_2 \rightarrow SO_2$ [fast]

$SO_2 + O_2 \rightarrow SO_3$ [slow, because it occurs by a termolecular elementary process catalyzed by V_2O_5]

$SO_3 + H_2SO_4 \rightarrow H_2S_2O_7$ [fast]

$H_2S_2O_7 + H_2O \rightarrow 2H_2SO_4$ [fast]

The reaction of SO_3 with water is very exothermic and causes extensive spattering and production of a fine mist of highly acidic water.

For this reason, direct reaction of SO_3 with water in the third step is impractical. Instead, SO_3 is bubbled into pure sulfuric acid, with which it reacts smoothly to give fuming sulfuric acid, $H_2S_2O_7$. This can then be treated with the stoichiometrically correct amount of water to give sulfuric acid. The contact process has been so perfected that sulfuric acid is very inexpensive to produce. Consequently, it is used in any industrial process requiring acid.

It finds it major uses in the production of phosphate fertilizers; in paper manufacture; in the petroleum industry; in steel production; and in the production of detergents. The importance of these products in our lives is obvious.

Catalytic Converters

For some years now, catalysts have been placed within the exhaust systems of automobiles to reduce the amount of poisonous or otherwise harmful emissions. These noble metal catalysts (based on platinum and palladium) carry out a dual function. First, they facilitate oxidation of carbon monoxide, resulting from incomplete hydrocarbon combustion, to carbon dioxide:

$$CO(g) + 1/2\ O_2(g) \xrightarrow{Pt} CO_2(g)$$

Second, they catalyze decomposition of nitric oxide, produced during engine operation and oxidized rapidly to toxic NO_2 by atmospheric oxygen, to N_2 and O_2.

Unfortunately, catalytic converters also facilitate oxidation of SO_2 to SO_3, which is the precursor of acid rain. Low-sulfur petroleum distillates are therefore essential.

The Haber Process. Vast quantities of ammonia are synthesized each year for use as fertilizer. Currently the most efficient process for ammonia synthesis is the Haber-Bosch Process, developed during the ten-year period preceding 1913, in which nitrogen and hydrogen react directly at high temperature and pressure and in the presence of an activated iron catalyst to form ammonia.

$$N_2(g) + 3H_2(g) \xrightarrow{Fe} 2NH_3(g)$$

A catalyst and high temperature are necessary to cause the reaction to go at a reasonable rate. Unfortunately, high temperature makes the exothermic reaction less favored, so very high pressure is used to favour products.

Even with conditions optimized, reaction is incomplete, and unreacted hydrogen gas is recycled for maximum efficiency of ammonia production. Nitrogen fertilizers produced from ammonia are largely responsible for the incredible growth in agricultural production over the decades since the First World War, when the process was first put on line in Germany. Ironically, the original motivation for development of the process was the requirement of explosives for the war effort.

The processes discussed above have at least three features in common. First, catalysis is heterogeneous; the catalyst is in all cases a solid, interacting with the substrate in the gas phase. Second, the mechanisms for these processes are incompletely understood. Thus catalysts are used successfully on a huge scale, even though we do not understand how they work.

Third, in all cases the catalyst involves a transition metal, from the D block of the periodic table. Transition metals are often versatile catalysts because they are flexible in coordination number (that is, the number of atoms, ions, or molecules to which they may bind in a Lewis acid-base interaction); in stereochemistry (that is, in the shapes that their adducts assume); and in oxidation state (that is, in the charge that they carry).

Nature has chosen transition metals to serve as the centerpieces for many of its catalysts, the enzymes, most probably for these same reasons.

3

Thermal Equilibrium

The condition under which two substances in physical contact with each other exchange no heat energy. Two substances in thermal equilibrium are said to be at the same temperature.

Now clearly the collection of atoms in a gas can perform many different types of motion. We could imagine all the atoms standing completely still (or as still as they are allowed by quantum mechanics) or we could imagine half of them at rest and the other half moving back and forth in oscillatory motion. These are not the types of states of matter which we describe through thermodynamics. We wish to describe the state which ensues in a system of particles after a well defined set of external conditions have been in effect for sufficiently long time that these average properties have converged to their final values. We call this state the state of thermal equilibrium.

An example of a thermodynamic system which is *not* in thermal equilibrium is a gas which occupies one half of the volume V which is available to it. Clearly there will be a macroscopic evolution of the volume of gas to a state where it occupies all of V at which point the gas may be in its thermodynamic equilibrium state.

Another example of a system which is not in thermal equilibrium is a cup of hot coffee on the breakfast table. If you left it there for several hours it would cool off until it reached thermodynamic equilibrium with the surroundings. If there were two cups of coffee on the table and they were both left to evolve into thermal equilibrium with the same surroundings then clearly the two cups of coffee would be in thermal equilibrium with one another as well. This postulate is sometimes called the zeroth law of thermodynamics.

From the zeroth law of thermodynamics comes the idea of a thermometer and the concept of temperature. We can classify the thermodynamic equilibria of even the most complicated systems in terms of the state of a simple system with which it is in thermal equilibrium. Thus if we can classify the thermodynamic state of a simple physical system be a number then we can use this same number to classify the thermodynamic equilibrium state of even the most complicated of systems.

Naturally we have lots of freedom for specifying a temperature scale. We could for example choose the temperature to be the length of a bar of a specific material because as we shall see the dimensions of solids vary with the thermal equilibrium state of the solid. This so called thermal expansion effect is however a complicated which depends on details in the atomic interaction potential which we do not want to build into our definition of temperature. Instead we choose to define the temperature in terms of the simplest possible system which has a thermal equilibrium. Specifically the Kelvin temperature scale used in physics is defined as being proportional to the pressure of a very dilute gas held at constant volume.

This implies that zero temperature is the temperature of a dilute gas which is so cold that it exerts a vanishing pressure on the walls of the volume that contains it. We need a second fixed point to fully define the temperature scale and for this physicists have chosen the so-called triple point of water. The triple point of water is where solid, liquid, and gas of H_2O coexist. It is a common and well defined thermal equilibrium state which we label by the temperature 273.16 K. The Kelvin temperature scale is thus defined as

$$T = 273.16\text{K}\frac{p}{p_{\text{trip}}}$$

where p_{trip} is the pressure in the fixed volume of gas when it is in thermal equilibrium with a mixture of water ice and water vapour at its triple point. It is an advantage of this definition that it is independent of the detailed properties of any one material.

Other temperature scales in use for historical reasons are defined in terms of the Kelvin ideal gas temperature scale. Specifically the Celsius and Fahrenheit temperature scales are defined as

$$T_c = T_K - 273.15\text{K} T_f = \frac{9}{5}T_K - 459.67°\text{F}$$

Phase Equilibrium in Solutions

Many of the ideas presented in the discussion of phase equilibrium of pure substances are also applicable to mixtures of pure substances. In this section we discuss the so-called colligative properties of solutions (homogeneous mixtures) in terms of phase equilibrium.

Solutions and Concentration Units

We begin with definitions of some terms that are used in discussing solutions:

- *Solution*—a homogeneous mixture. This means that the components may be blended in any desired composition, as long as the result is homogeneous. Homogeneous means that the composition of the mixture is the same at all points and independent of time.
- *Solvent*—the component present in major amount. In most cases, the solvent is a liquid.
- *Solute*—a component present in minor amount. In general a solution may contain more than one solute.

If we add 1.0 g of sugar to 10 mL of water in a beaker, the sugar falls to the bottom of the beaker where it forms a pile. Over the period of a few minutes, the pile becomes smaller until finally no solid sugar remains visible. The sugar has dissolved in the water. The result is a solution of sugar in water. Because water is present in major amount, it is the solvent, and sugar is the solute. The solution is clear and displays all of the usual properties of a liquid. There is no cloudiness (opacity) to indicate the presence of the sugar.

In preparing a solution, it is usually important to specify, as precisely as possible, the amount of solute present per unit amount of solvent or per unit amount of solution. This is called the concentration of the solution. The concentration is an intensive property of the solution, independent of the amount of solution present. In this respect, concentration is similar to density. There are several ways to express concentration, discussed below.

- Molarity, *M*. If *A* represents the solute, the molarity of the solution is the number of moles of *A* per liter of solution. Symbolically,

  $$M_A = [A] = \text{moles } A/1 \text{ L solution}$$

- Molality, m. The molality of a solution of *A* in some solvent is the number of moles of *A* per kilogram of solvent. Symbolically,

  $$m_A = \text{moles } A/1 \text{ kg solvent}$$

- Mole fraction, *X*. The mole fraction of *A* in a solution containing *A* and at least one other substance is the ratio of the number of moles of *A* to the total number of moles of all substances. Symbolically,

  $$X_A = \text{moles } A/\text{total moles}$$

If *A* is the only solute, then X_A = moles *A*/(moles *A* + moles solvent)

There are several other ways to express concentration, but those above are most common. We will use molarity most frequently.

Example: How many mL of 0.26 M H_2SO_4 are required to react completely with 26.72 mL of 0.18 M NaOH according to

$$H_2SO_4(aq) + 2NaOH(aq) \rightarrow 2H_2O + Na_2SO_4(aq)$$

Solution. Moles NaOH = 26.72 mL NaOH * 0.18 mole NaOH/1000 mL NaOH = 4.810×10^{-3} moles NaOH

From the stoichiometry of the equation,

Moles H_2SO_4

= moles NaOH * (1 mole H_2SO_4/2 mole NaOH)

= 4.810×10^{-3} * 1/2

= 2.405×10^{-3} moles H_2SO_4

Volume H_2SO_4

= moles H_2SO_4 * (1000 mL H_2SO_4/0.26 mole H_2SO_4)

= $2.405 \times 10^{-3} \times 1000/0.26$

= 9.25 mL H_2SO_4

Suppose that we require 100 mL of a 0.10 M sulfuric acid solution, but all we have available is commercial concentrated sulfuric acid, which is 18 M in H_2SO_4.

We can prepare the required solution by dilution. Dilution is the process of adding a known volume of a concentrated solution of a reagent to water (or another solvent) to give a less concentrated solution.

It is a very frequently-used laboratory technique. The key to dilution is that the number of moles of H_2SO_4 in the required volume of 18 M H_2SO_4 is the same as the number of moles in 100 mL of 0.1 M H_2SO_4. The number of moles is the product of solution volume and molarity both before and after dilution. Using subscript "*i*" for initial quantities and "*f*" for final quantities,: $V_iM_i = V_fM_f$.

Here V_i is the volume of concentrated H_2SO_4, M_i is its molarity, V_f is the volume of dilute H_2SO_4, and M_f is its molarity. V_i can easily be calculated from the known values of the other 3 quantities. The result is 0.556 mL.

Solutions have some interesting properties called colligative properties. They depend on the nature of the solvent and the amount (but not the identity) of the solute. These properties may be understood in terms of phase equilibrium. We begin with the effect of a solute on the vapour pressure of a liquid solvent.

Raoult's Law

Consider a solution of a non-volatile solute, *B*, in a volatile solvent, *A*. A volatile substance has an appreciable vapour pressure at room temperature; a non-volatile substance has essentially zero vapour pressure. How is P_{vap} of the solvent in the solution related to P_{vap} of the pure solvent? Raoult answered this question experimentally in 1886 when he showed that equation is valid for ideal solutions: $P_A = X_A P_A^\circ$.

P_A = the vapour pressure above the solution due to solvent, X_A = the mole fraction of solvent, and P_A° = the vapour pressure of pure solvent. This equation is called Raoult's Law. We can make several statements about this law.

- $X_A < 1$ so the vapour pressure of the solution is less than that of pure solvent.
- No term in the equation involves any chemical or physical property of the solute. It doesn't matter what the solute is, only that it is non-volatile.
- The equation is ideal because it holds only for ideal solutions. An ideal solution is one in which intermolecular forces between A molecules, between B molecules, and between A and B molecules are the same. If these forces are the same, there is no enthalpy change when solute dissolves in solvent. It is important to realise that Raoult's Law has very limited applicability. Very few real solutions even approach the ideal, and most are definitely NOT ideal. These do

not obey Raoult's Law. Some solutions are nearly ideal when very dilute; thus Raoult's law approximately describes the vapour pressures above most dilute solutions.

- The law is purely statistical. It says that the tendency for solvent molecules to escape the liquid is in proportion to the relative abundance (mole fraction) of solvent molecules at the liquid surface.

Raoult's Law can be understood physically by considering the liquid surfaces of pure solvent and solution, shown in Figure.

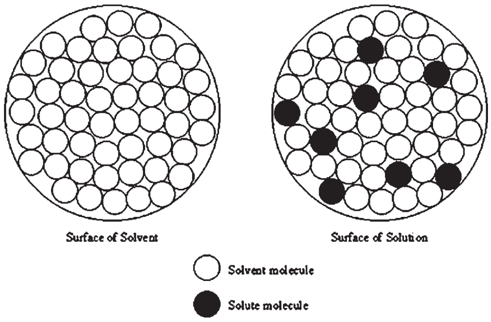


Fig. Raout's Law

In pure solvent, all surface molecules are solvent. However, in the solution, a fraction of molecules at the surface are solute molecules, which are non-volatile (cannot escape to the vapour phase). These reduce the surface area available for escape of solvent molecules, so that the evaporation rate of solvent is reduced from that in pure solvent. The fraction of surface area occupied by solvent molecules is directly related to the mole fraction of solvent.

The evaporation rate, and consequently the vapour pressure, is reduced by a factor equal to the ratio of surface areas, which is the mole fraction of solvent. Raoult's law, equation, follows.

Colligative Properties

The extent to which the vapour pressure is lowered depends quantitatively on the amount of solute present. Defining ΔP $= P_A^\circ\ P_A$, and substituting for P_A using Raoult's Law, gives

$$\Delta P = P_A^\circ - X_A P_A^\circ = P_A^\circ (1 - X_A) = X_B P_A^\circ$$

where X_B is the mole fraction of solute.

The vapour pressure lowering, ΔP, is the first of four colligative properties. The remaining three are consequences of ΔP, and may be examined in terms of the phase diagrams for the pure solvent and the solution. These are shown superimposed in Figure.

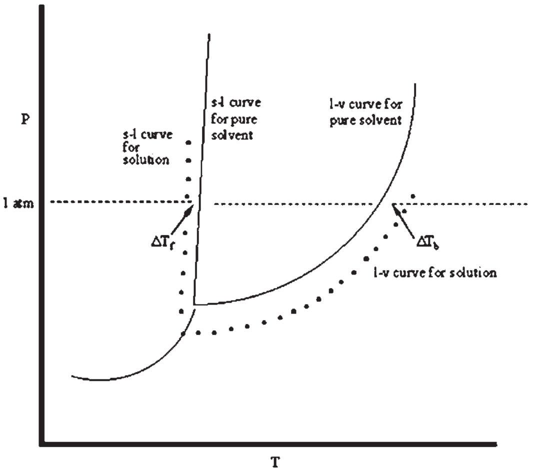


Fig. Phase Diagram for a Pure Substance and solution for which the Substance is the Solvent

The $l - v$ line for the solution (dashed line) is lower at all temperatures than that for the pure solvent (solid line). It therefore intersects the $P = 1$ atm line at a higher temperature. The boiling point of the solution is higher than that of pure solvent by an amount ΔT_b, which is called the boiling point elevation, and is indicated on the diagram.

The boiling point elevation is the second colligative property. ΔT_b is defined as T_b(solution) – T_b(solvent), which makes it a positive number. The boiling point elevation is directly proportional to the molality of the solute:

$$DT_b = K_b{*}m$$

The value of the constant, K_b, called the boiling point elevation constant for the solvent, depends only on properties of the solvent. Thus equation is valid for a particular solvent no matter what the solute is. Because the $l - v$ line for the solution is lower, it intersects the $s - v$ line at lower T than does the $l - v$ curve for the pure solvent. The $s - l$ line for the solution (dashed in the figure) therefore lies to the left of that for the pure solvent. Consequently the triple point for the solution is lower than that for the solvent by an amount ΔT_f, indicated on the diagram. Over small ranges of T and P, the $s - l$ lines are linear and roughly parallel. It follows that the freezing point for the solution is lower than that for the solvent by about the same amount, ΔT_f. ΔT_f is called the freezing point depression, and is defined to be a positive number: $\Delta T_f = T_f - T_f$(solution). It is the third colligative property. The freezing point depression is similar to the boiling point elevation in being directly proportional to the solute molality:

$$\Delta T_f = K_f{*}m$$

K_f is the freezing point depression constant and depends only on properties of the solvent. Table gives values of K_b and K_f for several common solvents.

Table. Molal Boiling Point and Freezing Point Constants

Solvent	***T_b(°C)***	***K_b***	***T_f(°C)***	***K_f***
acetic acid	118.2	2.93	17	3.90
chloroform	61.2	3.63		
naphthalene			80	6.8

water	100	0.52	0	1.86
camphor			179	40
carbon tetrachloride	76.6	5.03		
ethanol	78.6	1.22		
n-octane	125.7	4.02		

Unlike the vapour pressure lowering, which is usually small and difficult to measure accurately, ΔT_b and ΔT_f are relatively easily and accurately measured. The freezing point depression used to be applied in the determination of molar masses of unknown substances. However, because molar masses can now be determined much more accurately using mass spectrometry, the freezing point method is seldom used.

There are a number of practical uses of the freezing point depression and boiling point elevation colligative properties. For example, sodium chloride is often added to water for cooking, not only for flavour, but to raise the boiling temperature and accelerate the cooking chemistry. Calcium chloride is spread on icy roads in winter to lower the freezing point of the water. And antifreeze (ethylene glycol) is added to the cooling systems of automobiles to protect against boilover in the summer and coolant freeze in winter. The fourth colligative property is called osmotic pressure. It can be understood in terms of the apparatus, which consists of two arms, separated by a semi-permeable membrane.

This is a membrane with pores that allow passage of small molecules (solvent) but block larger molecules (solute). In the left arm of the apparatus is placed a pure solvent, usually water. In the right arm is placed a solution of the same solvent. The dots in the figure represent molecules of solute present in the solution. Solvent molecules can pass through the membrane in either direction. However, their passage from right to left (from solution to pure solvent) is impeded somewhat because solute molecules block their access to some of the pores. More solvent molecules per unit time pass from solvent to solution than in the reverse direction. The result is that the amount of solvent in the right arm increases with time and the solution becomes more dilute.

It is possible to prevent the net flow of solvent from left to right by applying pressure to the top of the liquid column in the right arm of the apparatus. The applied pressure increases the rate of passage of solvent from solution to solvent until it is equal to the rate of passage in the other direction. Under these conditions, the system is in equilibrium and the concentration of the solution does not change with time. The pressure that must be applied to stop the net flow of solvent is called the osmotic pressure, symbolized P. Its magnitude is directly proportional to the temperature and the molarity of the solution. The ideal gas constant, R, is the proportionality constant:

$$\Pi = M^*R^*T$$

Realizing that molarity is moles of solute per unit volume of solution, expressed in liters, we can convert equation to a form analogous to the ideal gas law:

$$\Pi V = n^*R^*T$$

It may seem odd that the ideal gas constant appears in an equation that describes a property of a liquid solution. However, a non-volatile solute dissolved in a solvent behaves much like a gas, because the solute molecules are far apart and are free to roam over the entire solution volume. This similarity between a gas and a dissolved solute causes osmotic pressure to obey a gas-law type equation.

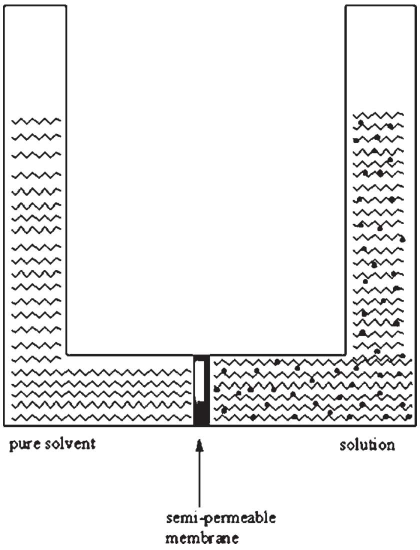


Fig. Osmotic Pressure

The similarity in fact extends further. The osmotic pressure calculated from equation has exactly the same value as the pressure of a sample of gas occupying the same volume at the same temperature. We know that the gas will expand if the pressure exerted on it is less than the pressure that it exerts. In the same way, the solution in Figure tends to “expand” (increase in volume) by dilution when in contact with pure solvent unless an external pressure equal to its osmotic (internal) pressure is applied.

A simple calculation using equation shows that concentrations as low as 10^{-4} M give readily measureable osmotic pressure. The osmotic pressure is therefore much more sensitive to the presence of solute than the other colligative properties. It can be used to determine the molar masses of huge molecules like proteins, which dissolve in water to give solutions that may be concentrated in terms of weight per cent, but are of very small molarity due to the large molar masses (on the order of 10000 μ).

Example: A solution of 0.0720 g of the blood protein, hemoglobin, in 100 mL water has an osmotic pressure of 2.10 torr at 300 K. What is the molar mass of hemoglobin?

Solution: Calculate the concentration in moles hemoglobin per liter using the osmotic pressure. Then equate the moles per liter with the grams per liter to get molar mass.

$C = \Pi/RT$ = (2.10 torr/760 torr per atm)/(0.08206 atm-L/Mole-K) (300 K)

$= 1.13 \times 10^{-4}$ moles/L

Since 100 mL of solution contains 0.0720 g, a liter would contain 0.720 g. Thus

$MM = 0.720$ g/1.13×10^{-4} moles = 64000 g/mole

You might think about whether freezing point depression or boiling point elevation measurements would be useful in determining this MM.

It may not be clear that osmotic pressure, the tendency for solvent to flow spontaneously from solvent to solution across the barrier, is a consequence of the vapour pressure lowering of the solvent in the solution. Figure shows two beakers, one containing pure solvent, the other the same solution that is in the right arm of the apparatus.

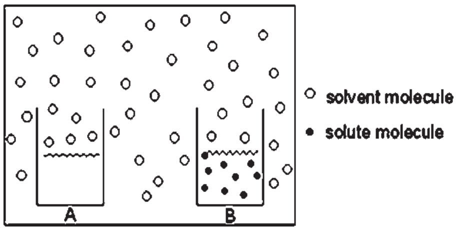


Fig. New Flow of Solvent to Solution via Gas Phase

The beakers are placed in a closed container. Solvent begins to evaporate from each beaker in an attempt to establish the equilibrium vapour pressure. However, this pressure is less for the solution than for the pure solvent. As pure solvent evaporates from the left beaker in an attempt to establish the vapour pressure, P°_{vap}, it condenses in the right beaker as the solution tries to lower the vapour pressure to its equilibrium value, P_{vap}. The solution gradually becomes more dilute due to spontaneous "flow" of solvent into it. The origin of the osmotic pressure phenomenon in the solvent vapour pressure lowering is clear.

Mechanical Equilibrium

We are now ready to consider objects in equilibrium. There are two conditions to equilibrium for most objects.

The first condition is stated by Newton's first law:

$$\sum \vec{F} = 0$$

The second condition of equilibrium is

$$\sum \vec{\tau} = 0$$

Basically, we say that a body is in equilibrium if the vector sum of the forces and torques are zero.

Usually, we will need to look at both translational equilibrium and rotational equilibrium. The rule of thumb is that if the body is a point source, or all of the forces act at the same point on the body, then we do not need to consider rotational equilibrium. If the forces act at different points on the body, then we must take rotation into account.

Centre of Mass

In order to simplify our calculations, it is convenient to talk in terms of the centre of mass, or centre of gravity, of a body.

We define the centre of mass to be the weighed average of the components of the body

$$\vec{X}_{CM} = \frac{\sum m_i \vec{x}_i}{\sum m_i} = \frac{\sum m_i x_i}{M}$$

If the object is a continuous mass distribution, we replace the summation with an integral. Also, notice that the centre of mass is a vector.

