

Thermodynamics: the Second Law

Some things happen; some things don't:

A gas expands to fill the vessel it occupies.

A hot object cools to the temperature of its surroundings.

Hydrogen and oxygen combine explosively (after a spark) and form water.

Spontaneous change – can occur without work being done to bring it about – has a natural tendency to occur.

A gas that already fills a vessel does not suddenly contract into a smaller volume. A cool object does not suddenly become hotter than its surroundings.

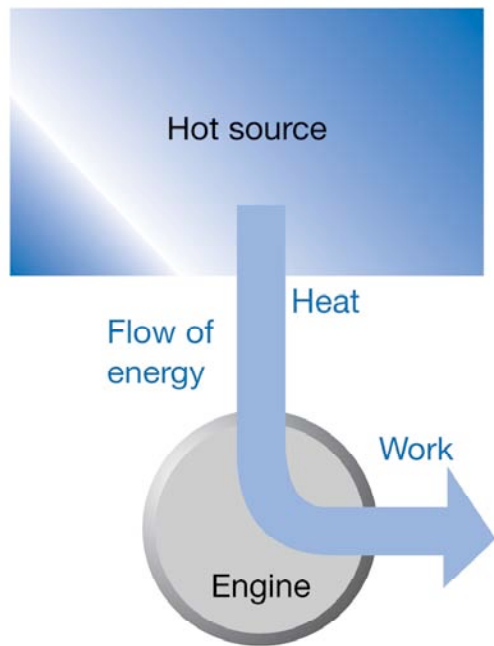
Water left standing in oceans does not gradually decompose into H_2 and O_2 .

Non-spontaneous change – can be brought about only by doing work – no natural tendency to occur- can be *made* to occur by doing work – gas can be compressed into a smaller volume by pushing in a piston; the temperature of a cool object can be raised by forcing an electric current through a heater attached to it; water can be decomposed by the passage of an electric current.

There must be a feature of the world that account for distinction between the two types of change. ‘Spontaneous’ and ‘non-spontaneous’ – signifies natural tendency, not speed.

Second Law of thermodynamics

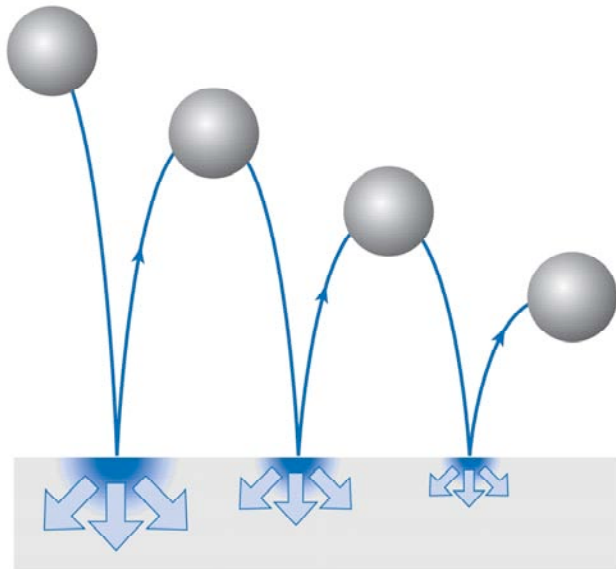
No process is possible in which the sole result is the absorption of heat from a reservoir and its complete conversion to work (formulated by Kelvin).



It has proved impossible to construct an engine, in which heat is drawn from a hot reservoir and completely converted into work. All real engines have both a hot source and a cold sink; some heat is always discarded into the cold sink and is not converted into work. Another everyday observation: a ball at rest on a surface has never been observed to leap spontaneously upwards. An upward leap of the ball would be equivalent to the conversion of heat from the surface into work.

The direction of spontaneous change

What determines the direction of spontaneous change? Not energy; it is conserved in any process (the First Law). Is it energy of the system? No. A perfect gas expands spontaneously into vacuum, yet its energy remains constant as it does so. Also, if the energy of the system does happen to decrease during a spontaneous change, the energy of its surroundings must increase by the same amount. So, the increase in energy of the surroundings is just as spontaneous as the decrease in energy of the system.

