Entropy and the Second Law[1]

Minimalist text: *Basic Chemical Thermodynamics*, E. B. Smith

Overview/History

The Second Law points the way to equilibrium. It may be used to calculate the equilibrium constant for an endothermic or exothermic reaction, to show that a perfect gas will expand to fill its container, and to show that heat flows from a hotter body to a cooler body.

Entropy: Movitation

The change of energy alone is not sufficient to determine the direction of a spontaneous process

At one time it was believed that a criterion for a reaction to occur spontaneously was that the reaction be *exothermic*.

More generally, it was believed that all systems evolve so as to *minimize their energy*, eg an object spontaneously slides downhill, not uphill.

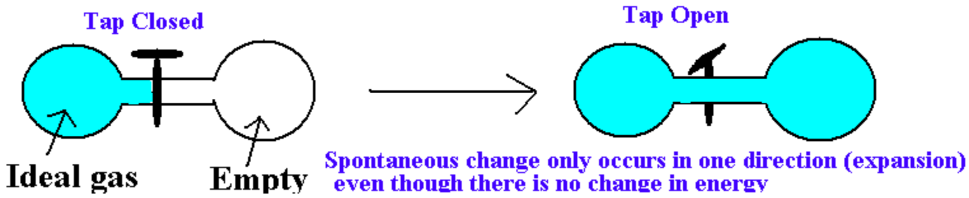
Counterexamples

Endothermic reaction

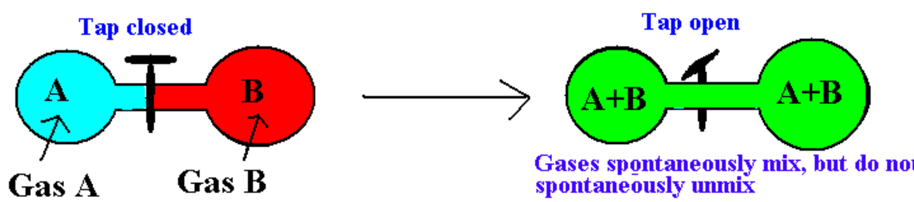
$$Ba(OH)_2(s) + 2NH_4NO_3(s) \rightarrow Ba(NO_3)_2(s) + 2H_2O(l) + 2NH_3(aq)$$

[1]Paul Maslen, Rm 428 B&S, ext 6282, maslen@crab.rutgers.edu
http://crab.rutgers.edu/ maslen/Courses/PChemI

No energy change In an *isolated* system the energy is constant, but in some cases spontaneous change only occurs in one direction. Eg when a tap is opened a gas will spontaneously expand but the reverse process never occurs,



Similarly, two gases will mix spontaneously, but the reverse never occurs,



Nonequilibrium isolated systems evolve in a direction that increases their disorder

- Looking at the two ideal-gas examples from a microscopic (molecular) point of view, each process involves an increase in disorder or randomness of the system.
- In the case of the expanding gas, we initially know that each gas molecule is in the left-hand container. But after the gas has expanded each molecule could be in either container, and so its location is more uncertain/random than before. The same considerations apply to the mixing of two gases
- These examples suggest that systems seek to evolve so as to
  - minimize their energy
  - maximize their disorder
- There is competition between minimizing energy and maximizing disorder.
  - In a simple mechanical system disorder is insignificant (few degrees of freedom), so energy minimization dominates.
  - In the mixing of two gases the energy changes are negligible and disorder dominates.
  - In general some compromise between the two processes must be met.

Entropy: a thermodynamic state function for disorder

Heat transfer $\not{d}q$ is related to disorder, since the disorder of a system increases when it is heated. [Eg when a crystal melts the disorder of the molecular arrangement increases.] But heat is not a very convenient mathematical quantity, because it is an inexact differential. We want an *exact* differential, ie we want a *state function*.

Maths review: Inexact differentials and integrating factors

Given an *inexact* differential df, eg

$$df(x, y) = xdy - ydx$$

it may be possible to produce an exact differential dg by multiplying df by an **integrating factor** $I(x, y)$,

$$dg(x, y) = I(x, y)\, df(x, y)$$

In this example

$$I = 1/y^2$$

is an integrating factor since

$$\begin{aligned} dg(x, y) &= \frac{1}{y^2}(xdy - ydx) \\ &= \frac{x}{y^2}dy - \frac{1}{y}dx \end{aligned}$$

is exact.