The usefulness of the centre of mass is that we will often need to calculate the torque of the centre of mass about some point. It can be shown that in terms of the centre of mass, the equilibrium conditions reduce to

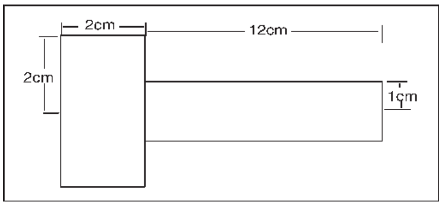
$$\sum \vec{F}_{\text{ext}} = 0$$

$$\sum \vec{\tau}_{\text{ext}} = \sum \vec{R} \times \vec{F}_{\text{ext}} = 0$$

where F_{ext} is all of the forces external to the body, and R is the distance from the centre of mass.

Example

Locate the centre of mass of the machine part in the diagram below



By symmetry, the centre of mass lies along the axis and the centre of mass of each part is midway between its ends. The volume of the disk is 8p cm^3 and that of the rod is 12p cm^3. Since the weights of the two parts are proportional to their volumes,

$$\frac{W_{\text{disk}}}{W_{\text{rod}}} = \frac{8\pi}{12\pi} = \frac{2}{3}$$

Taking the origin to be at the left face of the disc on the axis, we have

x_1 = 1 cm x_2 = 8 cm

and so

$$X_{CM} = \frac{W_{disk}X_1 + W_{rod}X_2}{W_{disk} + W_{rod}}$$

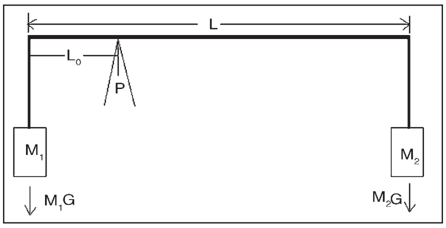
$$= \frac{\frac{2}{3}W_{rod}(1\text{ cm}) + W_{rod}(8\text{ cm})}{\frac{2}{3}W_{rod} + W_{rod}}$$

$$= 5.2\text{ cm}$$

Example

A 5 m long rigid rod whose own weight is negligible is pivoted at a point 2 m from the left end. A mass of $m_1 = 25$ kg is attached to the left end.

What must the mass be of a block attached to the right end so that the rod is in equilibrium? What is the force of the pivot on the rod?



There are no forces in the x direction. The forces in the y direction are

$$m_1g + m_2g - P = 0$$

The torque about the pivot is (taking counterclockwise to be positive)

$$m_1g(l_0) - m_2g(l - l_0) = 0$$

Solving this for m_2 yields

$$m_2 = m_1\frac{l_0}{l - l_0}$$

$$= (25\text{kg})\frac{(5m)}{(5m - 2m)}$$

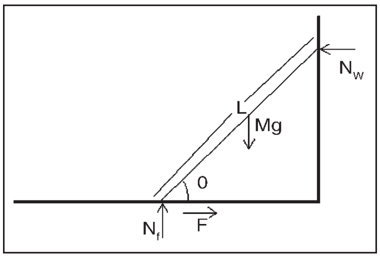
$$= 41.67\text{ kg.}$$

Thus, the force of the pivot must be

$$\begin{aligned} P &= m_1g + m_2g \\ &= (m_1 + m_2)g \\ &= (24 \text{ kg} + 41.67 \text{ kg})\left(9.8\frac{m}{s^2}\right) \\ &= 653.37 \text{ N}. \end{aligned}$$

Example

A 40 kg ladder is 10 m long. It leans in equilibrium against a frictionless vertical wall and makes an angle of 60° with the horizontal. Find the magnitude and direction of the force that the floor and wall exert against the ladder.



Since the wall is frictionless, the force from the wall is horizontal. The force from the floor consists of two parts: a normal component that is vertical, and a friction force that is horizontal. Setting up the force components

x component: $f - N_w = 0$

y component: $N_f - mg = 0$

Similarly, since the forces act at different locations on the ladder, there will also be a torque. Taking the torque to be positive in the counterclockwise direction around the point on the floor, the torques is

torques: $N_w l\text{sinq} - mg(l/2)\text{cosq} = 0$

where l is the length of the ladder. So we need to find N_w, N_f and f. From the y component equation, we see that

$$N_f = mg$$

while the x component yields

$$f = N_w$$

Similarly, from the torque equation, we have

$$F_1 = mg/2\text{tanq}$$

Thus,

$$F_1 = \frac{mg}{2\tan\theta}$$

$$= \frac{(40\text{ kg})\left(9.8\frac{m}{s^2}\right)}{2\tan(60°)}$$

$$= 113.2\text{N}$$

$$f = 113.2\text{ N}$$

$$\text{N} = \text{mg}$$

$$= (40\text{ kg})\left(9.8\frac{m}{s^2}\right)$$

$$= 392\text{ N.}$$

So, the total force from the floor is

$$\text{F} = \sqrt{N_f^2 + f^2}$$

$$= \sqrt{(392\,N)^2 + (113.2N)^2}$$

$$= 408\text{ N}$$

$$Q = \tan^{-1}\left(\frac{N_f}{f}\right)$$

$$= \tan^{-1}\frac{(392N)}{(113.2N)}$$

$$= 73.9°$$

Chemical Equilibrium

Chemical equilibrium, state of balance in which two opposing reversible chemical reactions proceed at constant equal rates with no net change in the system.

For example:

When hydrogen gas, H_2, and iodine gas, I_2, are mixed, and gaseous hydrogen iodide, HI, is formed according to the equation $H_2 + I_2 \rightarrow 2HI$, no matter how long the reaction is allowed to proceed some quantity of hydrogen and iodine will remain unreacted. The reason reactants in a reversible reaction are never completely converted to product is that an opposing reaction is taking place simultaneously, *i.e.*, some of the newly formed HI is being converted back into hydrogen and iodine.

For any particular temperature, a point of equilibrium is reached at which the rates of the two opposing reactions are equal and there is no further change in the system. This equilibrium point is characterized by specific relative concentrations of reactants and products and will also be reached from the opposite direction, *i.e.*, if one starts with hydrogen iodide and allows it to decompose into hydrogen and iodine. The equilibrium point can be described by the mass action expression, which defines the equilibrium constant, K_{eq}, in terms of the ratio of the molar concentrations of the products to those of the reactants.

For the reversible reaction used as an example, the equilibrium constant is

$$K_{eq} \quad =[HI]^2/[H_2][I_2]$$

for the general reversible reaction $nA + mB + \cdot \cdot \cdot\ pC + qD + \cdot \cdot \cdot$, the equilibrium constant is: where [A], [B], [C], [D], ... are the molar concentrations of the substances and *n, m, p, q, ...* are the coefficients of the balanced chemical equation. The larger the equilibrium constant for a given reaction, the more the reaction is favoured, since a larger value of K_{eq} means larger concentrations of the products relative to the reactants. The equilibrium constant is related to the change in the standard free energy, $G°$, of the system by the equation

$\Delta G^\circ = -RT. \ln K_{eq}$, where R is a constant, T is the temperature in degrees Kelvin, and $\ln K_{eq}$ is the natural logarithm of the equilibrium constant.

Chemical equilibrium can be defined for many types of chemical processes, such as dissociation of a weak acid in solution, solubility of slightly soluble salts, and oxidation-reduction reactions. In all of these cases, the equilibrium constant or its analogue is defined for certain conditions of temperature and other factors. If any of these factors change, the system will respond to establish a new equilibrium, in accordance with Le Chbtelier's principle.

Chemical equilibrium applies to reactions that can occur in both directions. In a reaction such as:

$CH_4(g) + H_2O(g) <\!\!\longrightarrow CO(g) + 3H_2(g)$

The reaction can happen both ways. So after some of the products are created the products begin to react to form the reactants. At the beginning of the reaction, the rate that the reactants are changing into the products is higher than the rate that the products are changing into the reactants. Therefore, the net change is a higher number of products.

Even though the reactants are constantly forming products and *vice-versa* the amount of reactants and products does become steady. When the net change of the products and reactants is zero the reaction has reached equilibrium. The equilibrium is a dynamic equilibrium. The definition for a dynamic equilibrium is when the amount of products and reactants are constant.

Chemical Equilibrium—A General Concept

The results of experiments on many different reactions over many years allow us to generalize as follows. For the generic reaction, in which the participating species are gases, the partial pressures at equilibrium obey the simple expression, independent of the initial pressures of the gases.

$$aA + bB \rightarrow dD + fF$$

$$K_{eq} = P_D{}^d P_F{}^f / P_A{}^a P_B{}^b$$

In words, the equation says that if we divide the product of the pressures of the products, each raised to the power of its stoichiometric coefficient in the equation for the reaction, by a similar product of reactant pressures, the result is a constant, K_{eq}, that depends only on temperature.

Every chemical reaction, simple or complex, obeys an equilibrium constant expression of the form of equation above.

This is a very simple result that makes possible calculations involving the direction and extent of reaction. If the value of K_{eq} for a reaction is large, the pressures of products will be large relative to those of reactants at equilibrium — the equilibrium lies to the right.

If K_{eq} is small, pressures of products will be small relative to those of reactants at equilibrium — the equilibrium lies to the left.Our conclusions are not restricted to gas phase reactions. An expression analogous to equation applies to reactions in solution, except that molarities must be used in place of pressures.

In fact, when we recognize that gas pressure is proportional to n/V (molarity) through the ideal gas law, we realise the equivalence of expressions in terms of pressure and molar concentration. Equation therefore applies to all reactions, in the gas phase, in solution, or in some combination:

$$K_{\mathrm{eq}} = [\Delta]^{\Delta}[F]^{f}/[A]^{a}[B]^{b}$$

The brackets signify molarity. One caution is in order for gas phase reactions. The numerical value and the units of the equilibrium constant depend on whether pressures or molarities are used. If K_{eq} is specified in units of bar, pressures are used in calculations; if in moles/L, concentrations are used. If K_{eq} has no units, either pressure or molarity may be used.

Rules for Writing Equilibrium Constant Expressions

It is important to become facile in writing and using equilibrium constant expressions for reactions. Several guidelines will help in this regard.

Conventions for expressing reagent concentrations:

- Partial pressure in bar is used for gaseous reagents;
- Molarity is used for a reagent dissolved in a solvent;
- Concentrations for pure liquids and solids are not written explicitly in K_{eq} expressions. The concentration of a pure liquid or solid is its density, which at a given temperature is constant for a condensed phase. It is usually included in the equilibrium constant rather than being explicitly written.

Example: Write the equilibrium constant expression for the reaction

$$N_2(g) + 3H_2(g) \rightarrow 2NH_3(g)$$

Solution: All species are gases, so we use their partial pressures:

$$K_{eq} = P_{NH3}{}^2/P_{H2}{}^3P_{N2}$$

Example: Write the equilibrium constant expression for the reaction

$$Fe(s) + 2Fe^{3+}(aq) \rightarrow 3Fe^{2+}(aq)$$

Solution: Only a pure solid and dissolved species are involved. We leave the pure solid out and use molarity for the ions:

$$K_{eq} = [Fe^{2+}]^3/[Fe^{3+}]^2$$

Example: The reaction of hydrogen and oxygen to form water may be written in many equivalent ways, two of which are

$H_2(g) + 1/2\ O_2(g) \rightarrow H_2O(g)\ K_1 = P_{H2O}/P_{H2}P_{O2}{}^{1/2}$

$2H_2(g) + O_2(g) \rightarrow 2H_2O(g)\ K_2 = P_{H2O}{}^2/P_{H2}{}^2\ P_{O2}$

How are K_1 and K_2 related?

Solution: Reaction (*b*) is clearly twice reaction (*a*). We see that K_2 is $K_1{}^2$. Generally,

If reaction (2) = *n* reaction (1), then $K_2 = K_1{}^n$

Reversing a reaction. If a reaction is reversed (turned around), its equilibrium constant is reciprocated (inverted).

Example: Write the equilibrium constant expression for the "reaction"

$$H_2O(l) \rightarrow H_2O(g)$$

Solution: Although this is not a chemical reaction, since no new substances are produced, we can treat it by the same rules. In writing the equilibrium constant expression, we leave out the pure liquid and use the partial pressure of the water vapour:

$$K_{eq} = P_{H2O(v)} = P_{vap}$$

Thus the equilibrium vapour pressure of a pure liquid (or solid) is a special case of an equilibrium constant.

Multiplication of a reaction by a constant: If all of the stoichiometric coefficients of an equation are multiplied by the same constant, the new equilibrium constant expression is obtained by raising the old one to a power equal to the constant. This is better appreciated by example.

Example: The reaction of nitrogen and hydrogen to form ammonia may be written in either direction:

$$(1)\ N_2 + 3H_2 \rightarrow 2NH_3\ K_1 = P_{NH3}{}^2/P_{N2}P_{H2}{}^3$$
$$(2)\ 2NH_3 \rightarrow N_2 + 3H_2\ K_2 = P_{N2}P_{H2}{}^3/P_{NH3}{}^2$$

How are the two K_{eq}'s related?

Solution: Reaction (*b*) is the negative of reaction (*a*): (*b*) = –(*a*). At the same time, $K_2 = 1/K_1$. This is a special case of equation.

Combining reactions by addition or subtraction: We use Hess's Law to obtain a desired reaction by adding (subtracting) two or more other reactions. How is K_{eq} for the sum related to the K_{eq}'s of the combined reactions? Again, example illustrates this clearly.

Example: The third reaction below can be obtained by adding the first two reactions.

(1) $C(s) + 1/2\ O_2(g) \rightarrow CO(g)$

$K_1 = P_{CO}/P_{O2}{}^{1/2}$

(2) $CO(g) + 1/2\ O_2(g) \rightarrow CO_2(g)$

$K_2 = P_{CO2}/P_{CO}P_{O2}{}^{1/2}$

(3) = (1) + (2) $C(s) + O_2(g) \rightarrow CO_2(g)$

$K_3 = P_{CO2}/P_{O2}$

How is K_3 related to K_1 and K_2?

Solution: Inspection of the equilibrium constant expressions shows that K_3 is the product of K_1 and K_2. Generalizing, when two reactions are added to give a third, their K_{eq}'s must be multiplied to obtain K_{eq} for the third:

$$(3) = (1) + (2)\ K_3 = K_1K_2$$

Units of equilibrium constants: These are easily obtained from the equilibrium constant expression and the units of concentration used in the expression.

Example: What are the units of the K_{eq} expression for the reaction

$$2H_2(g) + O_2(g) \rightarrow 2H_2O(g)$$

$$K_{eq} = P_{H2O}{}^2/P_{H2}{}^2P_{O2}$$

Solution: For pressures in atm, the units of the numerator of K_{eq} are atm^2, while those of the denominator are atm^3. The overall units are thus atm^{-1}.

Example: What are the units of K_{eq} for the reaction

$$H_2(g) + I_2(g) \rightarrow 2HI(g) \; K_{eq} = P_{HI}{}^2/P_{H2}P_{I2}$$

Solution: Units of both the numerator and denominator are bar^2, so K_{eq} is dimensionless. In general, K_{eq} is dimensionless when the total moles of gas (or dissolved species) is the same in reactants and products. Unless K_{eq} is dimensionless, we must use concentration units consistent with the specified units of K_{eq}.

4

Liquid-Vapour Equilibrium

The concept of vapour pressure by means of a thought experiment. Our observation following injection of water into the box was that the pressure rose gradually from zero to 23.8 torr at a temperature of 25°C, where it levelled off and remained constant indefinitely.

The pressure resulted from formation of water vapour by evaporation of some of the liquid water. We address two interesting questions: 1) Why does evaporation occur? 2) Why does the pressure rise to 23.8 torr, then stop changing? We take first a macroscopic, then a molecular, view. Consider the process in equation:

$$H_2O(l) \rightarrow H_2O(g)$$

$$\Delta PE > 0 \text{ favors liquid}$$

$$\Delta S > 0 \text{ favors gas}$$

The drive to minimum energy favors the liquid phase. However, the drive to increased disorder favors the gas phase.

Two natural tendencies try to drive the process in equation in opposite directions. The result is a compromise in which some water is present as liquid and some as vapour. This is our macroscopic interpretation of the vapour pressure phenomenon. We now seek an understanding at the molecular level.

An important result from our models of the gas, liquid, and solid phases can be stated succinctly as follows: at a given temperature, all molecules have the same average kinetic energy, whether they are present in the solid, liquid, or gas phase. Further, the distribution of kinetic energies follows the Maxwell-Boltzmann distribution, regardless of phase. The general form of the Maxwell-Boltzmann distribution is reproduced. In the ensuing discussion, we will apply this plot to the liquid phase of a pure substance.

As the curve indicates, at any moment there are some molecules moving very slowly, a large number moving with intermediate (near-average) kinetic energies, and a few molecules with very high kinetic energy. We focus now on the molecules near the surface of the liquid, because it is these that have a chance to escape from the liquid into the space above. Molecules near the surface possess a range of kinetic energies, like those in the bulk.

A molecule near the surface and moving toward the surface will escape the liquid if its kinetic energy is sufficient to overcome the attractive forces of nearby molecules in the liquid. In other words, the kinetic energy must be at least equal in magnitude to the depth of the liquid potential well. We will call this minimum required kinetic energy the escape kinetic energy. The number of liquid molecules having at least this kinetic energy is proportional to the area under the curve to the right of a vertical line passing through the escape *KE*.

When liquid water is injected into an evacuated box, it spreads out on the bottom and molecules begin to evaporate at a rate depending on two quantities. First, the number of molecules that evaporate per unit time is proportional to the number having at least the escape kinetic energy.

Second, the evaporation rate is proportional to the number of molecules at the surface — i.e., to the exposed liquid surface area. In equation form,

$R_E = k_E(T)*A$

R_E = evaporation rate, with units of amount per time

A = liquid surface area

$k_E(T)$ = rate constant for evaporation, with units of amount per unit area per unit time.

(The constant, k_E, is called a rate constant. It is a proportionality constant relating the evaporation rate to macroscopic variables on which rate depends. In this case, surface area is the only variable of importance, as long as temperature is constant. The size of the rate constant depends upon the fraction of molecules with *KE* greater than the escape KE. Because this depends on temperature, k_E is temperature-dependent.

This is indicated in the equation.) Evaporation leads to a buildup of molecules in the vapour phase over time. These exert pressure on the container walls, which increases directly as the number of molecules. Further, they collide occasionally with the liquid surface, where they may once again be captured by the intermolecular forces of the closely packed molecules at the liquid surface — in other words, they condense. The rate of condensation is proportional to the exposed surface area of liquid and to the number of molecules in the vapour phase. This number is directly proportional to the pressure exerted by the vapour. The rate of condensation, in equation form, is

$R_C = k_C{*}A{*}P$

R_C = condensation rate, with units of amount per time

k_C = rate constant for condensation, a proportionality constant that is independent of *T*, with units amount per time per area per unit pressure.

As the number of molecules in the vapour phase continues to increase as a result of a steady rate of evaporation, a point is eventually reached at which

$$R_E = R_C$$

Although both evaporation and condensation still occur, they occur at equal rates. There will be no further change in the number of molecules in the vapour phase, hence no further change in pressure. We describe this situation as a state of phase equilibrium. Attainment of phase equilibrium is shown graphically in Figure.

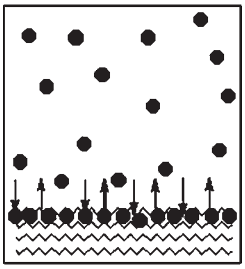


Fig. Phase Equilibrium

Equal rates of evaporation and condensation: equilibrium: Equation is used to represent the equilibrium between liquid and gas phases:

$$l \Leftrightarrow v$$

The double arrow indicates that the two processes, evaporation and condensation, occur simultaneously and at equal rates. Phase equilibrium is dynamic, rather than static, because although it appears at the macroscopic level that nothing is happening (vapour pressure is constant), there is a lot of action at the molecular level.

This can be easily substantiated by starting with a system consisting of H_2O in the liquid phase and D_2O (deuterium oxide) in the vapour phase.

After some time has elapsed, both forms of water will be found (by, for example, mass spectrometry) in both phases, indicating that evaporation and condensation are continuously occurring.

The pressure exerted by the vapour at equilibrium is called the equilibrium vapour pressure of the liquid, symbolized P_{vap}. Equations can be used to obtain an expression for P_{vap} in terms of the constants, k_E and k_C.

Since at equilibrium, R_E and R_C are equal, we write

$$k_E(T)A = k_C A P_{\text{vap}}$$

Solving for P_{vap} and cancelling the surface area terms in numerator and denominator gives equation.

$$P_{\text{vap}} = k_E(T)/k_C$$

This equation shows that for a particular liquid at a fixed temperature, P_{vap} is constant, in agreement with experiment.

The vapour pressure of a pure liquid provides the first example of an equilibrium constant, denoted K_{eq}. For a liquid in equilibrium with vapour, $P_{\text{vap}} = K_{\text{eq}}$. K_{eq} is a ratio of rate constants.

Each liquid has a characteristic vapour pressure at a given T whose value depends primarily on k_E. The greater the intermolecular forces, the greater the escape KE, and the smaller the value of k_E. Small k_E means smaller P_{vap}.

Since the constant k_C does not depend on the potential well depth, it is almost the same for all liquids. Equilibrium vapour pressures for several common laboratory liquids at 25°C are given in Table.

Table. Equilibrium P_{vap} at 25°C

Substance	***P_{vap} (torr)***
water (H_2O)	24
ethanol (H_2O)	65
chloroform (H_2O)	215
diethylether (H_2O)	545

Example: A sample of liquid of molecular weight 46.0 g/mole and density 1.04 g/mL is injected into a 150-mL closed container and spreads out to provide a surface area of 25 cm^2.

Over a period of 1.0 minute, the pressure due to vapour rises to an equilibrium value of 45 torr at 297 K. Calculate the average net rate of evaporation of liquid in moles/s, molecules/s, and mL/s.

Solution: Use the ideal gas law to calculate the moles of gas present in the gas phase at the end of the 1 minute period:

$n = PV/RT = (45/760 \text{ atm})(0.150 \text{ L})/(0.08206 \text{ L-atm/K-mole})(297 \text{ K}) = 3.64 \times 10^{-4}$ moles

This corresponds to $nN_0 = 2.20 \times 10^{20}$ molecules.

The volume of liquid converted to vapour is calculated by multiplying the moles of liquid by the molar mass, then dividing by density to convert to mL:

V of liquid $= n(MM)/\rho$ mL

$= (3.64 \times 10^{-4})$

$(46.0 \text{ g/mole})/(1.04 \text{ g/mL})$

$= 0.0161$ mL

The average evaporation rates in moles/s, molecules/s, and mL/s can now be calculated by dividing the amount evaporated by the total time required, which is 60 s:

Evaporation rate

$= 3.64 \times 10^{-4}$ moles/60 s $= 6.10 \times 10^{-6}$ moles/s

$= 2.20 \times 10^{20}$ molecules/60 s $= 3.67 \times 10^{18}$ molecules/s

$= 0.0161$ mL/60 s $= 2.68 \times 10^{-4}$ mL/s

The Temperature Dependence of Vapour Pressure

When the temperature of a liquid-vapour equilibrium system is increased, the equilibrium vapour pressure increases. There are two reasons for this.

- The pressure due to the molecules already in the gas phase increases by the ideal gas law. This makes a small contribution to the vapour pressure increase.
- More molecules enter the gas phase. This is by far the larger contribution.

We now attempt to justify these statements at the molecular level. An increase in temperature means that the kinetic energy of the molecules increases in both phases. Molecules at the liquid surface jiggle more vigorously, and a greater number of them have sufficient *KE* to escape the potential well of the liquid and enter the vapour phase. The increase in the number of molecules in the vapour phase results in an increased vapour pressure. The effect of increased temperature on the Maxwell-Boltzmann kinetic energy distribution. As the curve shifts right with increasing T, the area under the curve to the right of the escape KE increases exponentially. P_{vap} therefore increases exponentially with T. Mathematically, the T-dependence of P_{vap} can be understood in terms of equation. The minimum KE requirement for escape from the liquid is imbedded in the constant k_E, which depends markedly on T. k_C has almost no temperature dependence because no minimum KE is required for a molecule to fall into a potential well. The temperature dependence of P_{vap} therefore parallels that of k_E, which directly reflects the shift in the Maxwell-Boltzmann distribution.