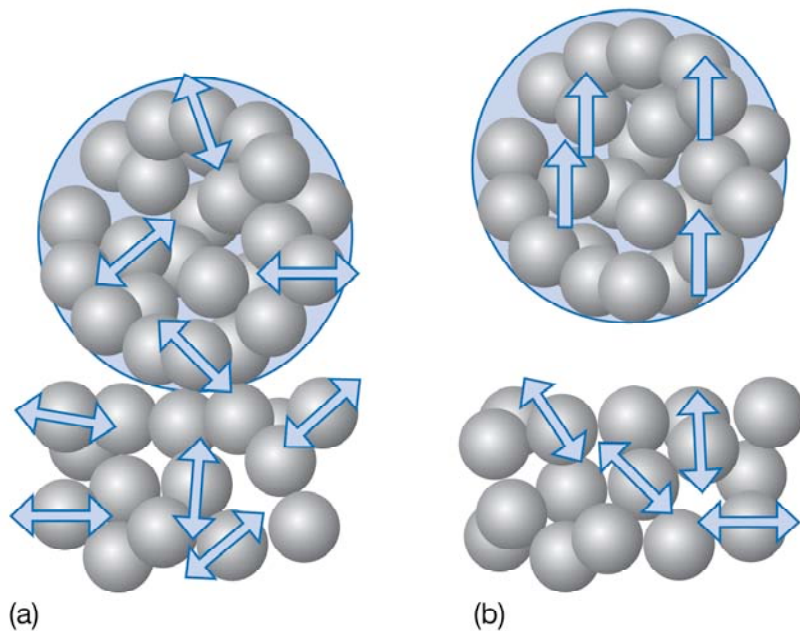


When a change occurs, the total energy of an isolated system remains constant but it is parceled out in different ways. Can it be that the direction of change is related to the distribution of energy?

The dispersal of energy

Consider a ball (the system) bouncing on the floor (the surroundings). The ball does not rise as high after each bounce because there are inelastic forces in the materials of the ball and floor and the kinetic energy of the ball's overall motion is converted into the energy of thermal motion. The direction of spontaneous change is towards a state in which the ball is in

rest with all its energy degraded into the thermal motion of floor atoms.



A ball resting on a warm floor has never been observed to start bouncing, something special needs to happen. Some of the thermal motion of the atoms in the floor would have to accumulate in a single small object, the ball. This requires a spontaneous localization of energy from the myriad of vibrations of the floor atoms into the much smaller number of atoms of the ball. The thermal motion is disorderly but for the ball to move upwards its atoms must all move in the same direction. The localization of random motion as orderly motion is so unlikely that it can be considered as virtually impossible.

Spontaneous change: *we look for the direction of change that leads to more disorderly dispersal of the total energy of the isolated system.*

A gas does not contract spontaneously, because to do so the disordered motion of its molecules would have to take them all into the same region of the container. The opposite change – spontaneous expansion – a natural consequence of increasing disorder. An object does not spontaneously become warmer than its surroundings because it is highly improbable that the jostling of randomly vibrating atoms in the surroundings will lead to the accumulation of excess thermal motion in the object. The opposite change – the spreading of the object's energy into the surroundings as thermal motion, is natural.

Entropy and the Second Law

A measure of the molecular disorder of a system – **entropy**, S .

Second Law of thermodynamics in terms of entropy:

The entropy of an isolated system increases in the course of a spontaneous change:

$\Delta S_{\text{tot}} > 0$, where S_{tot} – the total entropy of the system and its surroundings.

Thermodynamically irreversible processes (cooling to the temperature of the surroundings and the free expansion of gases) are spontaneous, and hence must be accompanied by an increase in total entropy.

The thermodynamic definition of entropy:

A change in the extent to which energy is dispersed in a disorderly manner depends on how

much energy is transferred as heat:

$$dS = \frac{dq_{\text{rev}}}{T}$$

$$\Delta S = \int_i^f \frac{dq_{\text{rev}}}{T}$$

The change in entropy of a substance – the energy transferred as heat to it *reversibly* divided by the temperature at which the transfer takes place.

To transfer energy as heat we make use of the disorderly motion of molecules. To transfer energy as work we make use of orderly motion. The change of degree of disorder is proportional to the energy transfer that takes place by making use of disorderly motion.

The presence of temperature in the denominator – takes into account the disorder that is already present. If a given quantity of energy is transferred as heat to a hot object (in which the atoms have a lot of disorderly thermal motion), then the additional disorder generated is less significant than if the same amount of energy is transferred as heat to a cold object in which the atoms have less thermal motion.

The units of entropy: J K^{-1} ; of molar entropy: $\text{J K}^{-1} \text{mol}^{-1}$.

Example 1. Calculating the entropy change for the isothermal expansion of a perfect gas.

We need to find the heat absorbed for reversible path between the initial and final states.