Another example: $\not{d}w$ can be converted to an exact differential by multiplying by $\frac{1}{P}$,

$$dV = \frac{1}{P}\not{d}w$$

so $\frac{1}{P}$ is an integrating factor for $\not{d}w$.

If we can find an integrating factor for heat then we'll have the differential of the desired state function for disorder!

An integrating factor for heat

$$\not{d}q = dU - \not{d}w = dU + PdV$$

For a **monoatomic ideal gas**

$$U(T) = \frac{3}{2}nRT$$

So

$$dU = \frac{3}{2}nRdT$$

So in this case

$$\not{d}q = \frac{3}{2}nRdT + PdV = \frac{3}{2}nRdT + \frac{nRT}{V}dV$$

Exercise Show that $\not{d}q$ is not exact.

Dividing by T produces the desired exact differential,

$$dS = \frac{\not{d}q}{T} = \frac{3}{2}\frac{nR}{T}dT + \frac{nR}{V}dV$$

V.I.P. Exercise Show that dS is exact.

Bonus Exercise Integrate dS to obtain $S(T, V)$ for a monoatomic ideal gas.

In conclusion, for a monoatomic ideal gas the integrating factor for $\not{d}q$ is $\frac{1}{T}$, and the new state function S is called Entropy.

Definition of Entropy

Entropy is defined as

$$\boxed{\mathbf{ds} = \frac{\text{đ}\mathbf{q}_{\text{rev}}}{\mathbf{T}}}$$

where $đq_{\text{rev}}$ is the heat absorbed by the system during a **reversible** process.

N.B. **S is a state function**, and dS is an exact differential, even though q is not. Thus ΔS is independent of path and hence is much more convenient to use than Δq. For example, it is often convenient to calculate the energy along a reversible path, even though the process of interest is irreversible. All that matters is the initial and final states.

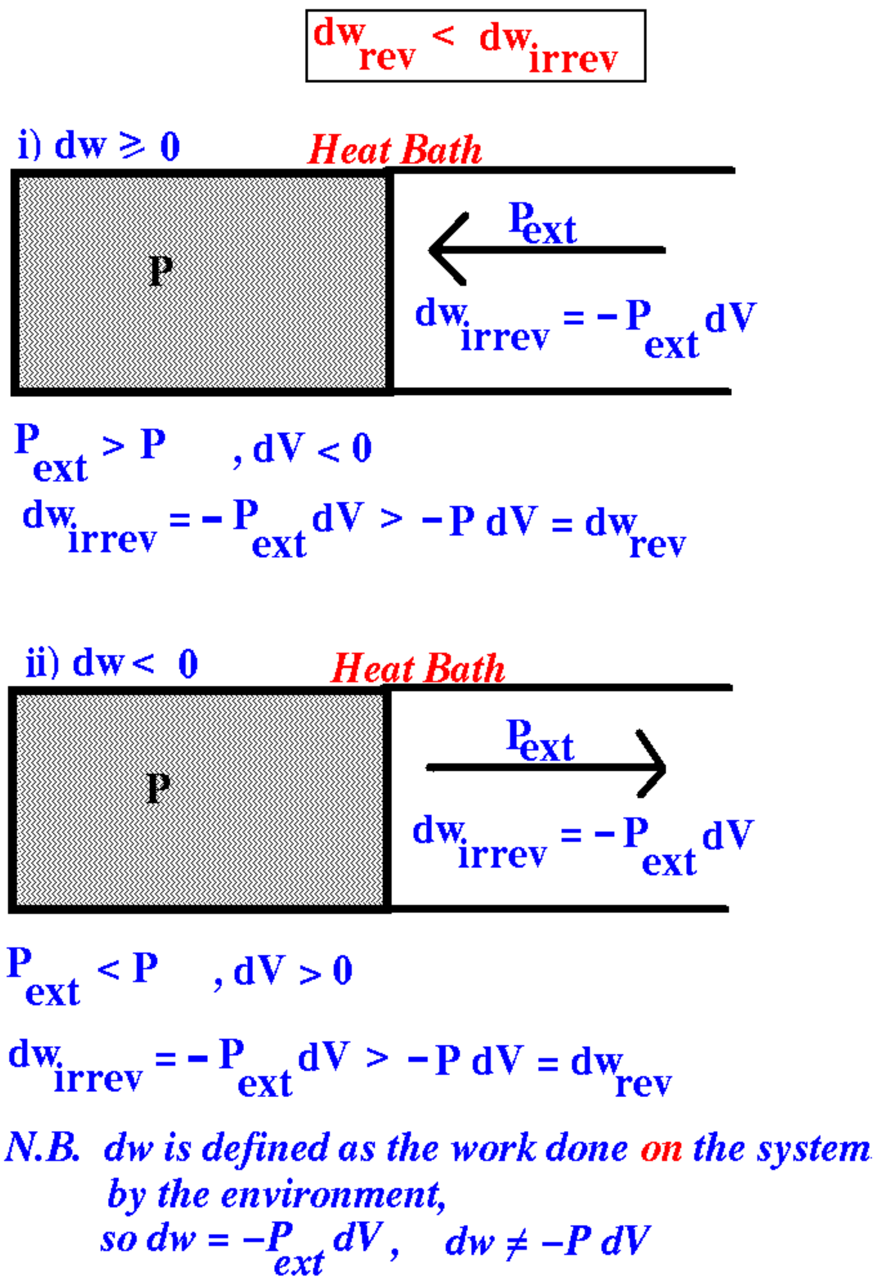
Entropy is the cornerstone of thermodynamics. Although it not initially as familiar as heat, it may be readily understood in terms of a microscopic picture outlined later in this section.