It can be shown, both experimentally and theoretically, that vapour pressure varies with temperature according to equation:

$$P_{\text{vap}} = e^{-\Delta H^\circ/RT} e^{\Delta S^\circ/R}$$

This is usually written in logarithmic form as the Clausius-Clapeyron equation, equation:

$$\ln P_{\text{vap}} = -\Delta H^\circ_{\text{vap}}/RT + \Delta S^\circ_{\text{vap}}/R$$

$\Delta H^\circ_{\text{vap}}$ and $\Delta S^\circ_{\text{vap}}$ are the standard molar enthalpy and entropy of vaporization, respectively. Equation suggests that a plot of ln P_{vap} vs. $1/T$ should yield the enthalpy of vaporization, $\Delta H^\circ_{\text{vap}}$, from the slope, and the entropy of vaporization, $\Delta S^\circ_{\text{vap}}$, from the intercept. This is a convenient experimental approach to the measurement of these quantities. The form of the Clausius-Clapeyron equation is general in physical science; all molecular processes exhibit temperature dependence of this form.

The vapour pressure is plotted against temperature for several common laboratory liquids. The magnitude of P_{vap}

for a liquid at a particular temperature and the rate of change of P_{vap} with temperature depend on the magnitude of the intermolecular forces in the liquid phase. The stronger the forces, the lower P_{vap} at a given T and the steeper the rise in the curve, water clearly has the largest intermolecular forces, due to strong hydrogen bonding.

Having seen how P_{vap} depends on T, we consider a problem involving conceptual aspects of *l-v* phase equilibrium.

Example: In the system, the liquid and vapour of a pure substance are in equilibrium at some temperature, in a cylinder fitted with a moveable piston. Under these conditions, rates of evaporation and condensation are equal. We carry out two sequential processes that perturb the equilibrium and examine how the system reattains equilibrium.

At time t_1, T is instantly increased. The system returns to equilibrium while the piston is held at position A throughout. What effect will the T increase have on the equilibrium? Increasing T will cause R_E to immediately increase (the Maxwell-Boltzmann distribution). However, because k_C is independent of temperature, R_C will be unaffected by the increase of T. Therefore, immediately following the T increase, R_E will exceed R_C; the system is no longer at equilibrium.

There will be a net flow of molecules from liquid to vapour. As the number of molecules in the vapour phase increases, the vapour pressure increases, causing R_C to increase, until R_E and R_C are once again equal. The system eventually reaches a new equilibrium, with a higher P_{vap}. It is important to realise that it takes time for the population of molecules in the gas phase to build up. Thus R_C adjusts much more slowly to the T change than does R_E. At time t_2, the piston is instantly pulled up to position B. The system returns to equilibrium. T is constant throughout.

Moving the piston has no effect on the rate of evaporation, which depends only on temperature. However, the increase in volume of the vapour space causes an instantaneous decrease in the vapour pressure and R_C. There is again an imbalance of rates that results in a net flow of molecules from liquid to vapour. As the number of molecules in the vapour builds up, R_C increases correspondingly. This change is gradual, but eventually R_C again becomes equal to R_E. Equilibrium is reestablished with the original values of R_E and R_C, but with a larger amount of vapour.

Note that the liquid (R_E) is unaffected by movement of the piston and adjusts instantly to a temperature change; the vapour (R_C) is affected by both processes, and is slow to adjust after they are carried out. The shape of the P_{vap}-time curve during adjustment is a typical kinetics curve, or dynamics curve. The slope of the curve is steep at first, far from equilibrium, and gradually decreases as the P_{vap} tapers smoothly and continuously to its equilibrium value.

Boiling — The Boiling Point

The boiling point of a liquid is the temperature at which the vapour pressure of the liquid is equal to the pressure above the liquid. The normal boiling point is the temperature at which the vapour pressure is 1 atm, the “normal” value of pressure above a liquid when it stands open to the atmosphere.

When a liquid boils, pockets of vapour form in the liquid and rise to its surface, where the vapour escapes to the atmosphere. The bubbles are not bubbles of air — they are pockets of the gaseous form of the substance. At temperatures where the vapour pressure of liquid is less than the pressure above the liquid, pockets cannot form because they are immediately collapsed by the greater outside pressure. Only when the vapour pressure becomes equal to the outside pressure do the pockets become self-supporting. Under these conditions, boiling can occur.

The temperature at which a liquid boils can be lowered by reducing the pressure above it. Under these conditions the pockets become self-supporting at a lower value of P_{vap}, hence at a lower temperature. A plot of P_{vap} versus T such as those in Figure shows how the boiling point changes with external pressure.

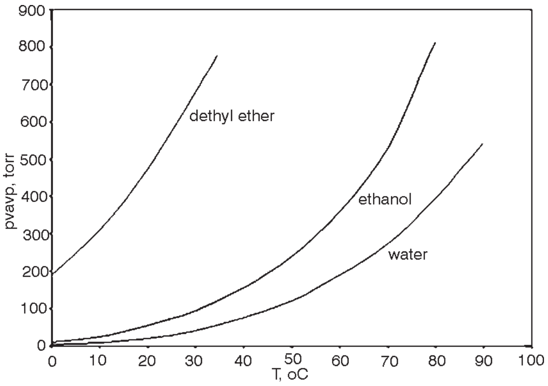


Fig. Vapour Pressure Versus Temperature

A practical manifestation of this phenomenon is the longer cooking time required at high altitude, where atmospheric pressure is substantially less than 1 atm. The boiling point of water is less than 100°C, so food takes longer to cook than at lower altitude. If you wanted to boil water at room temperature (25°C), to what value would you have to lower the pressure above it?

A thought experiment in which a liquid is boiled under controlled conditions will illustrate the volume-temperature characteristics of the process. We begin with a sample of a pure liquid in a cylinder fitted with a piston, at an initial temperature T_i which is below the normal boiling point, T_b, of the liquid. The outside pressure on the piston is 1 atm. This situation is pictured in Figure.

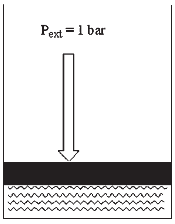


Fig. Liquid in Cylinder/Piston

At T_i, P_{vap} of the liquid is less than 1 atm so vapour cannot exist in the cylinder. We justify this statement as follows. Suppose there were some vapour above the liquid in the cylinder. It would exert a pressure P_{vap} on the piston. Because $P_{\text{vap}} < 1$ atm, the piston would begin to move in. In response, vapour would condense to maintain the equilibrium value of P_{vap}. This would cause the piston to move further in. This process of vapour condensation and inward movement of the piston would continue until there was no vapour left. Thus in the beginning, there can be no vapour present.

We now slowly heat the liquid to its normal boiling point, and boil it. As long as $T < T_b$, $P_{\text{vap}} < 1$ atm and the piston will not move. But at the T where P_{vap} becomes equal to 1 atm, vapour begins to form in the cylinder, and the piston begins to recede. More and more liquid evaporates in order to maintain P_{vap} at 1 atm until all of the liquid disappears.

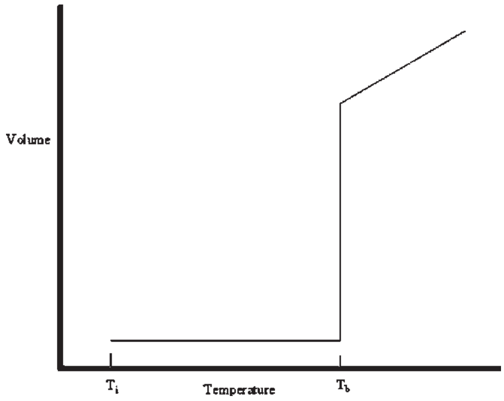


Fig. Volume Change During Heating and Boiling

At this point only vapour will be present in the cylinder. Finally, we continue heating the vapour. The volume of vapour increases with T according to the ideal gas law. A plot of the volume of the system as a function of T for the boiling process is shown in above figure. Several features of the plot are important:

- At $T > T_i$ but $< T_b$, the system volume remains essentially constant and small, because in this T range no vapour exists in the system, and the volume of the liquid does not vary much with T.
- Once T reaches T_b, the liquid begins to boil. Throughout the boiling process, T remains constant because all added heat is used to overcome the intermolecular forces in the liquid, increasing the *PE* of the molecules, and to push back the atmosphere. The *KE* of the molecules does not change.
- When all liquid has evaporated, added heat is used to increase the *KE* of the vapour molecules. T and V increase in a manner consistent with the ideal gas law.

5

Thermodynamics in Rotational Dynamics

The physical objects that we encounter in the world consist of collections of atoms that are bound together to form systems of particles. When forces are applied, the shape of the body may be stretched or compressed like a spring, or sheared like jello. In some systems the constituent particles are very loosely bound to each other as in fluids and gasses, and the distances between the constituent particles will vary. We shall begin our study of extended objects by restricting ourselves to an ideal category of objects, rigid bodies, which do not stretch, compress, or shear.

A body is called a rigid body if the distance between any two points in the body does not change in time. Rigid bodies, unlike point masses, can have forces applied at different points in the body. For most objects, treating as a rigid body is an idealization, but a very good one. In addition to forces applied at points, forces may be distributed over the entire body. Distributed forces are difficult to analyze; however, for example, we regularly experience the effect of the gravitational force on bodies. Based on our experience observing the effect of the gravitational force on rigid bodies, we note that the gravitational force can be concentrated at a point in the rigid body called the center of gravity, which for small bodies (so that $\vec{g}$ may be taken as constant within the body) is identical to the center of mass of the body.

Let's consider a rigid rod thrown in the air so that the rod is spinning as its center of mass moves with velocity $\vec{v}_{\mathrm{cm}}$. Rigid bodies, unlike point-like objects, can have forces applied at different points in the body. We have explored the physics of translational motion; now, we wish to investigate the properties of rotation exhibited in the rod's motion, beginning with the notion that every particle is rotating about the center of mass with the same angular (rotational) velocity.

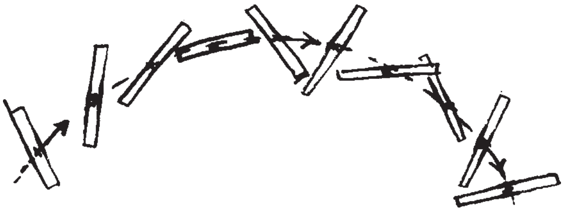


Fig. The Center of Mass of a thrown Rigid Rod follows a Parabolic Trajectory while the Rod Rotates about the Center of Mass.

We can use Newton's Second Law to predict how the center of mass will move. Since the only external force on the rod is the gravitational force (neglecting the action of air resistance), the center of mass of the body will move in a parabolic trajectory.

How was the rod induced to rotate? In order to spin the rod, we applied a torque with our fingers and wrist to one end of the rod as the rod was released. The applied torque is proportional to the angular acceleration. The constant of proportionality is called the moment of inertia. When external forces and torques are present, the motion of a rigid body can be extremely complicated while it is translating and rotating in space. We shall begin our study of rotating objects by considering the simplest example of rigid body motion, rotation about a fixed axis.

Fixed Axis Rotation: Rotational Kinematics

Fixed Axis Rotation

Static equilibrium, we demonstrated the need for two conditions: The total force acting on an object is zero, as is the total torque acting on the object. If the total torque is non-zero, then the object will start to rotate.

A simple example of rotation about a fixed axis is the motion of a compact disc in a CD player, which is driven by a motor inside the player. In a simplified model of this motion, the motor produces angular acceleration, causing the disc to spin. As the disc is set in motion, resistive forces oppose the motion until the disc no longer has any angular acceleration, and the disc now spins at a constant angular velocity. Throughout this process, the CD rotates about an axis passing through the center of the disc, and is perpendicular to the plane of the disc. This type of motion is called fixed-axis rotation.

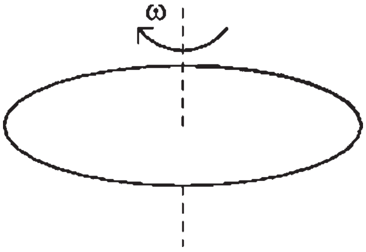


Fig. Rotation of a Compact Disc about a Fixed Axis.

When we ride a bicycle forward, the wheels rotate about an axis passing through the center of each wheel and perpendicular to the plane of the wheel. As long as the bicycle does not turn, this axis keeps pointing in the same direction. This motion is more complicated than our spinning CD because the wheel is both moving (translating) with some center of mass velocity, $\vec{v}_{cm}$, and rotating.

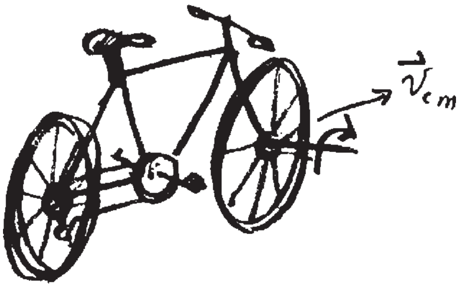


Fig. Fixed Axis Rotation and Center of Mass Translation for a Bicycle Wheel.

When we turn the bicycle's handlebars, we change the bike's trajectory and the axis of rotation of each wheel changes direction. Other examples of non-fixed axis rotation are the motion of a spinning top, or a gyroscope, or even the change in the direction of the earth's rotation axis.

This type of motion is much harder to analyze. Angular Velocity and Angular Acceleration. When we considered the rotational motion of a point-like object an angle coordinate è, and then defined the angular velocity as

$$\omega \equiv \frac{d\theta}{dt},$$

and angular acceleration (Equation 6.3.4) as

$$\alpha \equiv \frac{d^2\theta}{dt^2}.$$

For a rigid body undergoing fixed-axis rotation, we can divide the body up into small volume elements with mass Δm_i. Each of these volume elements is moving in a circle of radius r_1, i, about the axis of rotation

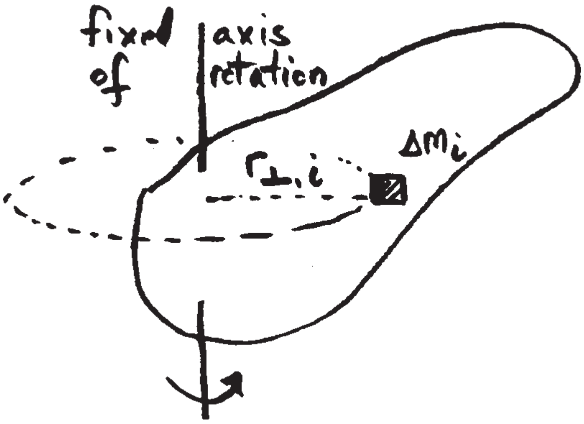


Fig. Coordinate System for Fixed-axis Rotation.

We will adopt the notation implied and denote the vector from the axis to the point where the mass element is located as $\vec{r}_{\perp i}$ with $\vec{r}_{\perp i} = |\vec{r}_{\perp i}|$,

Because the body is rigid, all the volume elements will have the same angular velocity ù and hence the same angular acceleration á. If the bodies did not have the same angular velocity, the volume elements would "catch up to" or "pass" each other, precluded by the rigid-body assumption.

Angular Velocity and Angular Acceleration

Suppose we choose Δ to be increasing in the counterclockwise direction as

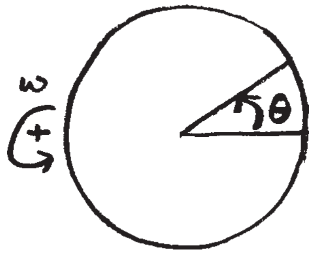


Fig. Sign Conventions for Rotational Motion.

If the rigid body rotates in the counterclockwise direction, then the angular velocity is positive, If the rigid body rotates in the clockwise direction, then the angular velocity is negative,

- If the rigid body increases its rate of rotation in the counterclockwise (positive) direction then the angular acceleration is positive, $\alpha \equiv {}^{\circ}d^2\theta/dt^2 = d\omega/dt > 0$.
- If the rigid body decreases its rate of rotation in the counterclockwise (positive) direction then the angular acceleration is negative, $\alpha \equiv {}^{\circ}d^2\theta/dt^2 = d\omega/dt > 0$.
- If the rigid body increases its rate of rotation in the clockwise (negative) direction then the angular acceleration is negative, $\alpha \equiv {}^{\circ}d^2\theta/dt^2 = d\omega/dt > 0$.
- If the rigid body decreases its rate of rotation in the clockwise (negative) direction then the angular acceleration is positive,

To phrase this more generally, if á and ù have the same sign, the body is speeding up; if opposite signs, the body is slowing down. This general result is independent of the choice of positive direction of rotation.

Tangential Velocity and Tangential Acceleration

Since the small volume Δm_i element of mass is moving in a circle of radius $r_{\perp i} = |\vec{r}_{\perp i}|$ with angular velocity ù, the element has a tangential velocity component

$$v_{\tan,i} = r_{\perp,i}\omega.$$

If the magnitude of the tangential velocity is changing, the volume element undergoes a tangential acceleration given by

$$a_{\tan,i} = r_{\perp,i}\alpha.$$

that the volume element is always accelerating inward with magnitude

$$|a_{\tan,i}| = \frac{v_{\tan,i}^2}{r_{\perp,i}} = r_{\perp,i}\ \omega^2.$$

Torque

A torque (τ) in physics, also called a moment (of force), is a pseudo-vector that measures the tendency of a force to rotate an object about some axis (center). The magnitude of a torque is defined as the product of a force and the length of the lever arm (radius). Just as a force is a push or a pull, a torque can be thought of as a twist.

The SI unit for torque is the newton meter (N m). In U.S. customary units, it is measured in foot pounds (ft·lbf) (also known as 'pound feet'). The symbol for torque is τ, the Greek letter tau. The concept of torque, also called moment or couple, originated with the studies of Archimedes on levers. The rotational analogues of force, mass, and acceleration are torque, moment of inertia, and angular acceleration, respectively.

Explanation

The force applied to a lever multiplied by its distance from the lever's fulcrum, the length of the lever arm, is its torque. A force of three newtons applied two meters from the fulcrum, for example, exerts the same torque as one newton applied six meters from the fulcrum.

This assumes the force is in a direction at right angles to the straight lever. The direction of the torque can be determined by using the right hand grip rule: curl the fingers of your right hand the direction of rotation and stick your thumb out so it is aligned with the axis of rotation. Your thumb points in the direction of the torque vector.

Mathematically, the torque on a particle (which has the position r in some reference frame) can be defined as the cross product:

$$\tau = r \times F$$

where

r is the particle's position vector relative to the fulcrum

F is the force acting on the particle.

The torque on a body determines the rate of change of its angular momentum,

$$\tau = \frac{dL}{dt}$$

where

L is the angular momentum vector

t stands for time.

As can be seen from either of these relationships, torque is a vector, which points along the axis of the rotation it would tend to cause.

Units

Torque has dimensions of force times distance and the SI unit of torque is the "newton meter" (N m). Even though the order of "newton" and "meter" are mathematically interchangeable, the BIPM (Bureau International des Poids et Mesures) specifies that the order should be N m not m N. N·m is also acceptable.

The joule, which is the SI unit for energy or work, is also defined as 1 N m, but this unit is not used for torque. Since energy can be thought of as the result of "force times distance", energy is always a scalar whereas torque is "force cross distance" and so is a (pseudo) vector-valued quantity. The dimensional equivalence of these units, of course, is not simply a coincidence: a torque of 1 N m applied through a full revolution will require an energy of exactly 2ð joules. Mathematically,

$$E = \tau\theta$$

where

E is the energy

τ is torque

θ is the angle moved, in radians.

Other non-SI units of torque include "pound-force-feet" or "foot-pounds-force" or "ounce-force-inches" or "meter-kilograms-force" or "kilogrammeter" (kgm).

Extended units in relation with rotation angles

As a consequence of the previous equation, if you introduce the radian (rad) as part of the dimensional units in the SI units system, the torque could be measured using "newton meters per radian" (N m/rad), or "joules per radian" (J/rad), while the energy needed and spent to perform the rotation would be measured simply in "newton meters" or "joules".

In the strict SI system, angles are not given any dimensional unit, because they do not designate physical quantities, despite the fact that they are measurable indirectly simply by dividing two distances (the arc length and the radius): one way to conciliate the two systems would be to say that arc lengths are not measures of distances (given they are not measured over a straight line, and a full circle rotation returns to the same position, i.e. a null distance).

So arc lengths should be measured in “radian meter” (rad·m), differently from straight segment lengths in “meters” (m). In such extended SI system, the perimeter of a circle whose radius is one meter, will be two pi rad·m, and not just two pi meters.

If you apply this measure to a rotating wheel in contact with a plane surface, the center of the wheel will move across a distance measured in meters with the same value, only if the contact is efficient and the wheel does not slide on it: this does not happen in practice, unless the surface of contact is constrained and is then not perfectly plane (and can resist to the horizontal linear forces applied to the irregularities of the pseudo-plane surface of movement and to the surface of the pseudo-circular rotating wheel); but then the system generates friction that loses some energy spent by the engine: this lost energy does not change the measurement of the torque or the total energy spent in the system but the effective distance that has been made by the center of the wheel.

The difference between the efficient energy spent by the engine and the energy produced in the linear movement is lost in friction and sliding, and this explains why, when applying the same non-null torque constantly to the wheel, so that the wheel moves at a constant speed according to the surface in contact, there may be no acceleration of the center of the wheel: in that case, the energy spent will be directly proportional to the distance made by the center of the wheel, and equal to the energy lost in the system by friction and sliding. For this reason, when measuring the effective power produced by a rotating engine and the energy spent in the system to generate a movement, you will often need to take into account the angle of rotation, and then, adding the radian in the unit system is necessary as well as making a difference between the measurement of arcs (in radian meter) and the measurement of straight segment distances (in meters), as a way to effectively compute the efficiency of the mobile system and the capacity of a motor engine to convert between rotational power (in radian watt) and linear power (in watts): in a friction-free ideal system, the two measurements would have equal value, but this does not happen in practice, each conversion losing energy in friction (it's easier to limit all losses of energy caused by sliding, by introducing mechanical constraints of forms on the surfaces of contacts).

Depending on works, the extended units including radians as a fundamental dimension may or may not be used.

Special cases and other facts

Moment Arm Formula

A very useful special case, often given as the definition of torque in fields other than physics, is as follows:

$$|\tau| = \text{(moment arm)} \,.\, \text{force}$$

The construction of the “moment arm” along with the vectors r and F mentioned above.

The problem with this definition is that it does not give the direction of the torque but only the magnitude, and hence it is difficult to use in three-dimensional cases.

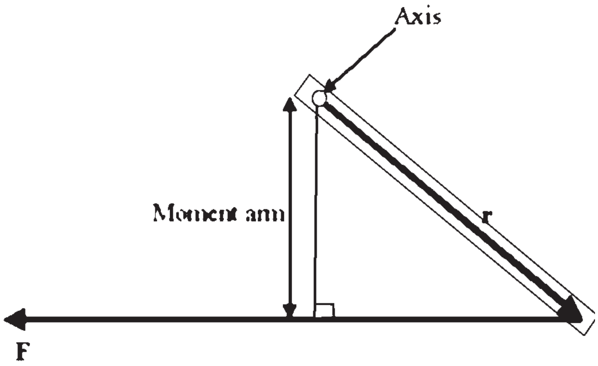


Fig. Moment Arm Diagram

If the force is perpendicular to the displacement vector r, the moment arm will be equal to the distance to the centre, and torque will be a maximum for the given force. The equation for the magnitude of a torque arising from a perpendicular force:

$$|\tau| = \text{(distance to center)} \,.\, \text{force}$$

For example, if a person places a force of 10 N on a spanner (wrench) which is 0.5 m long, the torque will be 5 N m, assuming that the person pulls the spanner by applying force perpendicular to the spanner.