The heat absorbed during a reversible isothermal expansion:

$$\Delta U = q + w \quad \Delta U = 0 \quad q = -w \quad q_{\text{rev}} = -w_{\text{rev}}$$

The expansion is isothermal, so the temperature is constant and may be taken outside the integral:

$$\Delta S = \frac{1}{T} \int_i^f dq_{\text{rev}} = \frac{q_{\text{rev}}}{T} \quad q_{\text{rev}} = -w_{\text{rev}} = nRT \ln \frac{V_f}{V_i} \quad \Delta S = nR \ln \frac{V_f}{V_i}$$

We can use the definition of entropy to calculate the entropy change in the surroundings in contact with system ΔS_{sur} . Consider an infinitesimal transfer of heat dq_{sur} to the surroundings. The surroundings – a reservoir of constant volume – the heat supplied to them can be identified with the change in their internal energy, dU_{sur} . The internal energy is a state function, dU_{sur} is an exact differential and is independent of whether the process is reversible or irreversible. The same is true for dq_{sur} here because $dq_{\text{sur}} = dU_{\text{sur}}$ in this case.

$$dS_{\text{sur}} = \frac{dq_{\text{sur,rev}}}{T} = \frac{dq_{\text{sur}}}{T}$$

Because the temperature of the surroundings is constant whatever the change:

$$\Delta S_{\text{sur}} = \frac{q_{\text{sur}}}{T}$$

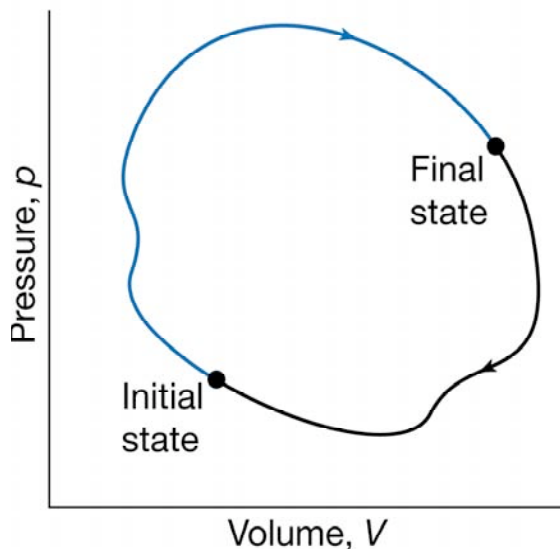
This expression makes it simple to calculate the changes in entropy of the surroundings in any process. For instance, for any adiabatic change, $q_{\text{sur}} = 0$, so

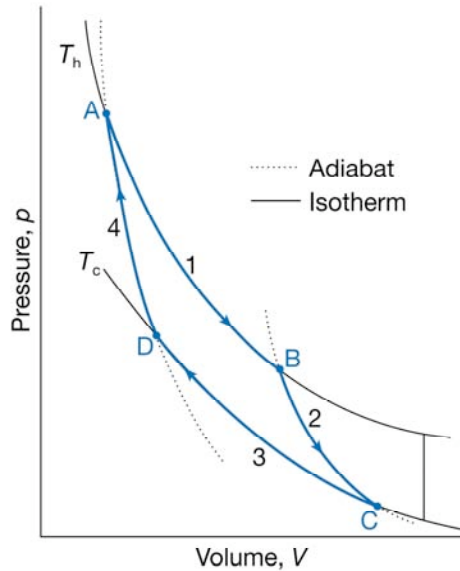
$$\Delta S_{\text{sur}} = 0$$

The entropy a state function

Entropy is a state function. To prove this, we need to show that the integral of dS is independent of path. To do so, it is sufficient to prove that the integral around an arbitrary cycle is zero; that guarantees that the entropy is the same at the initial and final states of the system regardless of the path taken between them. We need to show that

$$\oint \frac{dq_{\text{rev}}}{T} = 0$$





To prove this, we first consider the special cycle, so-called **Carnot cycle**, which consists of four reversible changes.

1. Reversible isothermal expansion from A to B at T_h ; the entropy change is q_h/T_h , q_h – the heat supplied to the system from the hot source.
2. Reversible adiabatic expansion from B to C. No heat leaves the system, $\Delta S = 0$, the temperature falls from T_h to T_c , the temperature of the cold sink.
3. Reversible isothermal compression from C to D. Heat is released to the cold sink; the change in entropy of the system is q_c/T_c , q_c is negative.
4. Reversible adiabatic compression from D to A. No heat enters the system, $\Delta S = 0$, the temperature rises from T_c to T_h .

The total change in entropy around the cycle:
$$\oint dS = \frac{q_h}{T_h} + \frac{q_c}{T_c}$$

Now we will show that $\frac{q_h}{q_c} = -\frac{T_h}{T_c}$, which will give zero for the integral.