The Second Law *postulates* that entropy is a state function for all substances, not just for a monoatomic ideal gas. It cannot be proven, but it can be made highly plausible. If one considers a thermally isolated piston ($đq = 0$), then if the piston is compressed or expanded and finally returned to its initial volume the temperature will always be greater than or equal to the initial temperature. Caratheodory was able to show that this is all one needs to assume in order to deduce the equation for entropy. Historically entropy was discovered by considering the efficiency of heat-engines (Carnot engines). All of these approaches require considerable effort. We'll skip these more general 'derivations' of entropy, though if you're curious there is a section on heat-engines/Carnot engines in Alberty.

Reversible and Irreversible Heat and Work

Next we want to show that $\text{đ}q_{\mathrm{rev}} > \text{đ}q_{\mathrm{irrev}}$. It is easier to proceed indirectly, by showing that $\text{đ}w_{\mathrm{rev}} < \text{đ}w_{\mathrm{irrev}}$, and then combining this with the First Law:

1. $\text{đ}w_{\mathrm{rev}} < \text{đ}w_{\mathrm{irrev}}$
   The reversible work is less than the irreversible work.



2. $\boxed{đq_{\mathbf{rev}} > đq_{\mathbf{irrev}}}$
In the previous example the change of state dU can be caused by either a reversible or an irreversible process,

$$\begin{aligned} dU &= đq_{\text{rev}} + đw_{\text{rev}} = đq_{\text{irrev}} + đw_{\text{irrev}} \\ \text{therefore} \quad đq_{\text{rev}} - đq_{\text{irrev}} &= đw_{\text{irrev}} - đw_{\text{rev}} \\ \text{from part (1)} \quad & \quad đw_{\text{irrev}} - đw_{\text{rev}} > 0 \\ \text{so} \quad đq_{\text{rev}} - đq_{\text{irrev}} &> 0 \quad \text{as desired.} \end{aligned}$$

Entropy for Reversible and Irreversible Processes

Combining $dS = đq_{\text{rev}}/T$ with $đq_{\text{rev}} > đq_{\text{irrev}}$ gives

$$ds = \frac{đq_{\text{rev}}}{T} > \frac{đq_{\text{irrev}}}{T} \qquad \boxed{\mathbf{ds} \geq \frac{đ\mathbf{q}}{\mathbf{T}}}$$

It is often useful to rearrange this as

$$đq \leq TdS$$

Combined First and Second Laws

The first law is $dU = đq + đw = đq - P_{\text{ext}}dV$. Combining this with $đq \leq TdS$ gives,

$$\boxed{\mathbf{dU \leq TdS - PdV}}$$

where T and P are the **environmental** temperature and pressure, and the equality holds for reversible processes. This equation is useful because all the variables — $U, T, S, P, V,$ — are state functions. It can be rearranged to express dS in terms of dU and dV.