Force at an Angle

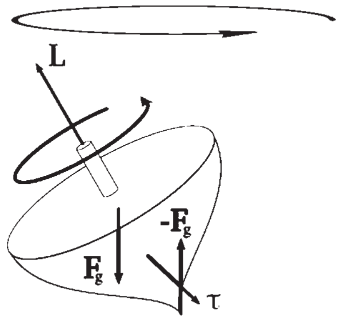
If a force of magnitude F is at an angle θ from the displacement arm of length r (and within the plane perpendicular to the rotation axis), then from the definition of cross product, the magnitude of the torque arising is:

$$\tau = rF\sin\theta$$

Static Equilibrium

For an object to be in static equilibrium, not only must the sum of the forces be zero, but also the sum of the torques (moments) about any point. For a two-dimensional situation with horizontal and vertical forces, the sum of the forces requirement is two equations: ΣH = 0 and ΣV = 0, and the torque a third equation: Στ = 0. That is, to solve statically determinate equilibrium problems in two-dimensions, we use three equations.

Torque as a Function of Time



The torque caused by the two opposing forces Fg and -Fg causes a change in the angular momentum L in the direction of that torque. This causes the top to precess. Torque is the time-derivative of angular momentum, just as force is the time derivative of linear momentum:

$$\tau = \frac{dL}{dt}$$

where

L is angular momentum.

Angular momentum on a rigid body can be written in terms of its moment of inertia I and its angular velocity ω:

$$L = I\,\omega$$

so if I is constant,

$$\tau = I \frac{d\omega}{dt} I\alpha$$

where á is angular acceleration, a quantity usually measured in radians per second squared.

Machine torque

Torque is part of the basic specification of an engine: the power output of an engine is expressed as its torque multiplied by its rotational speed of the axis. Internal-combustion engines produce useful torque only over a limited range of rotational speeds (typically from around 1,000–6,000 rpm for a small car). The varying torque output over that range can be measured with a dynamometer, and shown as a torque curve. The peak of that torque curve usually occurs somewhat below the overall power peak. The torque peak cannot, by definition, appear at higher rpm than the power peak.

Understanding the relationship between torque, power and engine speed is vital in automotive engineering, concerned as it is with transmitting power from the engine through the drive train to the wheels. Power is typically a function of torque and engine speed. The gearing of the drive train must be chosen appropriately to make the most of the motor's torque characteristics. Steam engines and electric motors tend to produce maximum torque close to zero rpm, with the torque diminishing as rotational speed rises (due to increasing friction and other constraints).

Therefore, these types of engines usually have quite different types of drivetrains from internal combustion engines.

Torque is also the easiest way to explain mechanical advantage in just about every simple machine.

Relationship between torque, power and energy

If a force is allowed to act through a distance, it is doing mechanical work. Similarly, if torque is allowed to act through a rotational distance, it is doing work. Power is the work per unit time. However, time and rotational distance are related by the angular speed where each revolution results in the circumference of the circle being travelled by the force that is generating the torque. The power injected by the applied torque may be calculated as:

$$\text{Power} = \text{torque} \;.\; \text{angular speed}$$

On the right hand side, this is a scalar product of two vectors, giving a scalar on the left hand side of the equation. Mathematically, the equation may be rearranged to compute torque for a given power output. Note that the power injected by the torque depends only on the instantaneous angular speed - not on whether the angular speed increases, decreases, or remains constant while the torque is being applied (this is equivalent to the linear case where the power injected by a force depends only on the instantaneous speed - not on the resulting acceleration, if any).

In practice, this relationship can be observed in power stations which are connected to a large electrical power grid. In such an arrangement, the generator's angular speed is fixed by the grid's frequency, and the power output of the plant is determined by the torque applied to the generator's axis of rotation. Consistent units must be used. For metric SI units power is watts, torque is newton meters and angular speed is radians per second (not rpm and not revolutions per second).

Also, the unit newton meter is dimensionally equivalent to the joule, which is the unit of energy. However, in the case of torque, the unit is assigned to a vector, whereas for energy, it is assigned to a scalar.

Conversion to other Units

For different units of power, torque, or angular speed, a conversion factor must be inserted into the equation. Also, if rotational speed (revolutions per time) is used in place of angular speed (radians per time), a conversion factor of 2ð must be added because there are 2ð radians in a revolution:

$$\text{Power} = \text{torque} \times 2\pi \times \text{rotational speed},$$

where rotational speed is in revolutions per unit time.

Useful formula in SI units:

$$\text{Power(kW)} = \frac{\text{torque (N.m)} \times 2\pi \times \text{rotational speed (rpm)}}{60000}$$

where 60,000 comes from 60 seconds per minute times 1000 watts per kilowatt.

Some people (e.g. American automotive engineers) use horsepower (imperial mechanical) for power, foot-pounds (lbf·ft) for torque and rpm (revolutions per minute) for angular speed. This results in the formula changing to:

$$\text{Power(hp)} = \frac{\text{torque (lbf.ft)} \times 2\pi \times \text{rotational speed (rpm)}}{33000}$$

The constant below in, ft·lbf./min, changes with the definition of the horsepower; for example, using metric horsepower, it becomes ~32,550.

Use of other units (e.g. BTU/h for power) would require a different custom conversion factor.

Derivation

For a rotating object, the linear distance covered at the circumference in a radian of rotation is the product of the radius with the angular speed. That is: linear speed = radius x angular speed. By definition, linear distance=linear speed x time=radius x angular speed x time.

By the definition of torque: torque=force x radius. We can rearrange this to determine force=torque/radius. These two values can be substituted into the definition of power:

$$\text{Power} = \frac{\text{force} \times \text{linear distance}}{\text{time}} = \frac{\left(\frac{\text{torque}}{\text{r}}\right) \times (r \times \text{angular speed} \times t)}{t}$$

$$= \text{torque} \times \text{angular speed}$$

The radius r and time t have dropped out of the equation. However angular speed must be in radians, by the assumed direct relationship between linear speed and angular speed at the beginning of the derivation. If the rotational speed is measured in revolutions per unit of time, the linear speed and distance are increased proportionately by 2ð in the above derivation to give:

$$\text{Power} = \text{toqrque} \times 2\pi \times \text{rotational speed}$$

If torque is in lbf·ft and rotational speed in revolutions per minute, the above equation gives power in ft·lbf/min. The horsepower form of the equation is then derived by applying the conversion factor 33,000 ft·lbf/min per horsepower:

power = torque × 2π × rotational speed.

$$\frac{\text{ft.lbf}}{\text{min}} \times \frac{\text{horse power}}{33000.\frac{\text{ft.lbf}}{\text{min}}} \approx \frac{\text{torque} \times \text{RPM}}{5252}$$

because 5252.113122... = $\frac{33,000}{2\pi}$.

Moment of inertia

Newton's second law, Force = mass x acceleration, relates the acceleration that an object of a certain mass experiences when subject to a given force. There is an analogous relation between torque and angular acceleration, which introduces the concept of moment of inertia:

Torque = moment of inertia × angular acceleration

Just as mass is a measure of how readily an object accelerates due to a given force, the moment of inertia of an object measures how easily an object rotates about a particular point of rotation.

Thus, objects with a larger moment of inertia about a given point will be harder to rotate with a set torque. Correspondingly, a larger torque will cause a larger acceleration on a particular body.

The moment of inertia of a body, which is always measured relative to a point of rotation, depends in general on the object's mass and on its shape. It is perhaps evident that for a single mass going in a circle of fixed radius, the greater the radius the harder it is to change the angular velocity.

This is because the actual displacement, and hence linear velocity of the mass is proportional to the radius, so greater radius, for a given angular displacement means greater linear displacement.

In an extended object the parts that are further from the axis of rotation contribute more to the moment of inertia than the parts closer to the axis. So as a general rule, for two objects with the same total mass, the object with more of the mass located further from the axis will have a greater moment of inertia.

For example, the moment of inertia of a solid cylinder of mass M and radius R about a line passing through its center is MR2, whereas a hollow cylinder with the same mass and radius has a moment of inertia of MR2.

Similarly when a spinning figure skater pulls her arms in to her body she places more of her body weight closer to the axis of rotation and decreases her moment of inertia.

Rotational kinetic energy

Recall that an object of a certain mass moving with particular speed will have an associated kinetic energy$\frac{1}{2}$ mass *x* speed2. An object spinning about an axis will also have associated with it a kinetic energy, composed of the kinetic energies of each individual part of the object. These individual contributions may be summed up to give an expression for the total kinetic energy of the spinning object:

Kinetic energy = $\frac{1}{2}$ moment of inertia × (angular speed)^2

As with linear motion, where a force did work on an object and led to a change in the object's kinetic energy, for rotational motion the work done by a torque:

Work = torque × angular distance

goes into changing the rotational kinetic energy of an object:

Work done = change in kinetic energy

The rotational kinetic energy is treated like any other form of energy, in that it can be transformed into other forms (eg, potential), and also it is a component of the (conserved) total energy of a system. Sometimes objects rotate about an axis that is itself in motion. For example, if you roll a cylinder down a ramp without any slipping, the axis about which it rotates (the center of the cylinder) moves down the ramp. In this case the total kinetic energy of the cylinder is the sum of its rotational kinetic energy plus its translational kinetic energy. It is therefore easy to see that an object with a higher moment of inertia will take longer to roll down the ramp. As a specific case consider a solid cylinder and a hollow cylinder with the same mass and radius starting at rest and rolling down the same ramp side by side. Which do you expect will reach the bottom first? We know that the moment of inertia of the hollow cylinder is greater, so that for a given angular velocity it has more rotational kinetic energy.

Moreover, if they both roll without slipping the linear velocity (and hence linear kinetic energy) is the same for both cylinders when their angular velocity is the same. In addition, the change in gravitational potential energy is the same for both cylinders (the weight of the cylinder times the height of the ramp), so both cylinders must have the same total kinetic energy at the bottom of the ramp.

This necessarily implies that the angular velocity (and linear velocity) of the hollow cylinder must be less at the bottom of the ramp than that of solid cylinder (otherwise it would have more kinetic energy). Consequently we can conclude that the hollow cylinder moves slower and the solid cylinder arrives at the bottom first.

Angular momentum

Recall for linear motion that we introduced the concept of (linear) momentum, mass x velocity, by equating the force exerted on an object to the change in the object's momentum. An analogous quantity called angular momentum can be introduced in the same way. For an object rotating about an axis, the angular momentum is defined as

Angular momentum = moment of inertia × angular velcity

which leads to the net torque exerted on the object being expressed as

Torque = moment of inertia × angular acceleration
= change in angular momentum

Conservation of linear momentum is a powerful tool in analyzing, for example, collisions between objects undergoing linear motion.

Similarly, conservation of angular momentum is very useful in many situations. Consider again the ice skater spinning around. If she draws her arms inwards, she decreases her moment of inertia. Conservation of angular momentum requires that the skater's moment of inertia times her angular velocity remain constant.

Thus if her moment of inertia decreases, her angular velocity must increase, and this is what we observe: when the skater pulls in her arms, she immediately starts to rotate faster.

It is also worth noting that just like linear momentum, conservation of angular momentum is associated with a symmetry of the laws of physics. In this case, the relevant symmetry has to do with rotations about any axis.

The Parallel Axis Theorem

The swingweight of a racquet is measured by the Babolat RDC using an axis of rotation 10 cm from the butt. To find the swingweight about the axis used on the stroke requires application of the Parallel Axis Theorem.

Swingweight, also known as moment of inertia and rotational inertia, is the resistance to change in the speed of the rotation about the axis of rotation. High swingweight means that the racquet is hard to get rotating, but once it gets going it will not be pushed around so much on impact with the ball and will tend to produce better pace and spin. Swingweight is the infinite sum of all infinitely small mass elements times the square of their distance from the axis of rotation. Or in mathematical terms,

$$I = \int r^2 dm$$

Call the known swingweight I and the unknown swingweight (about the axis of rotation used in the stroke) will be called I'. The swingweight of the racquet about its mass center will be called Ic.

The distance of the mass center (balance point of the racquet) from the axis of rotation for the known swingweight is r, and the racquet mass is M. The distance of the mass center from the new axis of rotation is r + x. The Parallel Axis Theorem (from first year physics) tells us that the swingweight is the sum of the swingweight about the mass center (Ic) plus the product of the mass (M) and the square of the distance (r) from the axis of rotation to the mass center.

$$I = Ic + Mr2$$

So once we know the RDC swingweight about the 10 cm axis, we can find the swingweight about any other parallel axis by another application of the Parallel Axis Theorem. The first step is finding the swingweight about an axis through the mass center (Ic).

$$I = Ic + Mr2$$

$$\Rightarrow Ic = I - Mr2$$

The same holds for the unknown swingweight, which is about a parallel axis that is a distance $r + x$ from the mass center:

$$I' = Ic + M(r + x)2$$

Now substitute what we've already found is equal to Ic:

$$I' = (I - Mr2) + M(r + x)2$$

$$= (I - Mr2) + M(r2 + 2rx + x2)$$

Simplifying, we get a general formula for finding the unknown swingweight (I') about a different axis ($r + x$):

$$I' = I + M(2rx + x2)$$

For the First Benchmark Condition (groundstroke), the axis of rotation for the stroke is at 7 cm from the handle end, so x is 3. And in the Second Benchmark Condition (serve), the axis is even farther away, and x is 5. The variable r is the published balance point minus 10 cm, but in our formulas we use r, which is the published balance point minus 7 or 5 cm according to which benchmark condition we are using, so we need to substitute in the above formula so we can use r instead of r. We will use another variable (a) to denote the axis used. So:

$$x = 10 - a$$

$$r = r + (10 - a) \Rightarrow r = r - (10 - a)$$

When we substitute in the above formula, we get:

$I' = I + M(2rx + x2) = I + M[2(r - (10 - a))(10 - a) + (10 - a)2]$

Now simplifying the expression in the brackets:

$[2(r - (10 - a))(10 - a) + (10 - a)2]$

$= -2ar + 20a - 2a2 + 20r - 200 + 20a + 100 - 20a + a2$

$= -2ar + 20a - a2 + 20r - 100$

$= 20r - 2ar - 100 + 20a - a2$

$= 2r(10 - a) - (10 - a)2$

So in the formulas, the variable I, which represents the swingweight about the axis used on the stroke, where a is the distance from the butt to the axis, I10 is the RDC swingweight about the axis 10 cm from the butt, and r is the distance in cm from the mass center (balance point) to the axis used in the stroke:

I = Ia = I10 + M*[2*(10 – a)*r – (10 – a)^2]

The simple pendulum

Consider a mass suspended from a light inextensible string of length , such that the mass is free to swing from side to side in a vertical plane. This setup is known as a simple pendulum. Let be the angle subtended between the string and the downward vertical. Obviously, the equilibrium state of the simple pendulum corresponds to the situation in which the mass is stationary and hanging vertically down (i.e.,). The angular equation of motion of the pendulum is simply

$$I\ddot{\theta} = \tau,$$

where is the moment of inertia of the mass, and is the torque acting on the system. For the case in hand, given that the mass is essentially a point particle, and is situated a distance from the axis of rotation (i.e., the pivot point), it is easily seen that $I = ml^2$.

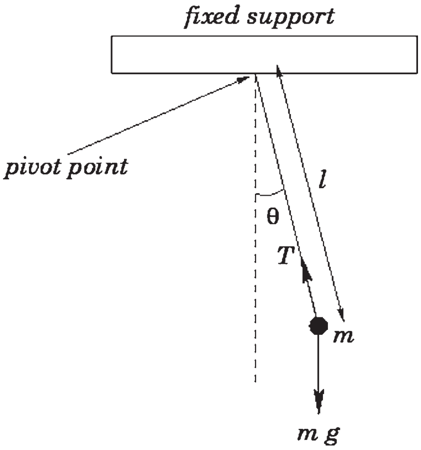


Fig. A Simple Pendulum.

The two forces acting on the mass are the downward gravitational force, mg, and the tension, T, in the string. Note, however, that the tension makes no contribution to the torque, since its line of action clearly passes through the pivot point.

From simple trigonometry, the line of action of the gravitational force passes a distance from the pivot point. Hence, the magnitude of the gravitational torque is $mg\ l \sin\theta$. Moreover, the gravitational torque is a restoring torque: i.e., if the mass is displaced slightly from its equilibrium state (i.e., $\theta = 0$) then the gravitational force clearly acts to push the mass back toward that state. Thus, we can write

$$\tau = -mgl\sin\theta.$$

Combining the previous two equations, we obtain the following angular equation of motion of the pendulum:

$$l\,\ddot{\theta} = -g\sin\theta.$$

Unfortunately, this is not the simple harmonic equation. Indeed, the above equation possesses no closed solution which can be expressed in terms of simple functions.

Suppose that we restrict our attention to relatively small deviations from the equilibrium state. In other words, suppose that the angle θ is constrained to take fairly small values. We know, from trigonometry, that for $|\theta|$ less than about 6° it is a good approximation to write

$$\sin\theta \simeq \theta.$$

Hence, in the small angle limit, Eq. reduces to

$$l\,\ddot{\theta} = -\,g\theta,$$

which is in the familiar form of a simple harmonic equation. Comparing with our original simple harmonic equation, Eq. and its solution, we conclude that the angular frequency of small amplitude oscillations of a simple pendulum is given by

$$\omega = \sqrt{\frac{g}{l}}.$$

In this case, the pendulum frequency is dependent only on the length of the pendulum and the local gravitational acceleration, and is independent of the mass of the pendulum and the amplitude of the pendulum swings (provided that $\sin\theta \simeq \theta$ remains a good approximation). Historically, the simple pendulum was the basis of virtually all accurate time-keeping devices before the advent of electronic clocks. Simple pendulums can also be used to measure local variations in$g$.

6

Ideal Monatomic Gases

Let us now practice calculating thermodynamic relations using the partition function by considering an example with which we are already quite familiar: i.e., an ideal monatomic gas. Consider a gas consisting of N identical monatomic molecules of mass m enclosed in a container of volume V. Let us denote the position and momentum vectors of the ith molecule by r_i and p_i, respectively.

Since the gas is ideal, there are no interatomic forces, and the total energy is simply the sum of the individual kinetic energies of the molecules:

$$E = \sum_{i=1}^{N} \frac{p_i^{\,2}}{2m},$$

where $p_i^2 = p_i \cdot p_i$.

Let us treat the problem classically. In this approach, we divide up phase-space into cells of equal volume $h_0^{\,f}$. Here, f is the number of degrees of freedom, and h_0 is a small constant with dimensions of angular momentum which parameterizes the precision to which the positions and momenta of molecules are determined. Each cell in phase-space corresponds to a different state. The partition function is the sum of the Boltzmann factor exp (– β E_r) over all possible states, where E_r is the energy of state τ. Classically, we can approximate the summation over cells in phase-space as an integration over all phase-space. Thus,

$$Z = \int \cdots \int \exp(-\beta\, E) \frac{d^3 r_1 \cdots d^3 r_N\; d^3 p_1 \cdots d^3{}_{PN}}{{h_0}^{3N}},$$

where $3N$ is the number of degrees of freedom of a monatomic gas containing N molecules. Making use of Eq. the above expression reduces to

$$Z = \frac{V^N}{{h_0}^{3N}} \int \cdots \int \exp[-\beta/2m)p_1{}^2]\, d^3 p_1 \cdots \exp[-(\beta/2m)p_N^2] d^3{}_{PN}.$$

Note that the integral over the coordinates of a given molecule simply yields the volume of the container, V, since the energy E is independent of the locations of the molecules in an ideal gas. There are N such integrals, so we obtain the factor V^N in the above expression. Note, also, that each of the integrals over the molecular momenta in Eq. are identical: they differ only by irrelevant dummy variables of integration. It follows that the partition function Z of the gas is made up of the product of N identical factors: i.e.,

$$Z = \zeta^N,$$

where

$$\zeta = \frac{V}{{h_0}^3} \int \exp[-(\beta/2m)p^2] d^3 p$$

is the partition function for a single molecule. Of course, this result is obvious, since we have already shown that the partition function for a system made up of a number of weakly interacting subsystems is just the product of the partition functions of the subsystems.

The integral in Eq. is easily evaluated:

$$\int \exp[-(\beta/2m)p^2]d^3p \;=\; \int_{-\infty}^{\infty}\exp[-(\beta/2m)\,{p_x}^2]dp_x$$

$$\int_{-\infty}^{\infty}\exp[-(\beta/2m)\,{p_y}^2]dp_y\;\times\int_{-\infty}^{\infty}\exp[-(\beta/2m)\,{p_z}^2]dp_z$$

$$=\left(\sqrt{\frac{2\pi m}{\beta}}\right)^3,$$

where use has been made of Eq. Thus,

$$\zeta = V\left(\frac{2\pi m}{{h_0}^2\beta}\right)^{3/2},$$

and

$$\ln Z = N\ln\zeta = N\left[\ln V-\frac{3}{2}\ln\beta+\frac{3}{2}\ln\left(\frac{2\pi m}{{h_0}^2}\right)\right].$$

The expression for the mean pressure yields

$$\bar{p}=\frac{1}{\beta}\frac{\partial \ln Z}{\partial V}=\frac{1}{\beta}\frac{N}{V},$$

which reduces to the ideal gas equation of state

$$pV = NkT = vRT,$$

where use has been made of $N = vN_A$ and $R = N_Ak$. According to Eq. the mean energy of the gas is given by

$$\bar{E}=-\frac{\partial \ln Z}{\partial\beta}=\frac{3}{2}\frac{N}{\beta}=v\frac{3}{2}RT.$$

Note that the internal energy is a function of temperature alone, with no dependence on volume.

The molar heat capacity at constant volume of the gas is given by

$$c_v=\frac{1}{v}\left(\frac{\partial\bar{E}}{\partial T}\right)_V=\frac{3}{2}R,$$

so the mean energy can be written

$$\bar{E}=v\,c_vT.$$

We have seen all of the above results before. Let us now use the partition function to calculate a new result. The entropy of the gas can be calculated quite simply from the expression

$$S = k(\ln Z + \beta \bar{E}) .$$

Thus,

$$S = vR\left[\ln V - \frac{3}{2}\ln\beta + \frac{3}{2}\ln\left(\frac{2\pi m}{h_0^{2}}\right) + \frac{3}{2}\right],$$

or

$$S = vR\left[\ln V + \frac{3}{2}\ln T + \sigma\right],$$

where

$$\sigma = \frac{3}{2}\ln\left(\frac{2\pi mk}{h_0^{2}}\right) + \frac{3}{2}.$$

The above expression for the entropy of an ideal gas is certainly new. Unfortunately, it is also quite obviously incorrect.

Gibb's paradox

What has gone wrong? First of all, let us be clear why Eq. is incorrect.

We can see that $S \to -\infty$ as $T \to 0$, which contradicts the third law of thermodynamics. However, this is not a problem. Equation was derived using classical physics, which breaks down at low temperatures. Thus, we would not expect this equation to give a sensible answer close to the absolute zero of temperature.

Equation is wrong because it implies that the entropy does not behave properly as an extensive quantity. Thermodynamic quantities can be divided into two groups, extensive and intensive. Extensive quantities increase by a factor α when the size of the system under consideration is increased by the same factor. Intensive quantities stay the same. Energy and volume are typical extensive quantities. Pressure and temperature are typical intensive quantities. Entropy is very definitely an extensive quantity. We have shown that the entropies of two weakly interacting systems are additive. Thus, if we double the size of a system we expect the entropy to double as well. Suppose that we have a system of volume *V* containing *υ* moles of ideal gas at temperature *T*. Doubling the size of the system is like joining two identical systems together to form a new system of volume 2*V* containing 2*υ* moles of gas at temperature *T*. Let

$$S = vR\left[\ln V + \frac{3}{2}\ln T + \sigma\right]$$

denote the entropy of the original system, and let

$$S' = 2vR\left[\ln 2V + \frac{3}{2}\ln T + \sigma\right]$$

denote the entropy of the double-sized system. Clearly, if entropy is an extensive quantity (which it is!) then we should have

$$S' = 2S.$$

But, in fact, we find that

$$S' - 2S = 2vR\ln 2.$$

So, the entropy of the double-sized system is more than double the entropy of the original system.