$$q_h = nRT_h \ln \frac{V_B}{V_A} \quad q_c = nRT_c \ln \frac{V_D}{V_C}$$

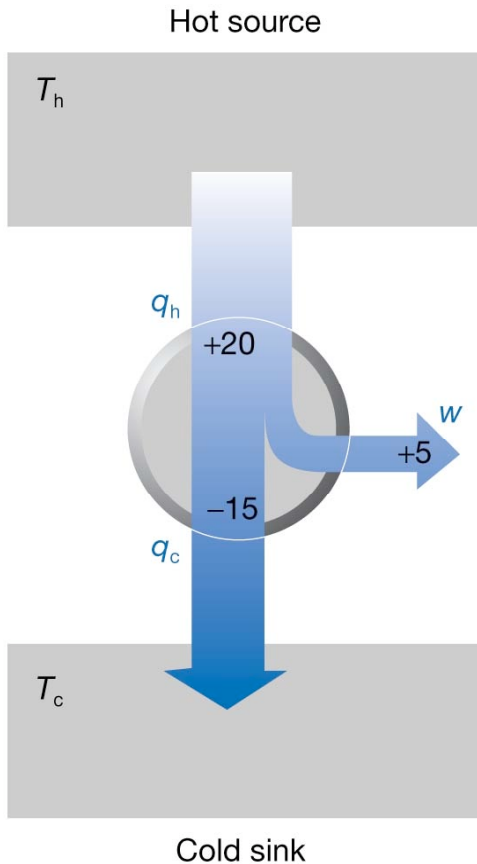
Relation between T and V for reversible adiabatic processes:

$$V_A T_h^c = V_D T_c^c \quad V_C T_c^c = V_B T_h^c \quad V_A V_C T_h^c T_c^c = V_D V_B T_h^c T_c^c$$

$$\frac{V_A}{V_B} = \frac{V_D}{V_C} \quad q_c = nRT_c \ln \frac{V_D}{V_C} = nRT_c \ln \frac{V_A}{V_B} = -nRT_c \ln \frac{V_B}{V_A}$$

$$\frac{q_h}{q_c} = \frac{nRT_h \ln(V_B/V_A)}{-nRT_c \ln(V_B/V_A)} = -\frac{T_h}{T_c}$$

Next we show that the same conclusion applies to any material.



Consider the **efficiency**, ϵ , of a heat engine:

$$\epsilon = \frac{\text{work_performed}}{\text{heat_absorbed}} = \frac{|w|}{q_h}$$

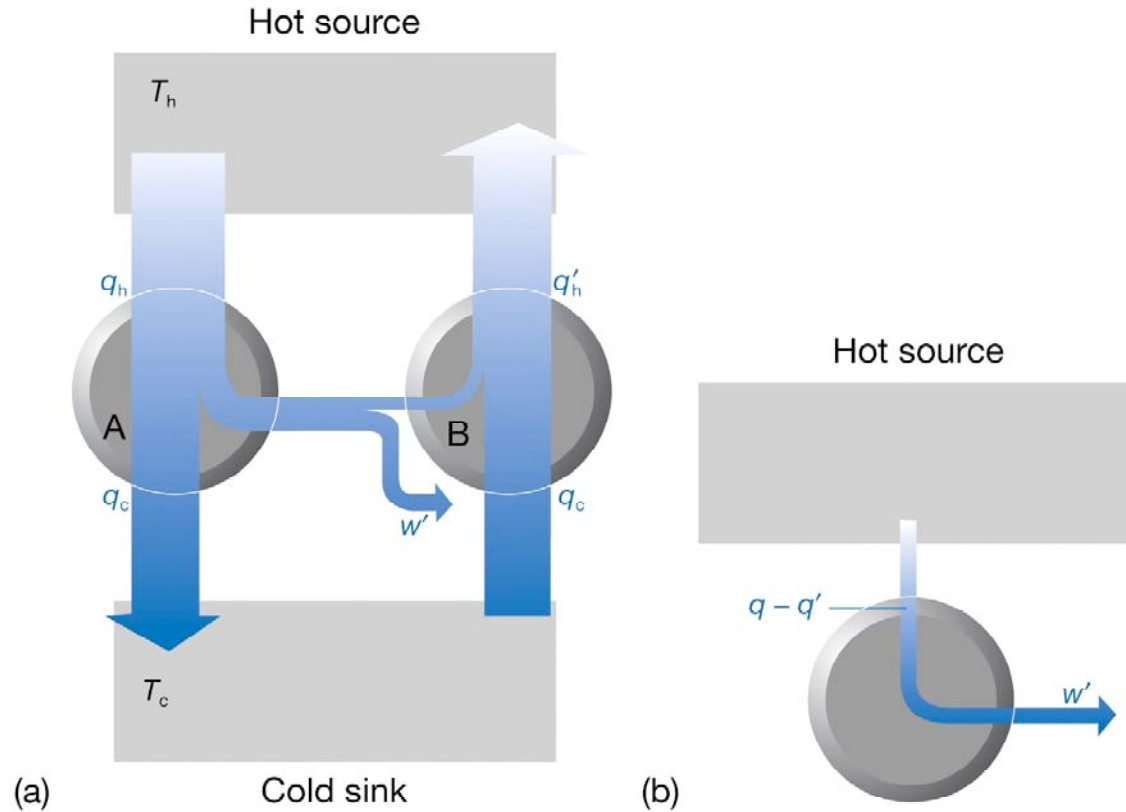
In terms of the heat transactions:

$$\epsilon = \frac{q_h + q_c}{q_h} = 1 + \frac{q_c}{q_h} = 1 - \frac{|q_c|}{q_h}$$