This equation, together with $dS \geq đq/T$, are the ones to remember. The preceding equations/derivation are not particularly important. It is important to remember that the equality only holds for reversible processes.

So far we haven't defined the Second Law. For our purposes, $dS \geq đq/T$ together with $T \geq 0$ constitute the Second Law.

Entropy Changes in an *Isolated* System

Consider an isolated system, $\boldsymbol{đq = đw = 0}$.

reversible change $dS = \dfrac{đq_{\text{rev}}}{T} = 0$

irreversible change $dS > \dfrac{đq_{\text{irrev}}}{T} = 0$

Thus,

$$\boxed{dS \geq 0 \qquad \text{isolated system} \quad đq = đw = 0}$$

Comment: the universe is (probably) an isolated system, so its entropy is increasing!

Exercise Suppose a cylinder is compressed rapidly (irreversibly), and then return it to its original volume and temperature. What can you say about

- ΔSsystem
- ΔSenvironment

Maximum entropy and minimum energy principles

The easiest way to show that entropy increases and energy decreases is to start from the combined first and second law,

$$dU \leq TdS - PdV$$

If S and V are constant then the right hand side is zero and we get the **minimum energy principle**,

$$\boxed{\mathbf{dU)_{S,V} \leq 0}}$$

Note that this only applies when the entropy and volume are constant, a rather inconvenient set of constraints.

The combined first and second law can be rearranged to express dS in terms of dU and dV,

$$dS \geq dU + PdV$$

If U and V are constant we recover the maximum entropy principle,

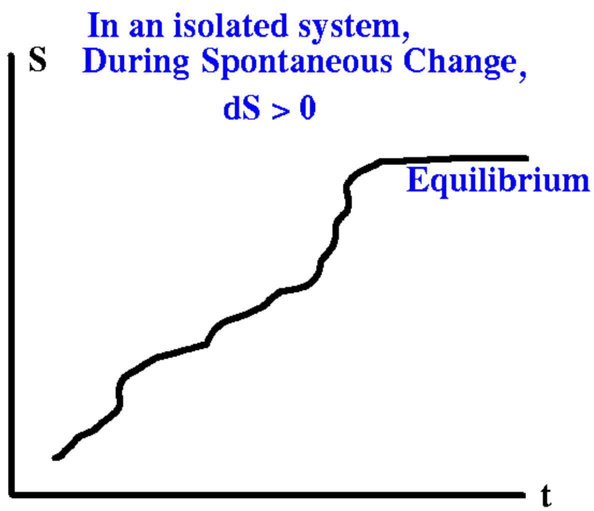
$$\boxed{\mathbf{dS)_{U,V} \geq 0}}$$

The point to remember is that the minimum energy principle and maximum entropy principle can easily be derived from the combined first and second law.

Exercise Show the the restrictions of constant (U, V) in the maximum entropy principle are equivalent to the restrictions $đq = đw = 0$ used earlier in this section.

Spontaneous Change and Equilibrium

Any change that spontaneously occurs in an *isolated* system leads to an increase in entropy, $dS > 0$. These changes can't spontaneously be reversed, because this would require $dS < 0$.



If an isolated system is left for long enough it will eventually reach a *state of maximum entropy*. Any further change would involve $dS < 0$, so it cannot occur spontaneously.

In an Isolated System ($\not{d}q = \not{d}w = 0$)
Equilibrium is the State of Maximum Entropy

This maximum-entropy principle can be used to derive a number of other variational principles for systems at equilibrium. One familiar example is that a mass in a graviational field moves to the position of minimum potential energy — the minimum energy principle. The maximum entropy principle is not always convenient to apply, because it requires an isolated system. One hint on how to adapt this to a non-isolated system such as a system in a heat bath is to use the combined first and second laws to write entropy as,