Where does this extra entropy come from? Well, let us consider a little more carefully how we might go about doubling the size of our system. Suppose that we put another identical system adjacent to it, and separate the two systems by a partition.

Let us now suddenly remove the partition. If entropy is a properly extensive quantity then the entropy of the overall system should be the same before and after the partition is removed. It is certainly the case that the energy (another extensive quantity) of the overall system stays the same. However, according to Eq. the overall entropy of the system increases by $2\upsilon R \ln 2$ after the partition is removed. Suppose, now, that the second system is identical to the first system in all respects except that its molecules are in some way slightly different to the molecules in the first system, so that the two sets of molecules are distinguishable. In this case, we would certainly expect an overall increase in entropy when the partition is removed. Before the partition is removed, it separates type 1 molecules from type 2 molecules. After the partition is removed, molecules of both types become jumbled together.

This is clearly an irreversible process. We cannot imagine the molecules spontaneously sorting themselves out again. The increase in entropy associated with this jumbling is called entropy of mixing, and is easily calculated. We know that the number of accessible states of an ideal gas varies with volume like $\Omega \propto V^N$. The volume accessible to type 1 molecules clearly doubles after the partition is removed, as does the volume accessible to type 2 molecules. Using the fundamental formula $S = k \ln \Omega$, the increase in entropy due to mixing is given by

$$S = 2k \ln \frac{\Omega_f}{\Omega_i} = 2Nk \ln \frac{V_f}{V_i} = 2\upsilon\, R \ln 2.$$

It is clear that the additional entropy $2\upsilon R \ln 2$, which appears when we double the size of an ideal gas system by joining together two identical systems, is entropy of mixing of the molecules contained in the original systems. But, if the molecules in these two systems are indistinguishable, why should there be any entropy of mixing? Well, clearly, there is no entropy of mixing in this case.

At this point, we can begin to understand what has gone wrong in our calculation. We have calculated the partition function assuming that all of the molecules in our system have the same mass and temperature, but we have never explicitly taken into account the fact that we consider the molecules to be indistinguishable.

In other words, we have been treating the molecules in our ideal gas as if each carried a little license plate, or a social security number, so that we could always tell one from another. In quantum mechanics, which is what we really should be using to study microscopic phenomena, the essential indistinguishability of atoms and molecules is hard-wired into the theory at a very low level. Our problem is that we have been taking the classical approach a little too seriously. It is plainly silly to pretend that we can distinguish molecules in a statistical problem, where we do not closely follow the motions of individual particles. A paradox arises if we try to treat molecules as if they were distinguishable. This is called Gibb's paradox, after the American physicist Josiah Gibbs who first discussed it. The resolution of Gibb's paradox is quite simple: treat all molecules of the same species as if they were indistinguishable. In our previous calculation of the ideal gas partition function, we inadvertently treated each of the *N* molecules in the gas as distinguishable.

Because of this, we overcounted the number of states of the system. Since the $N!$ possible permutations of the molecules amongst themselves do not lead to physically different situations, and, therefore, cannot be counted as separate states, the number of actual states of the system is a factor $N!$ less than what we initially thought. We can easily correct our partition function by simply dividing by this factor, so that

$$Z = \frac{\zeta^N}{N!}.$$

This gives

$$\ln Z = N \ln \zeta - N!,$$

or

$$\ln Z = N \ln \zeta - N \ln N + N,$$

using Stirling's approximation. Note that our new version of ln Z differs from our previous version by an additive term involving the number of particles in the system. This explains why our calculations of the mean pressure and mean energy, which depend on partial derivatives of ln Z with respect to the volume and the temperature parameter β, respectively, came out all right. However, our expression for the entropy S is modified by this additive term. The new expression is

$$S = vR\left[\ln V - \frac{3}{2}\ln \beta + \frac{3}{2}\ln\left(\frac{2\pi\, mk}{h_0^{\,2}}\right) + \frac{3}{2}\right] + k(-N \ln N + N).$$

This gives

$$S = vR\left[\ln \frac{V}{N} + \frac{3}{2}\ln T + \sigma_0\right]$$

where

$$\sigma_0 = \frac{3}{2}\ln\left(\frac{2\pi\, mk}{h_0^{\,2}}\right) + \frac{5}{2}.$$

It is clear that the entropy behaves properly as an extensive quantity in the above expression: i.e., it is multiplied by a factor α when v, V, and N are multiplied by the same factor.

The equipartition theorem

The internal energy of a monatomic ideal gas containing N particles. This means that each particle possess, on average, units of energy. Monatomic particles have only three translational degrees of freedom, corresponding to their motion in three dimensions. They possess no internal rotational or vibrational degrees of freedom. Thus, the mean energy per degree of freedom in a monatomic ideal gas is. In fact, this is a special case of a rather general result. Let us now try to prove this.

Suppose that the energy of a system is determined by some generalized coordinates and corresponding generalized momenta Pk, so that

$$E = E(q_1, \ldots, q_f, p_1, \ldots, p_f).$$

Suppose further that:

The total energy splits additively into the form

$$E = \in_i (p_i) + E'(q_1, \ldots, p_f),$$

where $\in_i$ involves only one variable p_i, and the remaining part E' does not depend on p_i.

The function $\in_i$ is quadratic in p_i, so that

$$\in_i (p_i) + bp_i^2,$$

where b is a constant.

The most common situation in which the above assumptions are valid is where p_i is a momentum. This is because the kinetic energy is usually a quadratic function of each momentum component, whereas the potential energy does not involve the momenta at all. However, if a coordinate q_i were to satisfy assumptions 1 and 2 then the theorem we are about to establish would hold just as well.

What is the mean value of $\in_i$ in thermal equilibrium if conditions 1 and 2 are satisfied? If the system is in equilibrium at absolute temperature $T \equiv (k\beta)^{-1}$then it is distributed according to the Boltzmann distribution. In the classical approximation, the mean value of $\in_i$ is expressed in terms of integrals over all phase-space:

$$\bar{\in}_i = \frac{\int_{-\infty}^{\infty} \exp[-\beta E(q_1,\ldots,p_f)] \in_i dq_1 \ldots dp_f}{\int_{-\infty}^{\infty} \exp[-\beta E(q_1,\ldots,p_f)] dq_1 \ldots dp_f}.$$

Condition 1 gives

$$\begin{aligned} \bar{\in}_i &= \frac{\int_{-\infty}^{\infty} \exp[-\beta(\in_i + E')] \in_i dq_1 \ldots dp_f}{\int_{-\infty}^{\infty} \exp[-\beta(\in_i + E')] dq_1 \ldots dp_f} \\ &= \frac{\int_{-\infty}^{\infty} \exp(-\beta\in_i) \in_i dp_i \int_{-\infty}^{\infty} \exp(-\beta E')\, dq_1 \ldots dp_f}{\int_{-\infty}^{\infty} \exp(-\beta\in_i)\, dp_i \int_{-\infty}^{\infty} \exp(-\beta E')\, dq_1 \ldots dp_f}, \end{aligned}$$

where use has been made of the multiplicative property of the exponential function, and where the last integrals in both the numerator and denominator extend over all variables $qk$and pk except p_i. These integrals are equal and, thus, cancel. Hence,

$$\bar{\in}_i = \frac{\int_{-\infty}^{\infty} \exp(-\beta\in_i) \in_i dq_i}{\int_{-\infty}^{\infty} \exp(-\beta\in_i) dp_i}.$$

This expression can be simplified further since

$$\int_{-\infty}^{\infty} \exp(-\beta\in_i) \in_i dp_i \equiv -\frac{\theta}{\partial\beta}\left[\int_{-\infty}^{\infty} \exp(-\beta\in_i) dp_i\right],$$

so

$$\bar{\epsilon}_i = -\frac{\partial}{\partial\beta}\ln\left[\int_{-\infty}^{\infty}\exp(-\beta\epsilon_i)dp_i\right].$$

According to condition 2,

where $y = \sqrt{\beta}\ p_i$. Thus,

$$\ln\int_{-\infty}^{\infty}\exp(-\beta\epsilon_i)\,dp_i = -\frac{1}{2}\ln\beta + \ln\int_{-\infty}^{\infty}\exp(-by^2)\,dy.$$

Note that the integral on the right-hand side does not depend on β at all. It follows from Eq. that

$$\bar{\epsilon}_i = -\frac{\partial}{\partial\beta}\left(-\frac{1}{2}\ln\beta\right) = \frac{1}{2\beta},$$

giving

$$\bar{\epsilon}_i = \frac{1}{2}kT.$$

This is the famous equipartition theorem of classical physics. It states that the mean value of every independent quadratic term in the energy is equal to (1/2)*kT*. If all terms in the energy are quadratic then the mean energy is spread equally over all degrees of freedom (hence the name “equipartition”).

Harmonic oscillators

Our proof of the equipartition theorem depends crucially on the classical approximation. To see how quantum effects modify this result, let us examine a particularly simple system which we know how to analyze using both classical and quantum physics: i.e., a simple harmonic oscillator. Consider a one-dimensional harmonic oscillator in equilibrium with a heat reservoir at temperature *T*. The energy of the oscillator is given by

$$E = \frac{p^2}{2m} + \frac{1}{2}kx^2,$$

where the first term on the right-hand side is the kinetic energy, involving the momentum p and mass m, and the second term is the potential energy, involving the displacement x and the force constant k. Each of these terms is quadratic in the respective variable. So, in the classical approximation the equipartition theorem yields:

$$\frac{\overline{p^2}}{2m} = \frac{1}{2}kT,$$

$$\frac{1}{2}k\overline{x^2} = \frac{1}{2}kT.$$

That is, the mean kinetic energy of the oscillator is equal to the mean potential energy which equals $(1/2)kT$. It follows that the mean total energy is

$$\overline{E} = \frac{1}{2}kT + \frac{1}{2}kT = kT.$$

According to quantum mechanics, the energy levels of a harmonic oscillator are equally spaced and satisfy

$$E_n = (n + 1/2)\,\hbar\omega,$$

where n is a non-negative integer, and

$$\omega = \sqrt{\frac{k}{m}}.$$

The partition function for such an oscillator is given by

$$Z = \sum_{n=0}^{\infty} \exp(-\beta E_n) = \exp[-(1/2)\beta\hbar\omega] \sum_{n=0}^{\infty} \exp(-n\beta\hbar\omega).$$

Now,

$$\sum_{n=0}^{\infty} \exp(-n\beta\hbar\omega) = 1 + \exp(-\beta\hbar\omega) + \exp(-2\,\beta\hbar\omega) + \cdots$$

is simply the sum of an infinite geometric series, and can be evaluated immediately,

$$\sum_{n=0}^{\infty}\exp(-n\beta\hbar\omega) = \frac{1}{1-\exp(-\beta\hbar\omega)}.$$

Thus, the partition function takes the form

$$Z = \frac{\exp[-(1/2)\beta\hbar\omega]}{1-\exp(-\beta\hbar\omega)},$$

and

$$\ln Z = -\frac{1}{2}\beta\hbar\omega - \ln[1-\exp(-\beta\hbar\omega)].$$

The mean energy of the oscillator is given by Eq.

$$\overline{E} = -\frac{\partial}{\partial\beta}\ln Z = -\left[-\frac{1}{2}\hbar\omega - \frac{\exp(-\beta\hbar\omega)\,\hbar\omega}{1-\exp(-\beta\hbar\omega)}\right],$$

or

$$\overline{E} = \hbar\omega\left[-\frac{1}{2} + \frac{1}{\exp(\beta\hbar\omega)-1}\right].$$

Consider the limit

$$\beta\hbar\omega = \frac{\hbar\omega}{kT} \ll 1,$$

in which the thermal energy kT is large compared to the separation $\hbar\omega$ between the energy levels. In this limit,

$$\exp(\beta\hbar\omega) \simeq 1 + \beta\hbar\omega,$$

so

$$\overline{E} \simeq \hbar\omega\left[\frac{1}{2} + \frac{1}{\beta\hbar\omega}\right] \simeq \hbar\omega\left[\frac{1}{\beta\hbar\omega}\right],$$

giving

$$\overline{E} \simeq \frac{1}{\beta} = kT.$$

Thus, the classical result (470) holds whenever the thermal energy greatly exceeds the typical spacing between quantum energy levels.

Consider the limit

$$\beta\hbar\omega\frac{\hbar\omega}{kT} >> 1,$$

in which the thermal energy is small compared to the separation between the energy levels. In this limit,

$$\exp(\beta\hbar\omega) >> 1,$$

Thus, if the thermal energy is much less than the spacing between quantum states then the mean energy approaches that of the ground-state (the so-called zero point energy). Clearly, the equipartition theorem is only valid in the former limit, where $kT >> \hbar\omega$, and the oscillator possess sufficient thermal energy to explore many of its possible quantum states.

Specific heats

We have discussed the internal energies and entropies of substances (mostly ideal gases) at some length. Unfortunately, these quantities cannot be directly measured. Instead, they must be inferred from other information. The thermodynamic property of substances which is the easiest to measure is, of course, the heat capacity, or specific heat. In fact, once the variation of the specific heat with temperature is known, both the internal energy and entropy can be easily reconstructed via

$$E(T,\ V) = v\int_0^T c_V(T,V)\,dT + E(0,V),$$

$$S(T,\ V) =$$

Here, use has been made of $dS = đQ/T$, and the third law of thermodynamics. Clearly, the optimum way of verifying the results of statistical thermodynamics is to compare the theoretically predicted heat capacities with the experimentally measured values.

Classical physics, in the guise of the equipartition theorem, says that each independent degree of freedom associated with a quadratic term in the energy possesses an average energy $(1/2)kT$ in thermal equilibrium at temperature T. Consider a substance made up of N molecules. Every molecular degree of freedom contributes $(1/2)N\,k\,T$, or $(1/2)\,\nu RT$, to the mean energy of the substance (with the tacit proviso that each degree of freedom is associated with a quadratic term in the energy). Thus, the contribution to the molar heat capacity at constant volume (we wish to avoid the complications associated with any external work done on the substance) is

$$\frac{1}{\nu}\left(\frac{\partial E}{\partial T}\right)_V = \frac{1}{\nu}\frac{\partial[(1/2)\nu RT]}{\partial T} = \frac{1}{2}R,$$

per molecular degree of freedom. The total classical heat capacity is therefore

$$c_V = \frac{g}{2}R,$$

where g is the number of molecular degrees of freedom. Since large complicated molecules clearly have very many more degrees of freedom than small simple molecules, the above formula predicts that the molar heat capacities of substances made up of the former type of molecules should greatly exceed those of substances made up of the latter. In fact, the experimental heat capacities of substances containing complicated molecules are generally greater than those of substances containing simple molecules, but by nowhere near the large factor predicted by Eq.

This equation also implies that heat capacities are temperature independent. In fact, this is not the case for most substances. Experimental heat capacities generally increase with increasing temperature. These two experimental facts pose severe problems for classical physics.

Incidentally, these problems were fully appreciated as far back as 1850. Stories that physicists at the end of the nineteenth century thought that classical physics explained absolutely everything are largely apocryphal.

The equipartition theorem (and the whole classical approximation) is only valid when the typical thermal energy *kT* greatly exceeds the spacing between quantum energy levels. Suppose that the temperature is sufficiently low that this condition is not satisfied for one particular molecular degree of freedom. In fact, suppose that *kT* is much less than the spacing between the energy levels.

In this situation the degree of freedom only contributes the ground-state energy, E_0, say, to the mean energy of the molecule. The ground-state energy can be a quite complicated function of the internal properties of the molecule, but is certainly not a function of the temperature, since this is a collective property of all molecules. It follows that the contribution to the molar heat capacity is

$$\frac{1}{v}\left(\frac{\partial[N\,E_0]}{\partial T}\right)_v = 0.$$

Thus, if *kT* is much less than the spacing between the energy levels then the degree of freedom contributes nothing at all to the molar heat capacity. We say that this particular degree of freedom is frozen out. Clearly, at very low temperatures just about all degrees of freedom are frozen out. As the temperature is gradually increased, degrees of freedom successively “kick in,” and eventually contribute their full (1/2)R to the molar heat capacity, as *kT* approaches, and then greatly exceeds, the spacing between their quantum energy levels. We can use these simple ideas to explain the behaviours of most experimental heat capacities. To make further progress, we need to estimate the typical spacing between the quantum energy levels associated with various degrees of freedom. We can do this by observing the frequency of the electromagnetic radiation emitted and absorbed during transitions between these energy levels. If the typical spacing between energy levels is ΔE then transitions between the various levels are associated with photons of frequency υ, where $h\upsilon = \Delta E$.

We can define an effective temperature of the radiation via $h\upsilon = kT_{\text{rad}}$. If $T >> T_{\text{rad}}$then $kT >> \Delta E$, and the degree of freedom makes its full contribution to the heat capacity. On the other hand, if $T << T_{\text{rad}}$ then $kT << \Delta E$, and the degree of freedom is frozen out. The “temperatures” of various different types of radiation. It is clear that degrees of freedom which give rise to emission or absorption of radio or microwave radiation contribute their full $(1/2)R$ to the molar heat capacity at room temperature.

Degrees of freedom which give rise to emission or absorption in the visible, ultraviolet, X–ray, or γ–ray regions of the electromagnetic spectrum are frozen out at room temperature. Degrees of freedom which emit or absorb infrared radiation are on the border line.

Table. Effective “Temperatures” of Various Types of Electromagnetic Radiation

Radiation type	Frequency (Hz)	T_{rad} (°K)
Radio	$< 10^{9}$	< 0.05
Microwave	$10^{9} - 10^{11}$	< 0.05
Infrared	$10^{11} - 10^{14}$	5. 5000
Visible	5×10^{14}	2×10^{4}
Ultraviolet	$10^{15} - 10^{17}$	5×10^{4} 5×10^{5}
X-ray	$10^{17} - 10^{20}$	5×10^{6} 5×10^{9}
g-ray	$> 10^{20}$	$> 5 \times 10^{9}3$

Specific Heats of Gases

Let us now investigate the specific heats of gases. Consider, first of all, translational degrees of freedom. Every molecule in a gas is free to move in three dimensions. If one particular molecule has mass m and momentum $p = mv$ then its kinetic energy of translation is

$$K = \frac{1}{2m}\left(p_x^2 + p_y^2 + p_z^2\right).$$

The kinetic energy of other molecules does not involve the momentum P of this particular molecule. Moreover, the potential energy of interaction between molecules depends only on their position coordinates, and, thus, certainly does not involve P. Any internal rotational, vibrational, electronic, or nuclear degrees of freedom of the molecule also do not involve P.

Hence, the essential conditions of the equipartition theorem are satisfied (at least, in the classical approximation). Since Eq. contains three independent quadratic terms, there are clearly three degrees of freedom associated with translation (one for each dimension of space), so the translational contribution to the molar heat capacity of gases is

$$(c_V)_{\text{translation}} = \frac{3}{2}R.$$

Suppose that our gas is contained in a cubic enclosure of dimensions L. According to Schrödinger's equation, the quantized translational energy levels of an individual molecule are given by

$$E = \frac{\hbar^2\pi^2}{2mL^2}\left(n_1^2 + n_2^2 + n_3^2\right),$$

where n_1, n_2, and n_3 are positive integer quantum numbers.

Clearly, the spacing between the energy levels can be made arbitrarily small by increasing the size of the enclosure. This implies that translational degrees of freedom can be treated classically, so that Eq. is always valid (except very close to absolute zero). We conclude that all gases possess a minimum molar heat capacity of (3/2) R due to the translational degrees of freedom of their constituent molecules.

The electronic degrees of freedom of gas molecules (i.e., the possible configurations of electrons orbiting the atomic nuclei) typically give rise to absorption and emission in the ultraviolet or visible regions of the spectrum. It follows from electronic degrees of freedom are frozen out at room temperature. Similarly, nuclear degrees of freedom (i.e., the possible configurations of protons and neutrons in the atomic nuclei) are frozen out because they are associated with absorption and emission in the X–ray and γ–ray regions of the electromagnetic spectrum. In fact, the only additional degrees of freedom we need worry about for gases are rotational and vibrational degrees of freedom. These typically give rise to absorption lines in the infrared region of the spectrum.

The rotational kinetic energy of a molecule tumbling in space can be written

$$K = \frac{1}{2} I_x \omega_x^2 + \frac{1}{2} I_y \omega_y^2 + \frac{1}{2} I_z \omega_z^2,$$

where the x–, y–, and z–axes are the so called principle axes of inertia of the molecule (these are mutually perpendicular), ω_x, ω_y, and ω_z are the angular velocities of rotation about these axes, and I_x, I_y, and I_z are the moments of inertia of the molecule about these axes. No other degrees of freedom depend on the angular velocities of rotation.

Since the kinetic energy of rotation is the sum of three quadratic terms, the rotational contribution to the molar heat capacity of gases is

$$(c_V)_{\text{rotation}} = \frac{3}{2}R,$$

according to the equipartition theorem. Note that the typical magnitude of a molecular moment of inertia is md^2, where m is the molecular mass, and d is the typical interatomic spacing in the molecule. A special case arises if the molecule is linear (e.g. if the molecule is diatomic).

In this case, one of the principle axes lies along the line of centers of the atoms. The moment of inertia about this axis is of order ma^2, where a is a typical nuclear dimension (remember that nearly all of the mass of an atom resides in the nucleus). Since $a \sim 10^{-5}\ d$,it follows that the moment of inertia about the line of centres is minuscule compared to the moments of inertia about the other two principle axes. In quantum mechanics, angular momentum is quantized in units of $\hbar$. The energy levels of a rigid rotator are written

$$E = \frac{\hbar^2}{2I} J(J+1),$$

where I is the moment of inertia and J is an integer. Note the inverse dependence of the spacing between energy levels on the moment of inertia.

It is clear that for the case of a linear molecule, the rotational degree of freedom associated with spinning along the line of centres of the atoms is frozen out at room temperature, given the very small moment of inertia along this axis, and, hence, the very widely spaced rotational energy levels.

Classically, the vibrational degrees of freedom of a molecule are studied by standard normal mode analysis of the molecular structure. Each normal mode behaves like an independent harmonic oscillator, and, therefore, contributes R to the molar specific heat of the gas [(1/2) R from the kinetic energy of vibration and (1/2)R from the potential energy of vibration].

A molecule containing n atoms has n–1 normal modes of vibration. For instance, a diatomic molecule has just one normal mode (corresponding to periodic stretching of the bond between the two atoms). Thus, the classical contribution to the specific heat from vibrational degrees of freedom is

$$(c_V)_{\text{vibration}} = (n-1)R.$$

The rotational and vibrational degrees of freedom actually make a contribution to the specific heats of gases at room temperature, once quantum effects are taken into consideration? We can answer this question by examining just one piece of data. The infrared absorption spectrum of Hydrogen Chloride. The absorption lines correspond to simultaneous transitions between different vibrational and rotational energy levels.

Hence, this is usually called a vibration-rotation spectrum. The missing line at about 3.47 microns corresponds to a pure vibrational transition from the ground-state to the first excited state (pure vibrational transitions are forbidden: HCl molecules always have to simultaneously change their rotational energy level if they are to couple effectively to electromagnetic radiation).

The longer wavelength absorption lines correspond to vibrational transitions in which there is a simultaneous decrease in the rotational energy level. Likewise, the shorter wavelength absorption lines correspond to vibrational transitions in which there is a simultaneous increase in the rotational energy level.

It is clear that the rotational energy levels are more closely spaced than the vibrational energy levels. The pure vibrational transition gives rise to absorption at about 3.47 microns, which corresponds to infrared radiation of frequency 8.5×10^{11} hertz with an associated radiation "temperature" of 4400 degrees kelvin.

We conclude that the vibrational degrees of freedom of HCl, or any other small molecule, are frozen out at room temperature. The rotational transitions split the vibrational lines by about 0.2 microns.

This implies that pure rotational transitions would be associated with infrared radiation of frequency 5×10^{12} hertz and corresponding radiation "temperature" 260 degrees kelvin. We conclude that the rotational degrees of freedom of HCl, or any other small molecule, are not frozen out at room temperature, and probably contribute the classical $(1/2)R$ to the molar specific heat. There is one proviso, however. Linear molecules (like HCl) effectively only have two rotational degrees of freedom (instead of the usual three), because of the very small moment of inertia of such molecules along the line of centres of the atoms.