For a Carnot engine:

$$\epsilon_{rev} = 1 - \frac{T_c}{T_h}$$

The Second Law of thermodynamics implies that *all reversible engines have the same efficiency regardless of their construction.*



Suppose two reversible engines are coupled together and run between the same two reservoirs. The working substances and details of construction are entirely arbitrary. Initially, suppose that engine A is more efficient than engine B, and that we choose a setting of the controls that causes engine B to acquire the heat q_c from the cold reservoir and to release a certain quantity of heat into the hot reservoir. In such an arrangement, engine A produces some work, while engine B uses

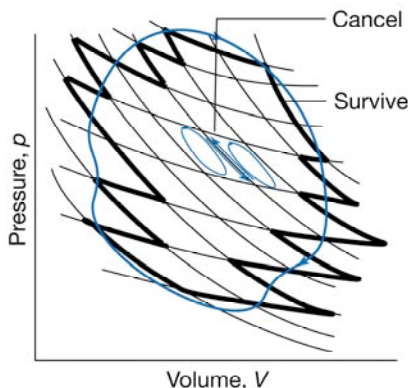
this work to pump heat from the cold sink to the hot source. However, because engine A is more efficient than B, not all the work that A produces is needed for this process, and the difference can be used to do extra work:

$$\varepsilon_A = 1 - \frac{|q_c|}{q_h} \quad \varepsilon_B = 1 - \frac{|q_c|}{q'_h} \quad \varepsilon_A > \varepsilon_B \quad q_h > q'_h \quad w' = q_h - q'_h$$

The net result is that the cold reservoir is unchanged, work has been produced, and the hot reservoir has lost a certain amount of energy. This is contrary to the Kelvin statement of the Second Law, because some heat has been converted directly into work.

In molecular terms: the disordered thermal motion of the hot reservoir has been converted into ordered motion characteristic to work. The conclusion is contrary to experience, so the initial assumption that engines A and B can have different efficiencies must be false. Hence, independent of working materials,

$$\epsilon_{rev} = 1 + \frac{q_c}{q_h} = 1 - \frac{T_c}{T_h} \quad \text{and} \quad \frac{q_h}{q_c} = -\frac{T_h}{T_c}$$



Finally, any reversible cycle can be approximated as a collection of Carnot cycles and the cyclic integral around an arbitrary path is the sum of integrals around each of the Carnot cycles. This becomes exact if the individual cycles become infinitesimal. The entropy change around each individual cycle is zero, so the sum of entropy changes for all the cycles is zero. However, in the sum, the entropy change along any individual path is cancelled by the entropy change along the path it shares with neighboring cycle. Therefore all the entropy changes cancel except those along the perimeter of the overall cycle:

$$\sum_{all} \frac{q_{rev}}{T} = \sum_{perimeter} \frac{q_{rev}}{T} = 0$$

In the limit of infinitesimal cycles, the non-cancelling edges of the Carnot cycles match the overall cycle exactly, and the sum becomes an integral. This result implies that dS is an exact differential and therefore S is a state function.

The Clausius inequality

We have verified that the entropy is a state function. Let's show that $\Delta S_{\text{tot}} \geq 0$ for any spontaneous change (the equality applies for a reversible process). Consider a system in thermal and mechanical contact with its surroundings at the same temperature T . Any change of state is accompanied by a change in entropy of the system, dS , and of the surroundings, dS_{sur} . Because the process might be irreversible, the total entropy will increase when a process occurs in the system:

$$dS + dS_{\text{sur}} \geq 0 \quad \text{or} \quad dS \geq -dS_{\text{sur}}$$

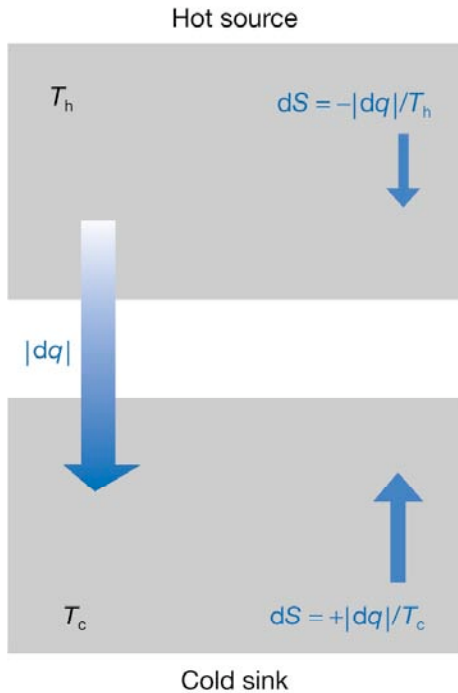
Because $dS_{\text{sur}} = -dq/T$, where dq is the heat supplied to the system during the process ($dq_{\text{sur}} = -dq$), it follows that for any change