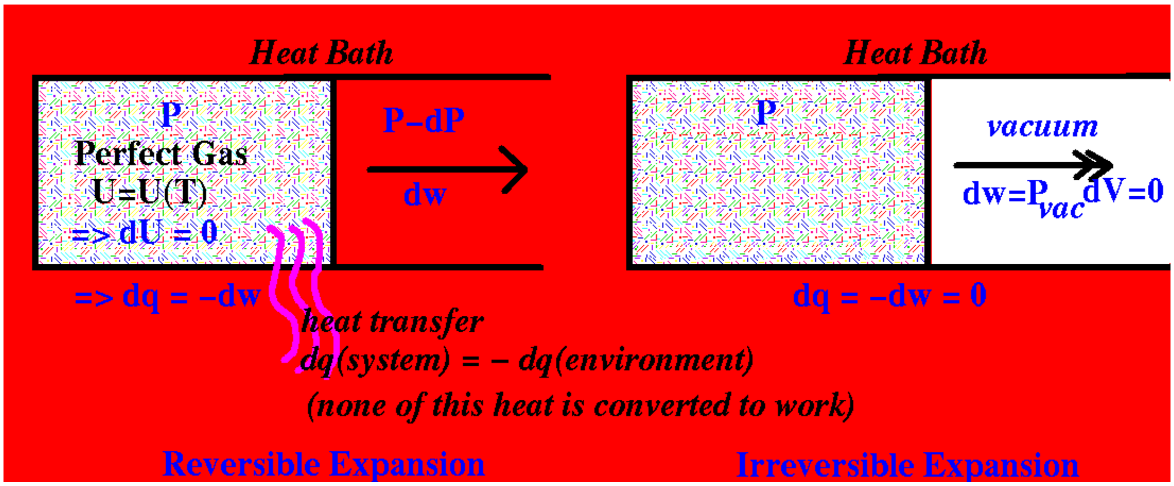
$$dS \geq \frac{1}{T}dU + \frac{P}{T}dV$$

The *independent* variables here are U and V, ie the *natural variables* for entropy are U and V, $S = S(U, V)$. The maximum entropy principle holds for an isolated system, where *the natural variables are constant.* This suggests that, to obtain a variational principle for a system at constant temperature and volume, we first transform entropy to be a state function whose natural variables are T and V. This is easily achieved by taking the $U \leftrightarrow T$ Legendre transform, $S(U, V) - > X(T, V)$ We'll meet several thermodynamic variational principles in the next sections.

Examples

Isothermal Expansion of a Perfect Gas

Consider the expansion of a gas in a piston.



In a reversible expansion $dS = \text{đ}q/T$. Heat flows directly from the system to the environment, or vice versa, so

$$\begin{aligned} \text{đ}q_{\text{system}} &= -\text{đ}q_{\text{environment}} \\ \text{and hence} \quad dS_{\text{system}} &= -dS_{\text{environment}} \\ \text{therefore} \quad dS_{\text{overall}} &= dS_{\text{system}} + dS_{\text{environment}} = 0 \end{aligned}$$

ie *There is no overall change in entropy during a reversible process.* It is easy to calculate dS_{system} for a perfect gas. A **perfect gas** is defined as an ideal gas whose internal energy U depends only on temperature, $U = U(T)$, not on pressure or volume. In an *isothermal* expansion the temperature is constant, so

$$\begin{aligned} dU &= 0 \\ \text{but} \quad dU &= \text{đ}q_{\text{rev}} + \text{đ}w \\ \text{so} \quad \boldsymbol{\text{đ}q_{\text{rev}}} &= \boldsymbol{-\text{đ}w} \\ &= PdV = \frac{nRT}{V}dV \\ \text{so} \quad \Delta q_{\text{rev}} &= nRT\int_A^B \frac{dV}{V} = nRT\ln\frac{V_B}{V_A} \end{aligned}$$

and hence

$$\boxed{\Delta S_{\text{system}} = \frac{\Delta q_{\text{rev}}}{T} = nR\ln\frac{V_B}{V_A}}$$

Irreversible expansion Consider now the isothermal expansion of the perfect gas into a *vacuum.* The change in entropy of the *system* is the same as for the reversible process, because the initial and final states of the system are the same in both cases.