We are now in a position to make some predictions regarding the specific heats of various gases. Monatomic molecules only possess three translational degrees of freedom, so monatomic gases should have a molar heat capacity $(3/2)R = 12.47$ joules/degree/mole.

The ratio of specific heats $\gamma = Cp/C_V = (C_V + R)/C_V$ should be 5/3 = 1.667. It can be seen from both of these predictions are borne out pretty well for Helium and Argon.

Diatomic molecules possess three translational degrees of freedom and two rotational degrees of freedom (all other degrees of freedom are frozen out at room temperature). Thus, diatomic gases should have a molar heat capacity (5/2)R = 20.8 joules/degree/mole.

The ratio of specific heats should be 7/5 = 1.4 It can be seen from these are pretty accurate predictions for Nitrogen and Oxygen. The freezing out of vibrational degrees of freedom becomes gradually less effective as molecules become heavier and more complex.

This is partly because such molecules are generally less stable, so the force constant k is reduced, and partly because the molecular mass is increased.

Both these effect reduce the frequency of vibration of the molecular normal modes and, hence, the spacing between vibrational energy levels.

This accounts for the obviously non-classical [i.e., not a multiple of $(1/2)R$] specific heats of Carbon Dioxide and Ethane. In both molecules, vibrational degrees of freedom contribute to the molar specific heat (but not the full R because the temperature is not high enough).

The variation of the molar heat capacity at constant volume (in units of R) of gaseous hydrogen with temperature. The expected contribution from the translational degrees of freedom is $(3/2)R$ (there are three translational degrees of freedom per molecule).

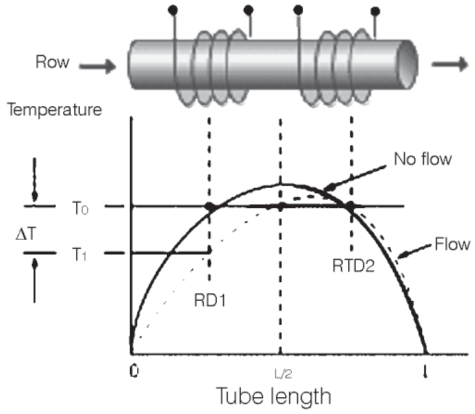


Fig. The Molar Heat Capacity at Constant Volume.

The expected contribution at high temperatures from the rotational degrees of freedom is *R* (there are effectively two rotational degrees of freedom per molecule). Finally, the expected contribution at high temperatures from the vibrational degrees of freedom is *R* (there is one vibrational degree of freedom per molecule). It can be seen that as the temperature rises the rotational, and then the vibrational, degrees of freedom eventually make their full classical contributions to the heat capacity.

Specific Heats of Solids

Consider a simple solid containing *N* atoms. Now, atoms in solids cannot translate (unlike those in gases), but are free to vibrate about their equilibrium positions. Such vibrations are called lattice vibrations, and can be thought of as sound waves propagating through the crystal lattice. Each atom is specified by three independent position coordinates, and three conjugate momentum coordinates.

Let us only consider small amplitude vibrations. In this case, we can expand the potential energy of interaction between the atoms to give an expression which is quadratic in the atomic displacements from their equilibrium positions. It is always possible to perform a normal mode analysis of the oscillations. In effect, we can find $3N$ independent modes of oscillation of the solid.

Each mode has its own particular oscillation frequency, and its own particular pattern of atomic displacements. Any general oscillation can be written as a linear combination of these normal modes.

Let q_i be the (appropriately normalized) amplitude of the ith normal mode, and p_i the momentum conjugate to this coordinate. In normal mode coordinates, the total energy of the lattice vibrations takes the particularly simple form

$$E = \frac{1}{2}\sum_{i=1}^{3N}(p_i^2 + \omega_i^2 q_i^2),$$

where ω_i is the (angular) oscillation frequency of the ith normal mode. It is clear that in normal mode coordinates, the linearized lattice vibrations are equivalent to $3N$ independent harmonic oscillators (of course, each oscillator corresponds to a different normal mode).

The typical value of ω_i is the (angular) frequency of a sound wave propagating through the lattice. Sound wave frequencies are far lower than the typical vibration frequencies of gaseous molecules.

In the latter case, the mass involved in the vibration is simply that of the molecule, whereas in the former case the mass involved is that of very many atoms (since lattice vibrations are non-localized).

The strength of interatomic bonds in gaseous molecules is similar to those in solids, so we can use the estimate ω

~ $\sqrt{k/m}$ (k is the force constant which measures the strength of interatomic bonds, and m is the mass involved in the oscillation) as proof that the typical frequencies of lattice vibrations are very much less than the vibration frequencies of simple molecules.

It follows from $\Delta E = \hbar\omega$ that the quantum energy levels of lattice vibrations are far more closely spaced than the vibrational energy levels of gaseous molecules. Thus, it is likely (and is, indeed, the case) that lattice vibrations are not frozen out at room temperature, but, instead, make their full classical contribution to the molar specific heat of the solid.

If the lattice vibrations behave classically then, according to the equipartition theorem, each normal mode of oscillation has an associated mean energy kTin equilibrium at temperature T [$(1/2)kT$ resides in the kinetic energy of the oscillation, and $(1/2)kT$ resides in the potential energy]. Thus, the mean internal energy per mole of the solid is

$$\bar{E} = 3NkT = 3vRT.$$

It follows that the molar heat capacity at constant volume is

$$c_V = \frac{1}{v}\left(\frac{\partial \bar{E}}{\partial T}\right)_V = 3R$$

for solids. This gives a value of 24.9 joules/mole/degree. In fact, at room temperature most solids (in particular, metals) have heat capacities which lie remarkably close to this value. This fact was discovered experimentally by Dulong and Petite at the beginning of the nineteenth century, and was used to make some of the first crude estimates of the molecular weights of solids (if we know the molar heat capacity of a substance then we can easily work out how much of it corresponds to one mole, and by weighing this amount, and then dividing the result by Avogadro's number, we can obtain an estimate of the molecular weight).

The experimental molar heat capacities *Cp* at constant pressure for various solids. The heat capacity at constant volume is somewhat less than the constant pressure value, but not by much, because solids are fairly incompressible. It can be seen that Dulong and Petite's law (i.e., that all solids have a molar heat capacities close to 24.9 joules/mole/degree) holds pretty well for metals. However, the law fails badly for diamond. This is not surprising.

As is well-known, diamond is an extremely hard substance, so its intermolecular bonds must be very strong, suggesting that the force constant k is large. Diamond is also a fairly low density substance, so the mass m involved in lattice vibrations is comparatively small. Both these facts suggest that the typical lattice vibration frequency of diamond ($\omega \sim \sqrt{k/m}$) is high. In fact, the spacing between the different vibration energy levels (which scales like $\hbar\omega$) is sufficiently large in diamond for the vibrational degrees of freedom to be largely frozen out at room temperature.

This accounts for the anomalously low heat capacity of diamond.

Table. Values of (Joules/Mole/Degree)
For Some Solids at T = 298° K. K. From Reif.

Solid	*Cp*	Solid	*Cp*
Copper	24.5	Aluminium	24.4
Silver	25.5	Tin (white)	26.4
Lead	26.4	Sulphur (rhombic)	22.4
Zinc	25.4	Carbon (diamond)	6.1

Dulong and Petite's law is essentially a high temperature limit. The molar heat capacity cannot remain a constant as the temperature approaches absolute zero, since, by Eq. this would imply S → ∞, which violates the third law of thermodynamics. We can make a crude model of the behaviour of C_V at low temperatures by assuming that all the normal modes oscillate at the same frequency, ω, say.

According to Eq. the solid acts like a set of $3N$ independent oscillators which, making use of Einstein's approximation, all vibrate at the same frequency. We can use the quantum mechanical result for a single oscillator to write the mean energy of the solid in the form

$$\bar{E} = 3N\hbar\omega\left(\frac{1}{2} + \frac{1}{\exp(\beta\hbar\omega) - 1}\right).$$

The molar heat capacity is defined

$$c_V = \frac{1}{v}\left(\frac{\partial \bar{E}}{\partial T}\right)_V = \frac{1}{v}\left(\frac{\partial \bar{E}}{\partial T}\right)_V \frac{\partial \beta}{\partial T} = -\frac{1}{vkT^2}\left(\frac{\partial \bar{E}}{\partial T}\right)_V,$$

giving

$$c_V = -\frac{3\,N_A\hbar\omega}{kT^2}\left[-\frac{\exp(\beta\hbar\omega)}{[\exp(\beta\hbar\omega) - 1]^2}\right],$$

which reduces to

$$c_V = 3R\left(\frac{\theta_E}{T}\right)^2 \frac{\exp(\theta_E / T)}{[\exp(\theta_E / T) - 1]^2}.$$

Here,

$$\theta_E = \frac{\hbar\omega}{k}$$

is called the Einstein temperature. If the temperature is sufficiently high that T>> θ_E then $kT >> \hbar\omega$, and the above expression reduces to $C_V = 3R$,, after expansion of the exponential functions. Thus, the law of Dulong and Petite is recovered for temperatures significantly in excess of the

Einstein temperature. On the other hand, if the temperature is sufficiently low that T<< θ_E then the exponential factors in Eq. become very much larger than unity, giving

$$C_V \sim 3R\left(\frac{\theta_E}{T}\right)\exp(-\theta_E/T).$$

So, in this simple model the specific heat approaches zero exponentially as $T \to 0$.

In reality, the specific heats of solids do not approach zero quite as quickly as suggested by Einstein's model when $T \to 0$. The experimentally observed low temperature behaviour is more like $C_V \propto T^3$. The reason for this discrepancy is the crude approximation that all normal modes have the same frequency. In fact, long wavelength modes have lower frequencies than short wavelength modes, so the former are much harder to freeze out than the latter (because the spacing between quantum energy levels, $\hbar\omega$, is smaller in the former case).

The molar heat capacity does not decrease with temperature as rapidly as suggested by Einstein's model because these long wavelength modes are able to make a significant contribution to the heat capacity even at very low temperatures.

A more realistic model of lattice vibrations was developed by the Dutch physicist Peter Debye in 1912. In the Debye model, the frequencies of the normal modes of vibration are estimated by treating the solid as an isotropic continuous medium. This approach is reasonable because the only modes which really matter at low temperatures are the long wavelength modes: i.e., those whose wavelengths greatly exceed the interatomic spacing. It is plausible that these modes are not particularly sensitive to the discrete nature of the solid: i.e., the fact that it is made up of atoms rather than being continuous.

Consider a sound wave propagating through an isotropic continuous medium. The disturbance varies with position vector *r* and time *t* like exp[–*i* (k.r – ω*t*)], where the wave-vector *k* and the frequency of oscillation ω satisfy the dispersion relation for sound waves in an isotropic medium:

$$\omega = kC_s.$$

Here, C_S is the speed of sound in the medium. Suppose, for the sake of argument, that the medium is periodic in the *x*–, *y*–, and *z*–directions with periodicity lengths L_x, L_y, and L_z, respectively. In order to maintain periodicity we need

$$k_x(x + L_x) = k_x + 2\pi n_x,$$

where n_x is an integer. There are analogous constraints on k_y and k_z. It follows that in a periodic medium the components of the wave-vector are quantized, and can only take the values

$$k_x = \frac{2\pi}{L_x} n_x,$$

$$k_y = \frac{2\pi}{L_y} n_y,$$

$$k_z = \frac{2\pi}{L_z} n_z,$$

where n_x, n_y, and n_z are all integers. It is assumed that L_x, L_y, and L_z are macroscopic lengths, so the allowed values of the components of the wave-vector are very closely spaced. For given values of k_y and k_z, the number of allowed values of k_x which lie in the range k_x to $k_x + dk_x$ is given by

$$\Delta n_x = \frac{L_x}{2\pi} 2k_x.$$

It follows that the number of allowed values of k (i.e., the number of allowed modes) when k_x lies in the range k_z to $k_z + dk_z$, k_z, $+ k_y$ lies in the range k_y to $k_y + dk_y$, and k_z lies in the range k_z to $k_z + dk_z$, is

$$\rho d^3k = \left(\frac{L_x}{2\pi} dk_x\right)\left(\frac{L_y}{2\pi} dk_y\right)\left(\frac{L_z}{2\pi} dk_z\right) = \frac{V}{(2\pi)^3} dk_x dk_y dk_z,$$

where $V = L_x L_y L_z$ is the periodicity volume, and $d^3k \equiv dk_x dk_y dk_z$. The quantity ρ is called the density of modes. Note that this density is independent of k, and proportional to the periodicity volume.

Thus, the density of modes per unit volume is a constant independent of the magnitude or shape of the periodicity volume. The density of modes per unit volume when the magnitude of k lies in the range k to $k + dk$ is given by multiplying the density of modes per unit volume by the "volume" in k-space of the spherical shell lying between radii k and $k + dk$. Thus,

$$\rho_k dk = \frac{4\pi k^2\, dk}{(2\pi)} = \frac{V^2}{2\pi^2} dk.$$

Consider an isotropic continuous medium of volume V. According to the above relation, the number of normal modes whose frequencies lie between ω and $\omega + d\omega$ (which is equivalent to the number of modes whose k values lie in the range ω/C_s to $\omega/C_s + d\omega/C_s$) is

$$\sigma_C(\omega)\, d\omega = 3\frac{k^2\, V}{2\pi^2} dk = 3\frac{V^2}{2\pi^2 C_S{}^3}\omega^2 d\omega.$$

The factor of 3 comes from the three possible polarizations of sound waves in solids. For every allowed wavenumber (or frequency) there are two independent torsional modes, where the displacement is perpendicular to the direction of propagation, and one longitudinal mode, where the displacement is parallel to the direction of propagation. Torsion waves are vaguely analogous to electromagnetic waves (these also have two independent polarizations). The longitudinal mode is very similar to the compressional sound wave in gases. Of course, torsion waves can not propagate in gases because gases have no resistance to deformation without change of volume.

The Debye approach consists in approximating the actual density of normal modes $\sigma(\omega)$ by the density in a continuous medium $\sigma_C(\omega)$, not only at low frequencies (long wavelengths) where these should be nearly the same, but also at higher frequencies where they may differ substantially.

Suppose that we are dealing with a solid consisting of N atoms. We know that there are only $3N$ independent normal modes. It follows that we must cut off the density of states above some critical frequency, ω_D say, otherwise we will have too many modes. Thus, in the Debye approximation the density of normal modes takes the form

$$\sigma_D(\omega) = \sigma_C(\omega) \text{ for } \omega < \omega_D$$

$$\sigma_D(\omega) = 0 \text{ for } \omega < \omega_D$$

Here, ω_D is the Debye frequency. This critical frequency is chosen such that the total number of normal modes is $3N$, so

$$\int_0^\infty \sigma_C(\omega)\, d\omega = \int_0^{\omega_D} \sigma_C(\omega)\, d\omega = 3N.$$

Substituting Eq. into the previous formula yields

$$\frac{3V}{2\pi^2 C_s^3}\int_0^{\omega_D} d\omega = \frac{3V}{2\pi^2 C_s^3}\omega_D^3 = 3N.$$

This implies that

$$\omega_D = C_s\left(6\pi^2 \frac{N}{V}\right)^{1/3}.$$

Thus, the Debye frequency depends only on the sound velocity in the solid and the number of atoms per unit volume. The wavelength corresponding to the Debye frequency is $2\pi\, C_s/\omega_D$, which is clearly on the order of the interatomic spacing $a \sim (V/N)^{1/3}$.

It follows that the cut-off of normal modes whose frequencies exceed the Debye frequency is equivalent to a cut-off of normal modes whose wavelengths are less than the interatomic spacing. Of course, it makes physical sense that such modes should be absent.

Compares the actual density of normal modes in diamond with the density predicted by Debye theory. Not surprisingly, there is not a particularly strong resemblance between these two curves, since Debye theory is highly idealized. Nevertheless, both curves exhibit sharp cut-offs at high frequencies, and coincide at low frequencies. Furthermore, the areas under both curves are the same. This is sufficient to allow Debye theory to correctly account for the temperature variation of the specific heat of solids at low temperatures.

We can use the quantum mechanical expression for the mean energy of a single oscillator, Eq. to calculate the mean energy of lattice vibrations in the Debye approximation. We obtain

$$\bar{E} = \int_0^\infty \sigma_D(\omega)\hbar\omega\left(\frac{1}{2} + \frac{1}{\exp(\beta\hbar\omega) - 1}\right) d\omega.$$

According to Eq. the molar heat capacity takes the form

$$C_V = \frac{1}{vkT^2}\int_0^\infty \sigma_D(\omega)\hbar\omega\left[\frac{\exp(\beta\hbar\omega)\hbar\omega}{[\exp(\beta\hbar\omega)-1]^2}\right]d\omega.$$

Substituting in Eq. we find that

$$C_V = \frac{k}{v}\int_0^{\omega_D}\frac{\exp(\beta\hbar\omega)(\beta\hbar\omega)^2}{[\exp(\beta\hbar\omega)-1]^2}\frac{3V}{2\pi^2 C_s^3}\omega^2 d\omega,$$

giving

$$C_V = \frac{3Vk}{2\pi^2 v(C_s\beta\hbar)^3}\int_0^{\beta\hbar\omega_D}\frac{\exp x}{(\exp x-1)^2}x^4 dx,$$

in terms of the dimensionless variable $x = \beta\hbar\omega$. According to Eq. the volume can be written

$$V = 6\pi^2 N\left(\frac{Cs}{\omega_D}\right)^3,$$

so the heat capacity reduces to

$$C_V = 3Rf_D(\beta\hbar\omega_D) = 3Rf_D(\theta_D/T),$$

where the Debye function is defined

$$f_D(y) \equiv \frac{3}{y^3}\int_0^y \frac{\exp x}{(\exp x-1)^2}x^4 dx.$$

We have also defined the Debye temperature θ_D as

$$k\theta_D = \hbar\omega_D.$$

Consider the asymptotic limit in which $T \gg \theta_D$. For small y, we can approximate exp x as $1 + x$ in the integrand of Eq. so that

$$f_D(y) \to \frac{3}{y^3}\int_0^y x^2 dx = 1.$$

Thus, if the temperature greatly exceeds the Debye temperature we recover the law of Dulong and Petite that $C_V = 3R$. Consider, now, the asymptotic limit in which $T \ll \theta_D$. For large y,

$$\int_0^y \frac{\exp x}{(\exp x-1)^2}x^4 dx \simeq \int_0^\infty \frac{\exp x}{(\exp x-1)^2}x^4 dx = \frac{4\pi^4}{15}.$$

Thus, in the low temperature limit

$$f_D(y) \rightarrow \frac{4\pi^4}{5}\frac{1}{y^3}.$$

This yields

$$c_V \simeq \frac{12\pi^4}{5}R\left(\frac{T}{\theta_D}\right)^3$$

in the limit $T \ll \theta_D$: i.e., c_V varies with temperature like T^3.

Table. Comparison of Debye Temperatures (In Degrees Kelvin)

Solid	θ_D *from low temp.*	θ_D *from sound speed*
NaCl	308	320
KCl	230	246
Ag	225	216
Zn	308	305

The fact that c_V goes like T^3 at low temperatures is quite well verified experimentally, although it is sometimes necessary to go to temperatures as low as 0.02 θ_D to obtain this asymptotic behaviour.

Theoretically, θ_D should be calculable from Eq. in terms of the sound speed in the solid and the molar volume.

A comparison of Debye temperatures evaluated by this means with temperatures obtained empirically by fitting the law to the low temperature variation of the heat capacity.

It can be seen that there is fairly good agreement between the theoretical and empirical Debye temperatures.

This suggests that the Debye theory affords a good, thought not perfect, representation of the behaviour of c_V in solids over the entire temperature range.

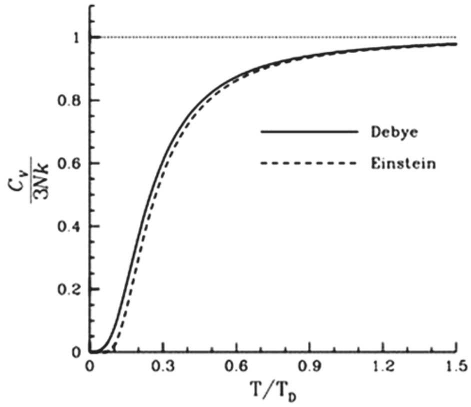


Fig. The Molar Heat Capacity of Various Solids.

Finally, the actual temperature variation of the molar heat capacities of various solids as well as that predicted by Debye's theory. The prediction of Einstein's theory is also show for the sake of comparison. Note that 24.9 joules/mole/degree is about 6 calories/gram-atom/degree (the latter are chemist's units).

7

Heat Capacity

The heat capacity of a substance is a measure of how well the substance stores heat. Whenever we supply heat to a material, it will necessarily cause an increase in the material's temperature. The heat capacity is defined as the amount of heat required per unit increase in temperature, so that

Heat added = heat capacity × (change in temperature)

Thus, materials with large heat capacities, like water, hold heat well - their temperature won't rise much for a given amount of heat - whereas materials with small heat capacities, like copper, don't hold heat well - their temperature will rise significantly when heat is added.

Heat capacity (usually denoted by a capital C, often with subscripts) is a measurable physical quantity that characterizes the ability of a body to store heat as it changes in temperature. It is defined as the rate of change of temperature as heat is added to a body at the given conditions and state of the body (foremost its temperature).

In the International System of Units, heat capacity is expressed in units of joules per kelvin. It is termed an "extensive quantity" because it is sensitive to the size of the object (for example, a bathtub of water has a greater heat capacity than a cup of water). Dividing heat capacity by the body's mass yields a specific heat capacity (also called more properly "mass-specific heat capacity" or more loosely "specific heat"), which is an "intensive quantity," meaning it is no longer dependent on amount of material, and is now more dependent on the type of material, as well as the physical conditions of heating.

Heat capacity is mathematically defined as the ratio of a small amount of heat δQ added to the body, to the corresponding small increase in its temperature dT:

$$C = \left(\frac{\delta Q}{dT}\right)_{cond.} = T\left(\frac{dS}{dT}\right)_{cond.}$$

For thermodynamic systems with more than one physical dimension, the above definition does not give a single, unique quantity unless a particular infinitesimal path through the system's phase space has been defined (this means that one needs to know at all times where all parts of the system are, how much mass they have, and how fast they are moving). This information is used to account for different ways that heat can be stored as kinetic energy (energy of motion) and potential energy (energy stored in force fields), as an object expands or contracts.

For all real systems, the path though these changes must be explicitly defined, since the value of heat capacity depends on which path from one temperature to another, is chosen. Of particular usefulness in this context are the values of heat capacity for constant volume, CV, and constant pressure, CP. These will be defined below.

Heat Capacity of Fluids

The state of a simple fluids with fixed mass is described by two thermodynamic parameters such as temperature T and pressure P. Therefore as mentioned above, one may distinguish between heat capacity at constant volume, C_V, and heat capacity at constant pressure, C_P:

$$C_V = \left(\frac{\delta Q}{dT}\right)_V = T\left(\frac{\partial S}{\partial T}\right)_V$$

$$C_P = \left(\frac{\delta Q}{dT}\right)_P = T\left(\frac{\partial S}{\partial T}\right)_P$$

where δQ is the infinitesimal amount of heat added, and dT is the subsequent rise in temperature.

The increment of internal energy is the heat added and the work added:

$$dU = T\,dS - P\,dV$$

So the heat capacity at constant volume is

$$C_V = \left(\frac{\partial U}{\partial T}\right)_V$$

The enthalpy is defined by H = U + PV. The increment of enthalpy is

$$dH = dU + (PdV + VdP)$$

which at dP=0, reduces to:

$$dH = T\,dS + V\,dP$$

So the heat capacity at constant pressure is

$$C_P = \left(\frac{\partial H}{\partial T}\right)_P$$

Note that this last "definition" is a bit circular, since the concept of "enthalpy" itself was invented to be a measure of heat absorbed or produced at constant pressures (the conditions in which chemists usually work). As such, enthalpy merely accounts for the extra heat which is produced or absorbed by pressure-volume work at constant pressure. Thus, it is not surprising that constant-pressure heat capacities may be defined in terms of enthalpy, since "enthalpy" was defined in the first place to make this so.