$$dS \geq dq/T$$

Clausius inequality

For an isolated system, $dq = 0$ and $dS \geq 0$. So, in an isolated system the entropy cannot decrease when a spontaneous change takes place. Irreversible adiabatic change: $dq = 0$, $dS \geq 0$. No heat flows into surroundings, $dS_{\text{sur}} = 0$, so $dS_{\text{tot}} \geq 0$.

Irreversible isothermal expansion of a perfect gas: $dU = 0$, $dq = -dw$. If the gas expands freely into vacuum, it does no work, $dw = 0$ and $dq = 0$. Therefore, according to the Clausius inequality, $dS \geq 0$. Next, consider the surroundings. No heat flows into surroundings, $dS_{\text{sur}} = 0$, so $dS_{\text{tot}} \geq 0$.



Spontaneous cooling: Consider a transfer of energy as heat from one system (the hot source at temperature T_h) to another system (the cold sink at temperature T_c). When $|dq|$ leaves the hot source, the entropy changes by $-|dq|/T_h$ (a decrease). When dq enters the cold sink the entropy changes by $+|dq|/T_c$ (an increase). The total entropy change is

$$dS = \frac{|dq|}{T_c} - \frac{|dq|}{T_h} = |dq| \left(\frac{1}{T_c} - \frac{1}{T_h} \right)$$

dS is positive because $T_h \geq T_c$. Hence, cooling is spontaneous. When $T_h = T_c$, $dS_{\text{tot}} = 0$: the two systems are in thermal equilibrium.

Entropy changes accompanying specific processes

The entropy of phase transition at the transition temperature

The degree of molecular order changes when a substance freezes or boils, so we should expect the transition to be accompanied by a change in entropy. Consider a system and its surroundings at the **normal transition temperature**, T_{trs} , the temperature at which two phases are in equilibrium at 1 atm. At the transition temperature, any transfer of heat between the system and its surroundings is reversible because the two phases in the system are in equilibrium. Because at constant pressure $q = \Delta_{\text{trs}}H$, the change in molar entropy of the system is $\Delta_{\text{trs}}S = \Delta_{\text{trs}}H/T_{\text{trs}}$.

Entropy of phase transitions

The entropy of a substance increases when it melts and when it boils because its molecules become more disordered as it changes from solid to liquid and from liquid to vapor.

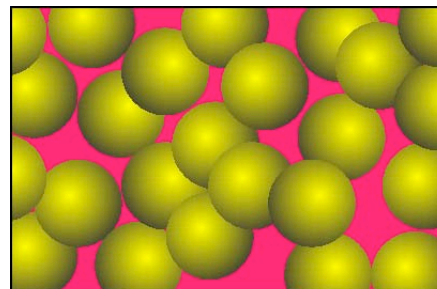
Suppose a solid is at its melting temperature. Transfer of energy as heat then occurs reversibly. If the temperature of the surroundings is infinitesimally lower than that of the system, then heat flows out of the system and the substance freezes. If the temperature is infinitesimally higher, then heat flows into the system and the substance melts. Because the transition occurs at constant pressure, we can identify the heat transferred per mole of substance with the enthalpy of melting.

Entropy of fusion at the melting temperature: $\Delta_{\text{fus}}S = \Delta_{\text{fus}}H/T_f$

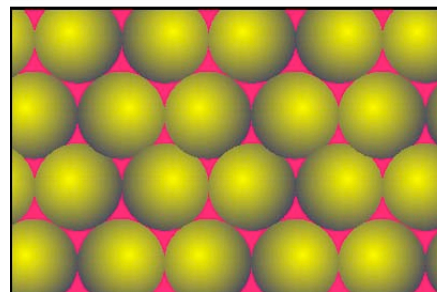
All enthalpies of fusion are positive – all entropies of fusion are positive too: disorder increases on melting.

Entropy of vaporization at the boiling temperature: $\Delta_{\text{vap}}S = \Delta_{\text{vap}}H/T_b$

All entropies of vaporization are positive.



(b)



(a)

Trouton's rule - $\Delta_{\text{vap}}H/T_b$ is approximately the same ($\sim 85 \text{ J K}^{-1} \text{ mol}^{-1}$) for most liquids.