For the vacuum,

$$\begin{aligned} P_{\text{ext}} &= 0 \\ \text{so} \quad đw &= -P_{\text{ext}} dV = 0 \\ \text{and} \quad đq &= -đw = 0 \end{aligned}$$

so this is an *adiabatic* expansion.

Some thought suggests that

$$\Delta S_{\text{vacuum}} = 0$$

[It is easiest to adopt a microscopic (molecular) point of view, and make the rather tenuous argument that a vacuum is 'nothing' and therefore can't have order/disorder, and therefore can't have entropy! A related way to think about it is that it is not possible to set up pressure-waves in a vacuum, so the vacuum is always equilibrated during the expansion of the piston. In fact the same final state of the *vacuum* could be reached by expanding the piston slowly (reversibly) and adiabatically, in which case $dS_{\text{vacuum}} = dq/T = 0$. See also Macquarrie sec. 20.6 and the top of page 835]

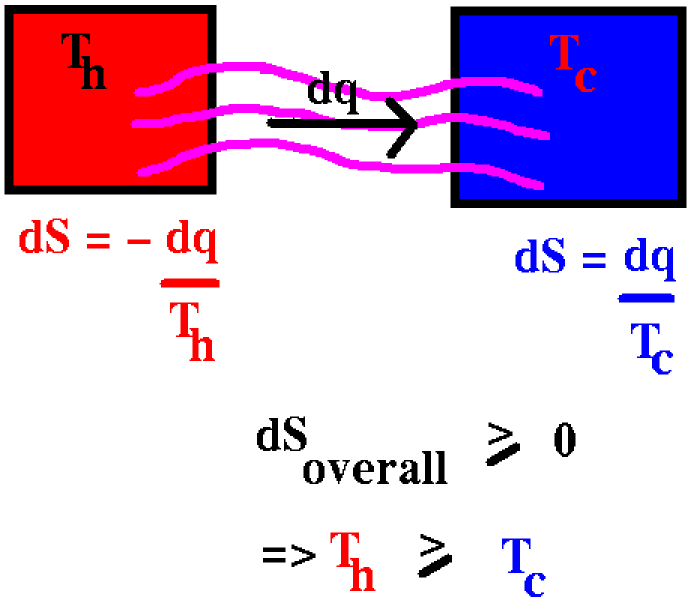
Thus in this case

$$\Delta S_{\text{overall}} = nR \ln \frac{V_B}{V_A} + 0 = nR \ln \frac{V_B}{V_A}$$

As $V_B > V_A$,
the overall entropy increases during the irreversible process.

The entropy change of the perfect gas is the same for the reversible and irreversible expansions, but the overall entropy change is different in the two cases.

Direction of Heat Flow



Heat flows from the hotter to the cooler body

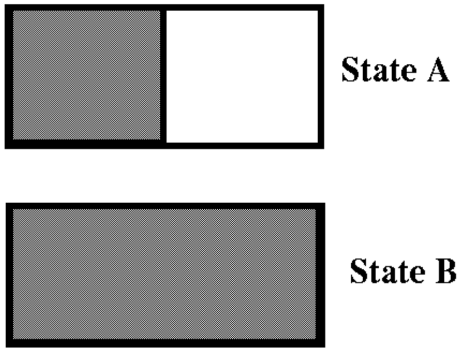
Consider heat flowing reversibly from a reservoir at temperature T_h to a reservoir at T_c.

$$\begin{aligned} dS &= -\frac{\not{d}q}{T_h} + \frac{\not{d}q}{T_c} \\ &= \not{d}q \frac{T_h - T_c}{T_h T_c} \end{aligned}$$

In order for entropy to increase we must have $T_h > T_c$,
ie *heat flows from the hotter to the cooler reservoir.*

Microscopic Basis for Entropy

Consider M gas molecules, first contained in one half of a container, and then allowed to occupy the entire volume.