Specific Heat Capacity

The specific heat capacity of a material is

$$c = \frac{\partial C}{\partial m}$$

which in the absence of phase transitions is equivalent to

$$c = c_m = \frac{C}{m} = \frac{C}{\rho V}$$

- C is the heat capacity of a body made of the material in question ($J \cdot K^{-1}$)
- m is the mass of the body (kg)
- V is the volume of the body (m^3)
- $\delta = mV^{-1}$ is the density of the material ($kg \cdot m^{-3}$)

For gases, and also for other materials under high pressures, there is need to distinguish between different boundary conditions for the processes under consideration (since values differ significantly between different conditions).

Typical processes for which a heat capacity may be defined include isobaric (constant pressure, dP = 0) and isochoric (constant volume, dV = 0) processes, and one conventionally writes for gases:

$$c_P = \left(\frac{\partial C}{\partial m}\right)_P$$

$$c_V = \left(\frac{\partial C}{\partial m}\right)_V$$

Units shown are SI units but, of course, any consistent set of units may be used.

A related parameter to c is CV–1, the volumetric heat capacity, (J·m–3·K–1 in SI units). In engineering practice, cV for solids or liquids often signifies a volumetric heat capacity, rather than a constant-volume one. In such cases, the mass-specific heat capacity (specific heat) is often explicitly written with the subscript m, as cm. Of course, from the above relationships, for solids one writes:

$$c_m = \frac{C}{m} = \frac{c_V}{\rho}$$

Dimensionless Heat Capacity

The dimensionless heat capacity of a material is

$$C^* = \frac{C}{nR} = \frac{C}{Nk}$$

where

- C is the heat capacity of a body made of the material in question ($J \cdot K^{-1}$)
- n is the amount of matter in the body (mol)
- R is the gas constant ($J \cdot K^{-1} \cdot mol^{-1}$)
- nR=Nk is the amount of matter in the body ($J \cdot K^{-1}$)

- N is the number of molecules in the body. (dimensionless)
- k is Boltzmann's constant ($J \cdot K^{-1} \cdot molecule^{-1}$)

Gas Phase

According to the equipartition theorem from classical statistical mechanics, for a system made up of independent and quadratic degrees of freedom, any input of energy into a closed system composed of N molecules is evenly divided among the degrees of freedom available to each molecule. It can be shown that, in the classical limit of statistical mechanics, for each independent and quadratic degree of freedom, that

$$E_i = \frac{k_B T}{2}$$

where

E_i is the mean energy (measured in joules) associated with degree of freedom i.

T is the temperature (measured in Kelvin)

k_B is Boltzmann's constant, ($1.380\ 6505(24) \times 10^{-23}$ J K^{-1})

In the case of a monatomic gas such as helium under constant volume, if it assumed that no electronic or nuclear quantum excitations occur, each atom in the gas has only 3 degrees of freedom, all of a translational type. No energy dependence is associated with the degrees of freedom which define the position of the atoms. While, in fact, the degrees of freedom corresponding to the momenta of the atoms are quadratic, and thus contribute to the heat capacity. There are N atoms, each of which has 3 components of momentum, which leads to 3N total degrees of freedom. This gives:

$$C_V = \left(\frac{\partial U}{\partial T}\right)_V = \frac{3}{2} N k_B = \frac{3}{2} n R$$

$$C_V, m = \frac{C_V}{n} = \frac{3}{2} R = 1.5R$$

where

C_V is the heat capacity at constant volume of the gas

$C_{V,m}$ is the molar heat capacity at constant volume of the gas

N is the total number of atoms present in the container

n is the number of moles of atoms present in the container (n is the ratio of N and Avogadro's number)

R is the ideal gas constant, (8.314570[70] J $K^{-1}mol^{-1}$). R is equal to the product of Boltzmann's constant k_B and Avogadro's number

In the somewhat more complex case of an ideal gas of diatomic molecules, the presence of internal degrees of freedom are apparent. In addition to the three translational degrees of freedom, there are rotational and vibrational degrees of freedom. In general, the number of degrees of freedom, f, in a molecule with n_a atoms is $3n_a$:

$$f = 3n_a$$

Mathematically, there are a total of three rotational degrees of freedom, one corresponding to rotation about each of the axes of three dimensional space. However, in practice we shall only consider the existence of two degrees of rotational freedom for linear molecules. This approximation is valid because the moment of inertia about the internuclear axis is vanishingly small with respect other moments of inertia in the molecule (this is due to the extremely small radii of the atomic nuclei, compared to the distance between them in a molecule). Quantum mechanically, it can be shown that the interval between successive rotational energy eigenstates is inversely proportional to the moment of inertia about that axis. Because the moment of inertia about the internuclear axis is vanishingly small relative to the other two rotational axes, the energy spacing can be considered so high that no excitations of the rotational state can possibly occur unless the temperature is extremely high. We can easily calculate the expected number of vibrational degrees of freedom (or vibrational modes). There are three degrees of translational freedom, and two degrees of rotational freedom, therefore

$$f_{\text{vib}} = f - f_{\text{trans}} - f_{\text{rot}} = 6 - 3 - 2 = 1$$

Each rotational and translational degree of freedom will contribute R/2 in the total molar heat capacity of the gas. Each vibrational mode will contribute R to the total molar heat capacity, however. This is because for each vibrational mode, there is a potential and kinetic energy component. Both the potential and kinetic components will contribute R/2 to the total molar heat capacity of the gas. Therefore, we expect that a diatomic molecule would have a molar constant-volume heat capacity of

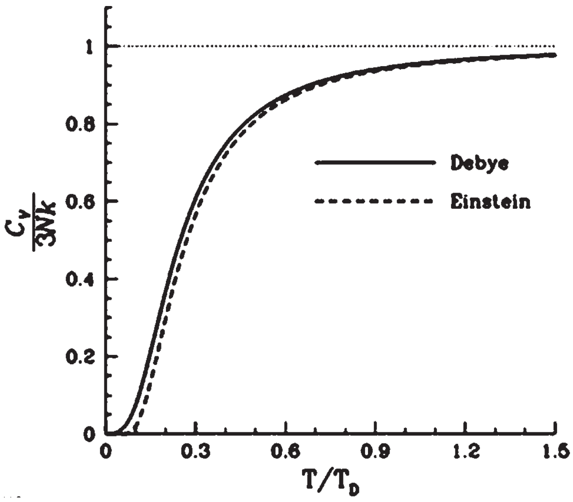
$$C_{V,m} = \frac{3R}{2} + R + R = \frac{7R}{2} = 3.5R$$

where the terms originate from the translational, rotational, and vibrational degrees of freedom, respectively. However, as the atoms composing the molecules become heavier, the heat capacities move closer to their expected values. One of the reasons for this phenomenon is the quantization of vibrational, and to a lesser extent, rotational states. In fact, if it is assumed that the molecules remain in their lowest energy vibrational state because the inter-level energy spacings are large, the predicted molar constant volume heat capacity for a diatomic molecule becomes

$$C_{V,m} = \frac{3R}{2} + R = \frac{5R}{2} = 2.5R$$

which is a fairly close approximation of the heat capacities of the lighter molecules in the above table. If the quantum harmonic oscillator approximation is made, it turns out that the quantum vibrational energy level spacings are actually inversely proportional to the square root of the reduced mass of the atoms composing the diatomic molecule. Therefore, in the case of the heavier diatomic molecules, the quantum vibrational energy level spacings become finer, which allows more excitations into higher vibrational levels at a fixed temperature.

Solid Phase



The dimensionless heat capacity divided by three, as a function of temperature as predicted by the Debye model and by Einstein's earlier model. The horizontal axis is the temperature divided by the Debye temperature. Note that, as expected, the dimensionless heat capacity is zero at absolute zero, and rises to a value of three as the temperature becomes much larger than the Debye temperature. The red line corresponds to the classical limit of the Dulong-Petit law

For matter in a crystalline solid phase, the Dulong-Petit law, which was discovered empirically, states that the dimensionless specific heat capacity assumes the value 3. Indeed, for solid metallic chemical elements at room temperature, heat capacities range from about 2.8 to 3.4 (beryllium being a notable exception at 2.0).

The theoretical maximum heat capacity for larger and larger multi-atomic gases at higher temperatures, also approaches the Dulong-Petit limit of 3R, so long as this is calculated per mole of atoms, not molecules. The reason is that gases with very large molecules, in theory have almost the same high-temperature heat capacity as solids, lacking only the (small) heat capacity contibution that comes from potential energy that cannot be stored between separate molecules in a gas.

The Dulong-Petit “limit” results from the equipartition theorem, and as such is only valid in the classical limit of a microstate continuum, which is a high temperature limit. For light and non-metallic elements, as well as most of the common molecular solids based on carbon compounds at standard ambiant temperature, quantum effects may also play an important role, as they do in multi-atomic gases. These effects usually combine to give heat capacities lower than 3 R per mole of atoms in the solid, although heat capacities calculated per mole of molecules in molecular solids may be more than 3 R. For example, the heat capacity of water ice at the melting point is about 4.6 R per mole of molecules, but only 1.5 R per mole of atoms. The lower number results from the “freezing out” of possible vibration modes for light atoms at suitably low temperatures, just as in many gases. These effects are seen in solids more often than liquids: for example the heat capacity of liquid water is again close to the theoretical 3 R/mole of atoms of the Dulong-Petit theoretical maximum.

Heat Capacity at Absolute Zero

From the definition of entropy

$$TdS = \delta Q$$

we can calculate the absolute entropy by integrating from zero temperature to the final temperature T_f

$$S(T_f) = \int_{T=0}^{T_j} \frac{\delta Q}{T} = \int_0^{T_f} \frac{\delta Q}{dT}\frac{\delta T}{T} = \int_0^{T_f} C(T)\frac{dT}{T}$$

The heat capacity must be zero at zero temperature in order for the above integral not to yield an infinite absolute entropy, thus violating the third law of thermodynamics. One of the strengths of the Debye model is that (unlike the preceding Einstein model) it predicts an approach of heat capacity toward zero as zero temperature is approached, and also predicts the proper mathematical form of this approach.

Standard states

Changes in energy content of a system are most easily compared if everyone agrees on a set of reference conditions. There are several conventions, but the commonly used set refers changes in chemical systems to defined standard states. The primary reference is to the standard states of the elements.

The standard state and the zero reference energy level

Elements in their standard states are considered to have chemical potentials and enthalpies of 0, or

$$\mu^o_{element} = 0$$

The standard state of an element is its natural state at 1 atms pressure, 25°C.

By defining the free energy of the elements in this way, we can regard any compound as having a chemical potential (partial free enrgy), or an enthalpy of formation, composed of the sum of all changes in chemical potential (or of enthalpy) for the reactions leading to its formation, by any convenient path.

Since free energy and enthalpy are variables of state, the value is a unique function of the state, so this approach can be used to define the the relative energy content of any chemical system by reference to the work needed to get there starting from the elements.

Standard states of Solutes and Gases, and Free Energy Changes of Reaction

In order to compare free energies for chemical processes, it is convenient to normalize free energy changes so as to eliminate differences in reaction volume. This is achieved by using ΔG^o, the molar free energy change, and a standard state for reactants in solution.

Under normal temperature and pressure (NTP) of 25°C and1 atms pressure:

Solutes are in their standard states when they have an activity of 1 M.

Gases are in their standard states when they are at a pressure of 1 atms.

Standard state of the Solvent

Treatment of the solvent represents a tricky issue. By convention, the solvent is assumed to have a standard state of 1 M (the units being necessary to avoid dimensions in logaritmic terms), which does not change under the conditions of biochemical reaction (solutes at dilute solution). In the case of aqueous solutions, this may seem odd, because the activity of liquid water is 55.35 M (at NTP). This convention is adopted because the interactions with the solvent are subsumed under the standard chemical potentials of the solutes (which are referred to the standard state of a 1 M solution), and under the activity coefficients relating activities to concentrations. For reactions, the interactions are subsumed under ΔG^o, since this is derived by summation of values for μ^o. The convention allows one to ignore interactions between solute and solvent; this is usually appropriate since they are not significantly affected by changes in the solvent. In effect, for biochemical reactions in which water is a substrate or product (mainly hydrolysis and lyase reactions), water is omitted from the thermodynamic equation. Thus for ATP hydrolysis:

$$\mathrm{ATP} + \mathrm{H_2O} \Leftrightarrow \mathrm{ADP} + \mathrm{Pi}$$

$$\Delta G' = \Delta G^{0'} + RT \ln \frac{(ADP).(Pi)}{(ATP)}$$

8

Work Transfer

Work is defined as force acting upon an object to cause a displacement. There are three key words in this definition - force, displacement, and cause. In order for a force to qualify as having done *work* on an object, there must be a displacement and the force must *cause* the displacement.

There are several good examples of work which can be observed in everyday life - a horse pulling a plow through the fields, a father pushing a grocery cart down the aisle of a grocery store, a freshman lifting a backpack full of books upon her shoulder, a weightlifter lifting a barbell above her head, an Olympian launching the shot-put, etc. In each case described here there is a force exerted upon an object to cause that object to be displaced.

Mathematically, work can be expressed by the following equation.

$$W = F \times d \times \cos \theta$$

where F = force, d = displacement, and the angle (theta) is defined as the angle between the force and the displacement vector. Perhaps the most difficult aspect of the above equation is the angle "theta.". The angle measure is defined as the angle between the force and the displacement. To gather an idea of its meaning, consider the following three casses.

- *A*: A force acts rightward upon an object as it is displaced rightward. In such an instance, the force vector and the displacement vector are in the same direction. Thus, the angle between F and d is 0 degrees.
- *B*: A force acts leftward upon an object which is displaced rightward. In such an instance, the force vector and the displacement vector are in the opposite direction. Thus, the angle between F and d is 180 degrees.
- *C*: A force acts upward upon an object as it is displaced rightward. In such an instance, the force vector and the displacement vector are at right angles to each other. Thus, the angle between F and d is 90 degrees.

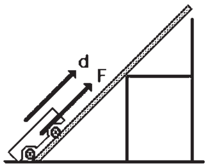
Let's consider case C above in more detail. case C involves a situation similar to the waiter who carried a tray full of meals above his head by one arm straight across the room at constant speed. The force supplied by the waiter on the tray is an upward force and the displacement of the tray is a horizontal displacement. As such, the angle between the force and the displacement is 90 degrees. If the work done by the waiter on the tray were to be calculated, then the results would be 0. Regardless of the magnitude of the force and displacement, F × d ×cosine 90 degrees is 0 (since the cosine of 90 degrees is 0). A vertical force can never cause a horizontal displacement; thus, a vertical force does not do work on a horizontally displaced object.

It can be accurately noted that the waiter's hand did push forward on the tray for a brief period of time to accelerate it from rest to a final walking speed. But once *up to speed*, the tray will stay in its straight-line motion at a constant speed without a forward force. And if the only force exerted upon the tray during the constant speed stage of its motion is upward, then no work is done upon the tray. Again, a vertical force does not do work on a horizontally displaced object.

The equation for work lists three variables - each variable is associated with one of the three key words mentioned in the definition of work (force, displacement, and cause). The angle theta in the equation is associated with the amount of force which causes a displacement. When a force is exerted on an object at an angle to the horizontal, only a part of the force contributes to (or causes) a horizontal displacement.

The Meaning of Theta

When determining the measure of the angle in the work equation, it is important to recognize that the angle has a precise definition - it is the angle between the force and the displacement vector. For instance, consider the activity performed in the given figure. A force was applied to a cart to pull it up an incline at constant speed. Several incline



Whenever F and d are
in the same direction,
θ = 0 degrees.

angles were used; yet, the force was always applied parallel to the incline. The displacement of the cart was also parallel to the incline. Since F and d were in the same direction, the angle was 0 degrees. The angle in the equation is defined as the angle between the force and the displacement vector.

Units

In the case of work (and also energy), the standard metric unit is the Joule (abbreviated "J"). One Joule is equivalent to one Newton of force causing a displacement of one meter. In other words,

The Joule is the unit of work.

1 Joule = 1 Newton × 1 meter

1 J = 1 Nm

In fact, any unit of force times any unit of displacement is equivalent to a unit of work. Some nonstandard units for work are shown below. Notice that when analysed, each set of units is equivalent to a force unit times a displacement unit.

Non-SI units of work include the erg, the foot-pound, the foot-poundal, and the liter-atmosphere.

Fluid

A fluid is any substance that conforms to the shape of its container. It may be either a liquid or a gas. A fluid is anything that would spill or float away if it weren't in a container (unless it's big enough to be held together by gravity like a star). If you can stir it up with a spoon or blow it through a straw, it's a fluid. Water is a fluid and so is air. In fact, all liquids and gases are fluids. In space and inside stars there's also another kind of fluid called a plasma.

The molecules in a solid are stuck together, but in a fluid they're free to move past each other. So if you had very small hands you could push one molecule of a fluid one way and another molecule the other way and off they would go in the direction you pushed them.

Compressibility of Fluids

All fluids are compressible. However, under some range of conditions, it is often possible to make the approximation that a fluid is incompressible. Water, for example, only changes its volume very slightly under extreme pressure.

Gases are much more compressible. The compressibility of air, for example, is part of our common experience. By blocking off a bicycle pump and pushing down on the handle, we can easily decrease the volume of the air by 50per cent, so that its density increases by a factor of two (the mass of air is constant). If we assume that the temperature remains constant (somehow), we know from the perfect gas law,

$$p = \rho RT$$

that the pressure must also increase by a factor of two. If the initial air was at atmospheric pressure, the pressure will rise by one atmosphere (14.696 psi, or 101,325 Pa). If we assume a pump diameter of 1.25 inch, then a force of 18.1 lbf will be required. This is not a large force, so that raising the pressure by two atmospheres above ambient pressure is easily done. We call pressures relative to zero pressure absolute pressure. This is the pressure that appears in the perfect gas law. Pressures measured relative to atmospheric pressure are called gauge pressures. The pressure measured by the most common types of pressure instruments is a gauge pressure since these instruments indicate the pressure relative to atmospheric pressure. A tire gauge, for instance, measures the pressure in a tire over and above the local atmospheric pressure. A vacuum gauge, in contrast, will measure the pressure below atmospheric: in common parlance a "vacuum" is any pressure lower than the ambient atmospheric pressure.

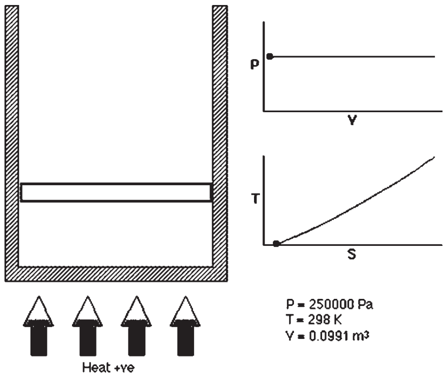
Even though gases are much more compressible than liquids (by perhaps a factor of 10^4), if the pressures are small the changes in density are also small. For example, if a 1per cent change in density is tolerated, then at constant temperature we can allow a 1per cent change in pressure. For air this corresponds to a change in altitude of about 85 meters, so that for changes in height of the order of tall buildings we can usually neglect the compressibility of air.

The compressibility of gases is also often discussed in terms of the parameter called the Mach number, which is the ratio of the fluid velocity to the speed of sound (the speed of sound for air at 20°C is 343 m/s = 1,126 ft/s = 768 mph). When a fluid increases its speed, there is a corresponding decrease in pressure. If the fluid velocity is small relative to the speed of sound (that is, the flow has a low Mach number), then the change in pressure when a fluid increases its velocity from zero to V is given by 1/2 the density times the velocity squared (in the absence of friction). This quantity is called the dynamic pressure:

$$\text{dynamic pressure} = \frac{1}{2}\rho V^2$$

If we again use a 1per cent level as a tolerable change in density, then if the temperature remains constant the allowed change in pressure is also equal to 1per cent (the process is more likely to be isentropic, but that does not change the argument very much). This requires a dynamic pressure less than 1per cent of the ambient pressure, so that at sea level where the density of air is about 1.2 kg/m^3 we are limited to velocities less than 40 m/s (132 ft/s or 90 mph), which corresponds to a Mach number of about 0.12. When we consider the flow of air over bicycles, we can always assume that the fluid has a constant density, and that the Mach number is not important.

Constant Pressure Process



Applying the first law of thermodynamics to the process

$$dU = dQ - dW$$

Replacing dW with the reversible work

$$dU = dQ - PdV$$

The volume will change as the gas is heated at constant pressure. To make calculations more straight forward, use ENTHALPY, H

$$H = U + PV$$

$$dH = dU + PdV + VdP$$

rearrange for dU

$$dU = dH - PdV - VdP$$

and substitute into the first law

$$dH - PdV - VdP = dQ - PdV$$

the PdV terms cancel out and since pressure is constant dP = 0, so that

$$dH = dQ$$

The definition of the specific heat at constant pressure

$$C_P = \frac{dH}{dT}$$

is used to replace dH in the first law

$$nC_p dT = dQ$$

$$Q = n\int_{T_1}^{T_2} C_p dT$$

During a constant pressure process, heat is added or removed and the temperature and volume change. T

he volume at the end of the process can be found using the ideal gas law and the work calculated from

$$W = P\Delta V$$

Entropy Change

Starting with the first law expression for the process

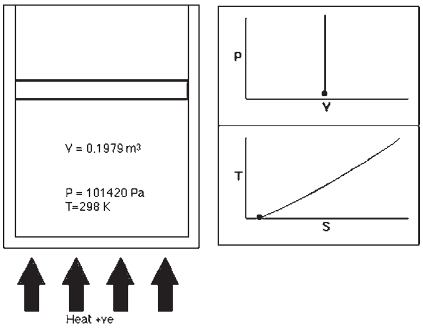
$$dH = dQ$$

and replacing dH from the definition of specific heat at constant pressure and Dq from the definition of entropy

$$nC_p dT = TdS$$

$$\Delta S = n\int_{T_1}^{T_2} \frac{C_p}{T} dT$$

Constant Volume Process



Applying the first law of thermodynamics to the process

$$dU = dQ - dW$$

Replacing dW with the reversible work

$$dU = dQ - PdV$$

since the volume is constant dV = 0 and

$$dU = dQ$$

using the definition of the specific heat at constant volume

$$C_v = \frac{dU}{dT}$$

to replace dU in the first law

$$dQ = nC_v dT$$

$$Q = n\int_{T_1}^{T_2} C_V dT$$

For a constant volume process, the addition or removal of heat will lead to a change in the temperature and pressure of the gas, as shown on the two graphs above

Entropy Change

To find the Entropy change, start with the expression derived from the first law

$$\mathbf{dU = dQ}$$

and replace **dU** using the definition of specific heat at constant volume and **dQ** using the definition of entropy

$$nC_V dT = TdS$$

$$\Delta S = n\int_{T_1}^{T_2} \frac{C_V}{T} dT$$

Effects of Pressure Changes on Fluid Properties

The predominant effect of an increase in pressure in a compressible fluid, such as a gas, is an increase in the density of the fluid. An increase in the pressure of an incompressible fluid will not have a significant effect on the density. For example, increasing the pressure of 100 °F water from 15 psia to 15,000 psia will only increase the density by approximately 6per cent. Therefore, in engineering calculations, it is assumed that incompressible fluids' density remain constant.

Effects of Temperature Changes on Fluid Properties

An increase in temperature will tend to decrease the density of any fluid. If the fluid is confined in a container of fixed volume, the effect of a temperature change will depend on whether the fluid is compressible.

If the fluid is a gas, it will respond to a temperature change in a manner predicted by the ideal gas laws. A 5per cent increase in absolute temperature will result in a 5per cent increase in the absolute pressure.