All liquids have approximately the same entropy of vaporization – when a liquid vaporizes, the compact condensed phase changes into a widely dispersed gas – the increase in disorder is approximately the same. Trouton's rule can be used to compute the standard enthalpy of vaporization of a substance from its boiling temperature:

$$\Delta_{\text{vap}}H = T_b \times (85 \text{ J K}^{-1} \text{ mol}^{-1})$$

The expansion of a perfect gas

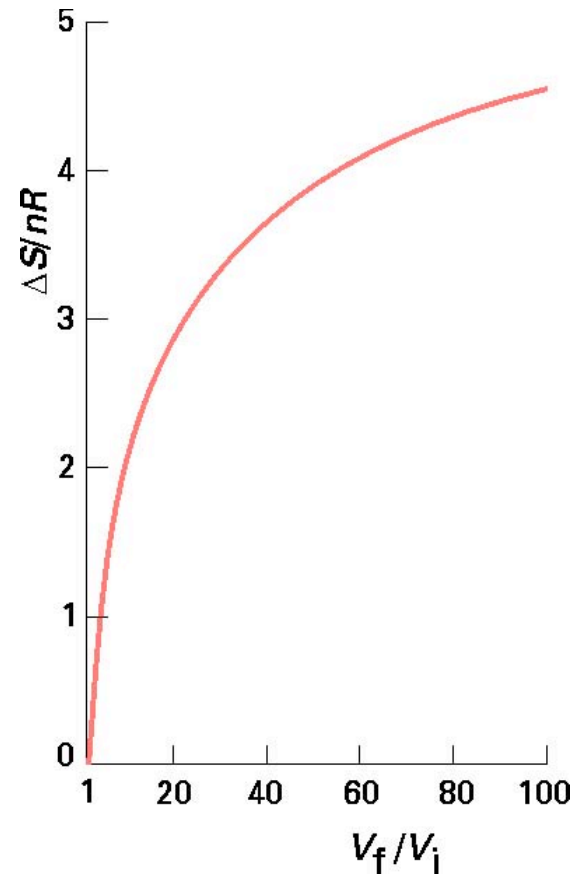
To calculate the entropy change, we need to know q_{rev} , the energy transferred as heat in the course of a reversible change at the temperature T . The heat transferred to a perfect gas when it undergoes reversible isothermal expansion:

$$q_{\text{rev}} = nRT \ln(V_f/V_i) \quad \Delta S = q_{\text{rev}}/T = nR \ln(V_f/V_i)$$

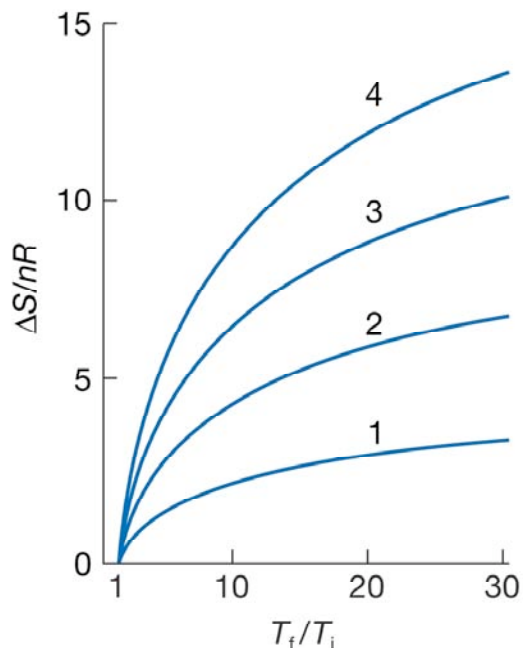
We see that if $V_f > V_i$, as in an expansion, then $V_f/V_i > 1$ and the logarithm is positive. Thus, ΔS is positive, the entropy increases.

Because S is a state function, the value of ΔS is independent of the path, and the expression applies whether the change of state occurs reversibly or irreversibly.

However, the total change of entropy does depend on how the expansion takes place. If the change is reversible, the entropy change in the surroundings must be such as to give $\Delta S_{\text{tot}} = 0$ and $\Delta S_{\text{sur}} = -\Delta S$. If the isothermal expansion occurs freely ($w = 0$) and irreversibly, then $q = 0$ (because $\Delta U = 0$). Consequently, $\Delta S_{\text{sur}} = 0$, and the total entropy change is positive for the expansion.



The variation of entropy with temperature



$$S(T_f) = S(T_i) + \int_i^f \frac{dq_{rev}}{T}$$

At constant pressure and with no non-expansion work done dq is identified with dH and, using the definition of constant pressure heat capacity, we can write

$$dq_{rev} = C_p dT \quad S(T_f) = S(T_i) + \int_i^f \frac{C_p dT}{T}$$

The same expression applies at constant volume, but with C_p replaced by C_V . When C_p is independent of T in the temperature range of interest,

$$S(T_f) = S(T_i) + \int_i^f \frac{C_p dT}{T} = S(T_i) + C_p \ln \frac{T_f}{T_i}$$

Example. Calculating the entropy change

Calculate the entropy change when argon at 25°C and 1 atm in a container of volume 500 cm³ is allowed to expand to 1000 cm³ and is simultaneously heated to 100°C.