The probability that any one molecule is in the left half is 1/2, and the probability all the molecules are in the left half is $\left(\frac{1}{2}\right)^M$. Thus the probability of being in state A relative to state B is

$$\frac{p_A}{p_B} = \left(\frac{1}{2}\right)^M$$

If instead the volumes V_A and V_B are allowed to vary, one can show

$$\frac{p_A}{p_B} = \left(\frac{V_A}{V_B}\right)^M \qquad i.e. \qquad \ln\frac{p_B}{p_A} = M \ln\frac{V_B}{V_A}$$

$$\text{cf} \quad \Delta S = nR \ln\frac{V_B}{V_A}$$

The relation between entropy and probability is

$$S_B - S_A = \frac{R}{N_A} \ln\frac{p_B}{p_A}$$

Defining *Boltzmanns constant* $k = R/N_A = 1.38 \times 10^{-23}$,

$$\boxed{S = k \ln W}$$

where **W** *is the number of microscopic states corresponding to a given thermodynamic state, ie the relative probability of being in the thermodynamic state.*

Exercise: Use the microscopic formula for entropy to calculate the entropy difference between two states of a mole of gas, one in which the gas is contained in a volume twice as large as the other.

Answer: $\Delta S = k \ln W_1 - kln W_2 = k \ln W_1/W_2 = k \ln 2^{N_A} = 5.8 JK^{-1}$.

Comment: The microscopic entropy can decrease. However, this requires the system to move from a state of higher probability to a state of lower probability — a rare event. Considering the previous example, the entropy will decrease if all the molecules spontaneously move into the left half of the container. However, the probability of this is vanishingly small, $\sim \left(\frac{1}{2}\right)^{N_A}$

Comment: In a typical *mechanical* system there is usually only one or two possible arrangements of the system ($W = 1$ or $W = 2$). Thus entropy is negligibly small for such systems and only energy need be considered when determining the equilibrium configuration.

The Third Law

As the temperature of a substance is decreased, the number of accessible molecular arrangements is steadily reduced. At absolute zero, many *pure* substances only have one possible molecular arrangement — a perfect crystal, in which case $S = k \ln 1 = 0$. This leads to the Third Law,

The entropy of a perfect crystal is zero at absolute zero.

There are a number of exceptions to this rule, including ice! These exceptions arise whenever $W > 1$ at absolute zero. In the case of ice, each oxygen atom has two hydrogen bonds and two covalent bonds, and these can be arranged in several ways.

Entropy of Solids, Liquids and Gases

We saw in the previous section that the entropy of a gas increases with volume. The entropy of a chemical system is closely related to the freedom possesed by the molecules in the system, so we expect entropy to increase as a compound goes from solid to liquid to gas. One can also reach the same conclusion from macroscopic thermodynamic considerations:

Recall that

$$dH = đq + VdP$$

so

$$đq = dH)_P$$

The entropy of vaporisation is,

$$\Delta S_{\text{vap}} = \left.\frac{\Delta q_{rev}}{T}\right)_P = \frac{\Delta H_{\text{vap}}}{T} >> 0$$

So

$$\boxed{\mathbf{S}_{\text{solid}} < \mathbf{S}_{\text{liquid}} < \mathbf{S}_{\text{gas}}}$$

Thus the reaction

$$CaCO_3(s) \rightarrow CaO(s) + CO_2(g) \quad \text{has} \quad \Delta S >> 0$$

because the gas has high entropy and the solids have low entropy.

Entropy as a function of Temperature and Pressure

Pressure: We have seen that, for the *isothermal* expansion of a perfect gas,

$$\Delta S = nR \ln \frac{V_B}{V_A} \qquad \text{isothermal expansion of a perfect gas}$$

Substituting in $PV = nRT$ gives,

$$\Delta S = -nR \ln \frac{P_B}{P_A} \qquad \text{isothermal expansion of a perfect gas}$$

For many problems it is convenient to express this as

$$S = S_o - nR \ln P \qquad \text{isothermal expansion of a perfect gas}$$

where S_o is the entropy at 1 atmosphere pressure and P is the pressure *in units of atmospheres.*