If the fluid is an incompressible liquid in a closed container, an increase in the temperature will have a tremendously greater and potentially catastrophic effect.

As the fluid temperature increases, it tries to expand, but expansion is prevented by the walls of the container. Because the fluid is incompressible, this results in a tremendous increase in pressure for a relatively minor temperature change. The change in specific volume for a given change in temperature is not the same at various beginning temperatures.

Resultant pressure changes will vary. A useful thumb rule for water is that pressure in a water-solid system will increase about 100 psi for every 1 °F increase in temperature.

Non Flow Energy Equation

Let a system boundary enclose only the water that is inside the reservoir. The underlying principle is that the net rate at which energy is transferred and transported into the system equals the rate of change of the energy of the system.

Internal energy is transported into and out of the system with the water flows and is lost from the system as heat transfer to the surroundings. When the relevant simplifying assumptions are made the situation is described by a first order differential equation in temperature. This can be integrated from the initial temperature of the water in the reservoir at time zero to give the temperature of the water at any future time. The flow rate of water into the system is steady. There is no flow out of the system until the overflow level is reached. Thereafter the flow rate out of the system is steady and equals the flow rate in. After a finite time the temperature of the water leaving will be within a specified tolerance of the eventual (infinite time) steady state value.

You may or may not agree with the simplifying assumptions mentioned here.

- The water can be regarded as an incompressible liquid.
- The specific heat of the water can be taken as constant.
- Kinetic energy of the water streams and the water in the reservoir can be neglected.
- Potential energy changes can also be neglected; they have no influence on the temperatures in this problem.
- Flow work terms (commonly dealt with by the use of the enthalpy property to include both flow work transfer and internal energy transport) and displacement work terms associated with the change in volume of the system boundary cancel out and do not affect the temperatures.
- A reservoir such as this may be subject to stratification and significant temperature variations may exist within it. For analysis purposes complete and continuous mixing of the water in the reservoir (without fluid friction) will be assumed.
- As a consequence of the ongoing mixing, the temperature of the water coming out of the reservoir is equal to the temperature of the water in the reservoir.

- From the mass balance point of view the loss of water from the surface can be neglected. However, the evapourative effect at the surface will be significant in energy terms (unless the air above the surface is saturated). It is common practice to deal with this as heat transfer between the water surface and the air.
- The rate of heat transfer from the water in the reservoir to the surroundings can be described and evaluated in terms of the temperature of the water, the temperature of the surroundings and the water level (if there is heat transfer through the side walls of the reservoir).

The non flow energy equation for the system can be written as follows:

$$\begin{aligned} \dot{m}_{\text{in}}u_{\text{in}} - \dot{m}_{\text{out}}u_{\text{out}} - \dot{Q}_{\text{out}} &= \frac{\mathrm{d}U}{\mathrm{d}t} \\ &= m\frac{\mathrm{d}u}{\mathrm{d}t} + u\frac{\mathrm{d}m}{\mathrm{d}t}] \\ &= m\frac{\mathrm{d}u}{\mathrm{d}t} + u\left(\dot{m}_{\text{in}} - \dot{m}_{\text{out}}\right) \end{aligned}$$

The following expressions describe the specific internal energy of the water, the rate of heat transfer out of the system to the surroundings and the mass of water in the system:

$$\begin{aligned} u &= c(T - T_{\text{ref}}) \\ Q_{\text{out}} &= k(T - T_{\text{surr}}) \\ m &= m_0 + (\dot{m}_{\text{in}} - \dot{m}_{\text{out}})t \end{aligned}$$

The differential equation describing the rate of change of the temperature reduces to:

$$\frac{\mathrm{d}T}{\mathrm{d}t} = \frac{\dot{m}_{\text{in}}c(T_{\text{in}} - T) - k(T - T_{surr})}{m_0 + (\dot{m}_{\text{in}} - \dot{m}_{\text{out}})t}$$

Where

T = Temperature
t = Time
m = Mass
U = Internal energy
u = Specific internal energy
Q = Heat transfer
c = Specific heat capacity
k = Heat transfer coefficient
$surr$ = Surroundings
ref = Reference zero state for u

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The Carnot Cycle

All standard heat engines (steam, gasoline, diesel) work by supplying heat to a gas, the gas then expands in a cylinder and pushes a piston to do its work. The catch is that the heat and/or the gas must somehow then be dumped out of the cylinder to get ready for the next cycle. We examine the first step, the expansion, then go on to the full cycle—Carnot's analysis. Carnot's aim was to figure out how to maximize the efficiency of a heat engine, and then work out what that efficiency was, that is, how much of the heat supplied was actually converted into the mechanical work done by the engine. Remember that he had in mind the analogy of the water wheel, at that time still a main driving force of industry. He knew that the most efficient water wheels were those that operated smoothly, the water went into the buckets at the top from the same level, it didn't fall through any height, and didn't splash around. In the limit of a frictionless wheel, with gentle flow on and off the wheel, the machine would be reversible—turning it in reverse to raise the water back would take the same amount of work the wheel had delivered as the water fell. This was clearly perfect efficiency, so these were to conditions to emulate in the heat engine. The analog to having the water flow into buckets at the same height, with no wasteful drop, is to have the heat from the heat supply flow into the gas at the same temperature. There must of course be a slight drop in temperature for the heat to flow at all, but this must be minimized. This means that as the heat is supplied and the gas expands, the temperature of the gas stays the same as that of the heat supply (the "heat reservoir") and the gas is expanding *isothermally*.

Isothermal Expansion

So the first question is: how much work is done by an isothermally expanding gas? Taking the temperature of the heat reservoir to be T_H (*H* for hot), the expanding gas follows the isothermal path $PV = nRT_H$ in the (P, V) plane.

The work done by the gas in a small volume expansion ΔV is just $P\Delta V$, the area under the curve.Hence the work done in expanding isothermally from volume V_a to V_b is the total area under the curve between those values,

$$\text{work done isothermally} = \int_{V_a}^{V_b} P\,dV = \int_{V_a}^{V_b} \frac{nRT_H}{V}\,dV = nRT_H \ln \frac{V_b}{V_a}.$$

Since the gas is at constant temperature T_H, there is no change in its internal energy during this expansion, so the total heat supplied must be $nRT_H \ln \frac{V_b}{V_a}$, the same as the external work the gas has done.

In fact, this isothermal expansion is only the first step: the gas is at the temperature of the heat reservoir, hotter than its other surroundings, and will be able to continue expanding even if the heat supply is cut off. To ensure that this further expansion is also reversible, the gas must not be losing heat to the surroundings. That is, after the heat supply is cut off, there must be no further heat exchange with the surroundings, the expansion must be *adiabatic*.

Adiabatic Expansion

The work done in an adiabatic expansion is like that done in allowing a compressed spring to expand against a force—equal to the work needed to compress the spring in the first place, for a perfect spring, and an adiabatically enclosed gas is essentially perfect in this respect. In other words, adiabatic expansion is reversible.

To find the work the gas does in expanding adiabatically from V_b to V_c, say, the above analysis is repeated with the isotherm $PV = nRT_H$ replaced by the adiabat $PV^{\gamma} = P_b V_b^{\gamma}$,

$$\text{work done adiabatically } W_{\text{adiabat}} = \int_{V_b}^{V_c} PdV = P_b V_b^{\gamma} \int_{V_b}^{V_c} \frac{dV}{V^{\gamma}} = P_b V_b^{\gamma} \frac{V_c^{1-\gamma} - V_b^{1-\gamma}}{1-\gamma}.$$

Again, this is the *area under the curve*, in this case under the adiabat, from *b* to *c* in the (*P*, *V*) plane.

Since points *b*, *c* are on the same adiabat, $P_c V_c^{\gamma} = P_b V_b^{\gamma}$, and the expression can be written more neatly:

$$W_{\text{adiabat}} = \frac{P_c V_c - P_b V_b}{1-\gamma}.$$

This is a useful expression for the work done since we are plotting in the (*P*, *V*) plane, but note that from the gas law $PV = nRT$, the numerator is just $nR(T_c - T_b)$, and from this $W_{\text{adiabat}} = nC_V(T_c - T_b)$, as of course it must be—this is the loss of internal energy that has been expended by the gas on expanding against external pressure.

We've looked in detail at the work a gas does in expanding as heat is supplied (isothermally) and when there is no heat exchange (adiabatically).

These are the two initial steps in a heat engine, but it is equally necessary for the engine to get back to where it began, for the next cycle. The general idea is that the piston drives a wheel, which continues to turn and pushes the gas back to the original volume.

But it is also essential for the gas to be as cold as possible on this return leg, because the *wheel* is now having to expend work on the *gas*, and we want that to be as little work as possible—it's costing us. The colder the gas, the less pressure the wheel is pushing against.

To ensure that the engine is as efficient as possible, this return path to the starting point (P_a,V_a) must also be reversible. We can't just retrace the path taken in the first two legs, that would take all the work the engine did along those legs, and leave us with no net output. Now the gas cooled during the adiabatic expansion from *b* to *c*, from T_H to T_C, say, so we can go some distance back along the reversible colder isotherm T_C.

But this won't get us back to (P_a,V_a), because that's on the T_H isotherm. The simplest option—the one chosen by Carnot—is to proceed back along the cold isotherm to the point where it intersects the adiabat through a, then follow that isotherm back to *a*. (One could follow a more complicated path: provided it was composed of segments each being adiabatic or isothermal, it would be reversible.) Carnot's cycle is around that curved quadrilateral having these four curves as its sides.

Efficiency of the Carnot Engine

In a complete cycle of Carnot's heat engine, the gas traces the path *abcd*. The important question is: what fraction of the heat supplied from the hot reservoir (along the red top isotherm) is turned into mechanical work? This fraction is called the *efficiency* of the engine.

The work output along any curve in the (*P*, *V*) plane is just $\int PdV$—the area under the curve, but it will be *negative* if the volume is decreasing! So the work done by the engine during the hot isothermal segment is the area *abfh*, then the adiabatic expansion adds the area *bcef*, but as the gas is compressed back, the wheel has to do work on the gas equal to the area *cdge* as heat is dumped into the cold reservoir, then *dahg* as the gas is recompressed to the starting point.

The bottom line is that the total work done by the gas is the area bounded by the four paths: the curved "parallelogram" in the picture above. We could compute this area by finding $\int PdV$ for each segment, but that is unnecessary—on completing the cycle, the gas is back to its initial temperature, so has the same internal energy. *Therefore, the work done by the engine must be just the difference between the heat supplied at* T_H *and that dumped at* T_C.

Now the heat supplies along the initial hot isothermal path *ab*, equal to the work done along that leg, is (from the paragraph above on isothermal expansion):

$$Q_H = nRT_H \ln \frac{V_b}{V_a}$$

and the heat dumped into the cold reservoir along *cd* is

$$Q_C = nRT_C \ln \frac{V_c}{V_d}.$$

The difference between these two is the net work output. This can be simplified using the adiabatic equations for the other two sides of the cycle:

$$T_H V_b^{\gamma-1} = T_C V_c^{\gamma-1}$$

$$T_H V_a^{\gamma-1} = T_C V_d^{\gamma-1}.$$

Dividing the first of these equations by the second,

$$\left(\frac{V_b}{V_a}\right) = \left(\frac{V_c}{V_d}\right)$$

and using that in the preceding equation for Q_C,

$$Q_C = nRT_C \ln \frac{V_a}{V_b} = \frac{T_C}{T_H} Q_H.$$

[illegible] w be written simply:

$$W = Q_H - Q_C = \left(1 - \frac{T_C}{T_H}\right) Q_H.$$

Therefore the efficiency of the engine, defined as the fraction of the ingoing heat energy that is converted to available work, is

$$\text{efficiency} = \frac{W}{Q_H} = 1 - \frac{T_C}{T_H}.$$

These temperatures are of course in degrees Kelvin, so for example the efficiency of a Carnot engine having a hot reservoir of boiling water and a cold reservoir ice cold water will be $1 - (273/373) = 0.27$, just over a quarter of the heat energy is transformed into useful work.

The Second Law of Thermodynamics

After all the effort to construct an efficient heat engine, making it reversible to eliminate “friction” losses, etc., it is perhaps somewhat disappointing to find this figure of 27per cent efficiency when operating between 0 and 100 degrees

Celsius. Surely we can do better than that? After all, the heat energy of hot water is the kinetic energy of the moving molecules, can't we find some device to channel all that energy into useful work? Well, we can do better than 27per cent, by having a colder cold reservoir, or a hotter hot one. But there's a limit: we can never reach 100per cent efficiency, because we cannot have a cold reservoir at $T_C = 0K$, and even if we did after the first cycle the heat dumped into it would warm it up!

The Second Law of Thermodynamics states that *we cannot devise an engine, working in a cycle, that simply extracts heat from a hot reservoir and delivers mechanical work*.

This means any engine that takes heat and delivers work also dumps out some of the initial heat to a reservoir at a lower temperature.

It's important to note that the First Law of Thermodynamics, the conservation of total energy including heat, would not be violated by an engine that powered a ship by extracting heat energy from the surrounding water. This Second Law is saying something new. And, this Second Law does not follow from the First by logical deduction—it comes (like the First) from experiment and observation.

The Most Efficient Engine

An important consequence of the second Law is that *no engine can be more efficient than the Carnot cycle*. Essentially, this is because a "super efficient" engine, if one existed, could be used to drive a Carnot cycle in reverse, which would pump back to the hot reservoir the heat the super efficient engine dumped in the cold reservoir, and the net effect of the two coupled engines would be to take heat from the hot reservoir and do work, contradicting the Second Law.

To see this, we plot the heat/energy flow for the Carnot cycle:

Here $Q_H = Q_C + W$ (all expressed in Joules, of course).

Since the engine is reversible, it can also be run backwards (this would be a refrigerator: outside work is supplied, and heat is extracted from a cold reservoir and dumped into a hot reservoir:

Suppose now we have a super efficient engine, represented by the first diagram above, and dumping the same heat per cycle Q_C into the cold reservoir, but taking in more heat energy $Q_H + \Delta$ Joules from the hot reservoir, and performing work $W + \Delta$. Now, we hook up our super efficient engine to the "Carnot refrigerator" in the diagram above. The refrigerator sucks out of the cold reservoir all the heat the super efficient engine dumped there, and needs W Joules of work per cycle to do it. The super efficient engine can provide this, and there are still Δ Joules of work to spare. Of course, the Carnot refrigerator has also dumped Q_H Joules of heat in the hot reservoir. But the bottom line is that between them, the super efficient engine and the Carnot refrigerator have extracted Δ Joules of heat from the hot reservoir and performed Δ Joules of work—contradicting the Second Law.

The Second Law therefore forces the conclusion that no amount of machine design will produce an engine more efficient than the Carnot cycle. The rather low ultimate efficiencies this dictated came as a shock to nineteenth century engineers.

Molecular Collisions

In analyzing the gas so far, we've ignored collisions between molecules, and in fact for air at ordinary temperatures the relationship between pressure, volume and temperature came out correctly. Furthermore, Maxwell's speed distribution can be used to find what fraction of the molecules in a planet's atmosphere are moving at above escape velocity, so we can predict what gases will remain surrounding a planet, given the gravitational force near the surface, and the temperature.

But there are other phenomena for which an understanding of collisions is all-important. For example, if two different gases, say oxygen and nitrogen, in a container at the same pressure and temperature are separated by a partition, how quickly will they mix once the partition is removed? Assuming room temperature, the molecules will be moving at hundreds of meters per second, so one might imagine the mixing will be over in hundredths of a second. But *that is not the case at all*—observationally, it might take an hour, for a box holding a few liters. This surprisingly slow penetration of one gas by another is called *diffusion*. The reason it takes the gases so long to mix becomes evident on tracking one molecule as it enters the other gas. Think of an oxygen molecule moving into nitrogen. We'll take O_2 and N_2 to be little spheres of diameter d. So now visualize the little O_2 sphere shooting into this space where all these other spheres are moving around. *Temporarily, for ease of visualization, let's imagine all the other spheres to be at rest.*

How far can we expect the O_2 to get before it hits an N_2? The *average* distance before a collision is called the *mean free path*. Let's try to picture how much room there is to fly between these fixed N_2 spheres. We do know that if it were *liquid* nitrogen, there would be *very little* room: liquids are just about incompressible, so the molecules must be touching. Roughly speaking, a molecule of diameter d will occupy a cubical volume of about d^3 (there has to be some space left over—we can pack cubes to fill space, but not spheres.) We also know that liquid nitrogen weighs about 800 kg per cubic meter, whereas N_2 gas at room temperature (and pressure) weighs about 1.2 kg per cubic meter, a ratio of 670. This means that *on average each molecule in the gas has 670 times more room*—that is, it has a space 670 times the volume d^3 we gave it in the liquid. So in the gas, the average center-to-center separation of the molecules will be the cube root of 670, which is about $8.75d$. So the picture is a gas of spheres of diameter d, placed at random, but separated on average by distances of order $10d$. It's clear that shooting an oxygen molecule into this it will get quite a way.

We now try to estimate just how far an O_2 will get, on average, as it shoots into this forest of spheres. Picture the motion of the center of the oxygen molecule. Before any collision, it will be moving on a straight-line path. Just how close does the O_2 center have to get to an N_2 center for a hit? Taking both O_2, N_2 to be spheres of diameter d, if an N_2 center lies within d of the O_2 center's path, there will be a hit. So we can think of the O_2 as sweeping out a volume, a cylinder of *radius d* centered on its path, hitting and deflecting if it encounters an N_2 *centered within that cylinder*. So how far will it get, on average, before a hit? In traveling a distance x, it sweeps out a volume $\pi d^2 x$. Now picture it going through the gas for some considerable length of time, so there are many collisions. The volume swept out will look like a stovepipe, long straight cylindrical sections connected by elbows at the collisions. The total volume of this stovepipe (ignoring tiny corrections from the elbows) will be just $\pi d^2 L$, L being the total length, that is, the total distance the molecule traveled. If the density of the nitrogen is n molecules per cubic meter, the number of N_2's in this stovepipe volume will be $\pi d^2 L n$, in other words, this will be the number of collisions. Therefore, the average distance *between* collisions, the mean free path l, is given by:

$$\text{mean free path } l = \frac{\text{total distance traveled}}{\text{number of collisions}} = \frac{L}{\pi d^2 L n} = \frac{1}{\pi d^2 n}$$

So what is n? We estimated above that each molecule has space $670d^3$ to itself, so n is just how many of those volumes there are in one cubic meter, that is, $n = 1/670d^3$.

Therefore, the mean free path is given by

$$l = \frac{1}{\pi d^2 n} = \frac{670d^3}{\pi d^2} = 200d.$$

Notice that this derivation of the mean free path *in terms of the molecular diameter* depends *only* on knowing the *ratio of the gas density to the liquid density—it does not depend on the actual size of the molecules*! But it *does* mean that if we can somehow measure the mean free path, by measuring how fast one gas diffuses into another, for example, we can deduce the size of the molecules, and historically this was one of the first ways the size of molecules was determined, and so Avogadro's number was found.

Let us now put in some numbers to find this mean free path: for O_2, N_2, $d = 0.3\text{nm}$, so the mean free path $l = 60\text{nm}$, or $6\times10^{-8}\text{m}$. The speed of the molecules at room temperature v is approximately 500 meters per sec., so the molecule has of order 10^{10} collisions per second!

Actually, there is one further correction we should make. We took the N_2 molecules to be at rest, whereas in fact they're moving as fast as the oxygen molecule, approximately. This means that even if the O_2 is temporarily at rest, it can undergo a collision as an N_2 comes towards it. Clearly, what really counts in the collision rate is the *relative* velocity of the molecules. Defining the average velocity as the root mean square velocity, if the O_2 has velocity $\vec{v}_1$ and the N_2 $\vec{v}_2$, then the square of the relative velocity $\overline{(\vec{v}_1-\vec{v}_2)^2} = \overline{\vec{v}_1^2} - 2\overline{\vec{v}_1\cdot\vec{v}_2}\cdot + \overline{\vec{v}_2^2} = \overline{\vec{v}_1^2} + \overline{\vec{v}_2^2}$, since $\overline{\vec{v}_1\cdot\vec{v}_2}$ must average to zero, the relative directions being random. So the average *square* of the relative velocity is twice the average square of the velocity, and therefore the average root-mean-square velocity is up by a factor “2, and the collision rate is increased by this factor. Consequently, the mean free path is *decreased* by a factor of “2 when we take into account that *all* the molecules are moving.

Our final result, then, is that the mean free path

$$l = \frac{1}{\sqrt{2}\pi d^2 n}.$$

Finding the mean free path is—literally—the first step in figuring out how rapidly the oxygen atoms will diffuse into the nitrogen gas, and of course vice versa.

What we really want to know is just how much we can expect the gases to have intermingled after a given period of time. We'll just follow the one molecule, and estimate how far it gets. To begin with, let's assume for simplicity that it tales steps all of the same length l, but after each collision it bounces off in a random direction. So after N steps, it will have moved to a point

$$\vec{L} = \vec{l}_1 + \vec{l}_2 + \vec{l}_3 + \ldots + \vec{l}_N ,$$

where each vector $\vec{l}_j$ has length l, but the vectors all point in random different directions.

If we now imagine many of the oxygen molecules following random paths like this, how far on average can we expect them to have drifted after N steps? (note that they could with equal likelihood be going backwards!) The appropriate measure is the root-mean-square distance,

$$\overline{\vec{L}^2} = \overline{\left(\vec{l}_1 + \vec{l}_2 + \vec{l}_3 + \ldots \vec{l}_N\right)^2} = Nl^2 + \sum_{i,j} \overline{\vec{l}_i \cdot \vec{l}_j}$$

Since the direction after each collision is completely random, $\overline{\vec{l}_i \cdot \vec{l}_j} = 0$, and the root-mean-square distance $\sqrt{\overline{\vec{L}^2}} = \sqrt{N}\, l$.

If we allow steps of different lengths, the same argument works, but now l is the root-mean-square path length.

The important factor here is the $\sqrt{N}$. Recall from above that $l = 60\,\mathrm{nm}$, or $6 \times 10^{-8}\,\mathrm{m.}$, and there are of order 10^{10} collisions per second. This means that the average distance diffused in one second is $\sqrt{10^{10}}\, l = 10^5 l$, say half a centimeter. The average distance in one hour would be only 60 times this, or 30 cm., one foot, and in a day about five feet—the average distance traveled is only increasing as the *square root* of the time elapsed!

This is a very general result. For example, suppose we have a gas in which the mean free path is l and the average speed of the molecules is v. Then the average time between collisions $\tau = l / v$. The number of collisions in time t will be t/τ, so the average distance a molecule moves in time t will be $r = l\sqrt{t/\tau}$.

A famous mystery cleared up by arguments like this was that Newton predicted the speed of sound would be given by $c^2 = B/\rho$, as we discussed earlier in the course, with *B* the bulk modulus. But when *B* was measured carefully by slowly compressing air, the result was in error by about 30per cent! The speed of sound predicted a higher (stiffer) bulk modulus.

The explanation turned out to be that in a slow measurement of the bulk modulus, the gas stays at the same temperature—the heating caused by slow compression leaks away. But if the compression is rapid, the gas heats up and so the pressure goes up more than if it had stayed at the same temperature. So the question is whether the compression and decompression as a sound wave passes through is so rapid that the heated-up gas doesn't have time to spread to the cooled regions. For sound at say 1000Hz, the wavelength is 34 cm. If compression heats gas locally, the hot molecules will diffuse away in a similar manner to that discussed above. They will be slightly faster than the average molecules. In 1/1000 th of a second, they will have 10^7 collisions, so will travel about $\sqrt{10^7}\,l = 3000l = 0.2\,\text{mm}$. This tiny distance compared with the wavelength of the sound wave means that during the compression/decompression cycles as the wave passes through, the heat has no chance to dissipate—so, effectively, it's like compressing a gas in an insulated container, it's harder to compress than it would be if the heat generated could flow away, and the bulk modulus is higher by an amount (around 30per cent) we shall work out in a forthcoming lecture.