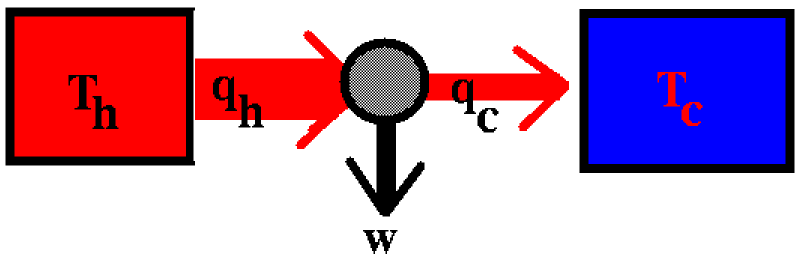
Temperature: Combining $dS = \frac{đq_{\text{rev}}}{T}$ together with $C_V = \left(\frac{đq_{\text{rev}}}{dT}\right)_V$ and $C_P = \left(\frac{đq_{\text{rev}}}{dT}\right)_P$ gives dS in terms of the heat capacities,

$$\boxed{\begin{aligned} \left(\frac{\partial S}{\partial T}\right)_V &= \frac{C_V}{T} \\ \left(\frac{\partial S}{\partial T}\right)_P &= \frac{C_P}{T} \end{aligned}}$$

Exercise: Integrate these expressions from T_A to T_B, assuming C_V and C_P are constant.

Maximum Efficiency of Heat Engines

A heat engine harnesses a heat-flow from a hot reservoir to a cold reservoir to produce work.



Ideally the engine would convert all the heat q_h from the hot reservoir into work, but the Second Law ($\Delta S \geq 0$) limits the efficiency of the engine, and some wasted heat is ejected to the cold reservoir. In the ideal case of a reversible engine $\Delta S = 0$,

$$\begin{aligned} \Delta S &= 0 = \frac{-q_h}{T_h} + \frac{q_c}{T_c} \\ \%\ \text{Heat energy wasted} &= \frac{q_c}{q_h} = \frac{T_c}{T_h} \end{aligned}$$

From a microscopic perspective, the kinetic energy of the molecules is being converted into work. If all the kinetic energy is converted to work then the molecules end up at absolute zero ($T_c = 0$).

Exercise: Assuming that a standard car engine operates at $800K$ and a diesel engine at $1300K$, estimate the relative efficiency of the two engines.

Exercise: A **heat pump** or refrigerator is a heat engine operated in reverse. Work is performed to move heat from a cold reservoir to a hot reservoir. For small temperature differences heat pumps are much more efficent that electric heaters. For example if you have a battery which can do $1J$ of work, an electric heater can produce at most $1J$ of heat. If $T_c = 280$ and $T_h = 300$, use conservation of energy, $q_h = q_c + w$, together with the efficiency formula above to calculate q_h. You should get $q_h >> 1$.

Homework: 1 atm = $10^5 Nm^{-2}$

1. What is the entropy change of a system during a cyclic process, i) When the entire cycle is reversible ii)When part of the cycle is irreversible. Give reasons for your answer.

2. True or False? For every process in an isolated system (a) $\Delta T = 0$, (b) $\Delta U = 0$, (c) $\Delta S = 0$.

3. Calculate ΔS when $0.011 m^3$ of a perfect gas at $273K$ and 1 atm pressure is isothermally compressed to 10 atm pressure.

4. The heat capacity of argon at constant pressure is $20.8 JK^{-1}mol^{-1}$. Estimate the entropy change when one mole of argon is heated from $300K$ to $1200K$ at 1 atm pressure.

5. Calculate the entropy change when one mole of ice at $268K$ is melted to form water at $323K$. The heat capacity of ice is $3.8 JK^{-1}mol^{-1}$, that of water is $75 JK^{-1}mol^{-1}$, and the enthalpy of fusion of ice at $273K$ is $6.02 kJmol^{-1}$.

6. Calculate the entropy change when one mole of cadium vapour at 1 atm pressure is heated from $1040K$ to $1100K$ and subsequently isothermally compressed to a pressure of 6 atm. You may assume that the vapour follows perfect gas behaviour, and $C_p = 12.5 JK^{-1}mol^{-1}$.

7. 1 mole of A at 1 atm pressure and 1 mole of B at 2 atm pressure are separated by a partition and surrounded by a heat reservoir. When the partition is withdrawn, how much does the entropy change? Assume perfect gases.

8. A household refrigerator operates between $35C$ and $-10C$. How many joules of heat can in principle be removed per joule of work?

9. ΔH for the graphite $\rightarrow$ diamond phase transition, which occurs at $10^{10} Nm^{-2}$ and $2000K$, is $1.9 kJmol^{-1}$. Calculate ΔS for the transition.