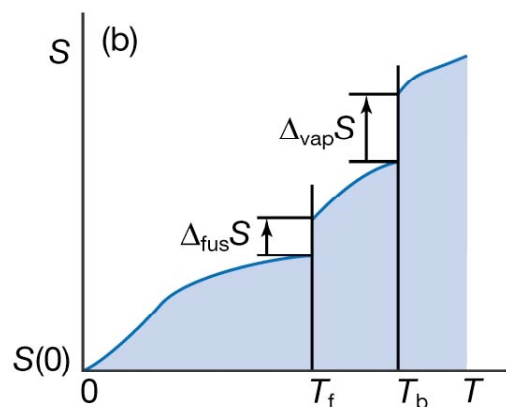
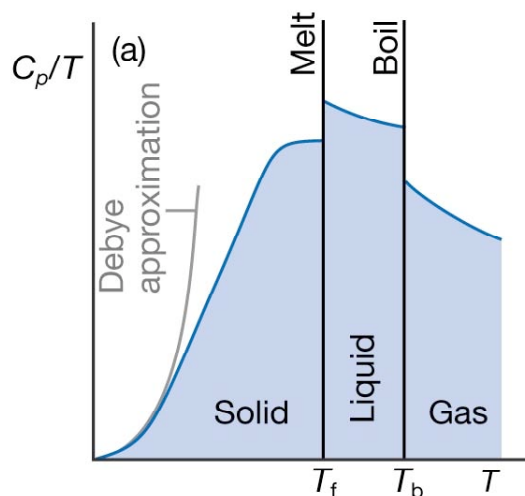
Because S is a state function, we are free to choose any convenient path from the initial state. We chose reversible isothermal expansion to the final volume followed by reversible heating at constant volume to the final temperature. Then,

$$\Delta_1 S = nR \ln \frac{V_f}{V_i} \quad \Delta_2 S = C_V \ln \frac{T_f}{T_i} = nC_{V,m} \ln \frac{T_f}{T_i} \quad C_{p,m} - C_{V,m} = R$$

The amount of Ar present: $n = pV/RT = 0.0204$ mol

$$\Delta_1 S = nR \ln 2.00 = +0.118 \text{ J K}^{-1} \quad \Delta_2 S = n C_{V,m} (373/298) = +0.057 \text{ J K}^{-1} \quad \Delta_{\text{tot}} S = +0.175 \text{ J K}^{-1}$$

The measurement of entropy



The entropy of a system at a temperature T is related to its entropy at $T = 0$ by measuring its heat capacity C_p at different temperatures and evaluating the integral. The entropy of transition ($\Delta_{\text{trs}}H/T_{\text{trs}}$) must be added for each phase transition between $T = 0$ and the temperature of interest.

$$S(T) = S(0) + \int_0^{T_f} \frac{C_p(s)dT}{T} + \frac{\Delta_{\text{fus}}H}{T_f} + \int_{T_f}^{T_b} \frac{C_p(l)dT}{T} + \frac{\Delta_{\text{vap}}H}{T_b} + \int_{T_b}^T \frac{C_p(g)dT}{T}$$

All the properties required, except $S(0)$, can be measured calorimetrically, and the integrals can be evaluated either graphically or by fitting data to a polynomial analytically.

One problem: it is difficult to measure heat capacities near $T = 0$. **Debye's extrapolation:** the heat capacity is proportional to T^3 when T is low. C_p is measured down to as low a temperature as possible, and a curve of the form aT^3 is fitted to the data. The fit determines the value of a , and the expression $C_p = aT^3$ is assumed.

Example. Calculating the entropy at low temperatures.

The molar constant-pressure heat capacity of a certain solid at 10 K is $0.43 \text{ J K}^{-1} \text{ mol}^{-1}$. What is S_m at that temperature?

$$S(T) = S(0) + \int_0^T \frac{aT^3 dT}{T} = S(0) + a \int_0^T T^2 dT = S(0) + \frac{1}{3} aT^3$$

$$S(T) = S(0) + (1/3)C_p(T) \quad S_m(10 \text{ K}) = S_m(0) + 0.14 \text{ J K}^{-1} \text{ mol}^{-1}$$

The Third Law of thermodynamics

At $T = 0$, all energy of thermal motion has been quenched and in a perfect crystal all the atoms or ions are in a regular, uniform array. The absence of both spatial disorder and thermal motion suggests that such materials have zero entropy. This conclusion is consistent with the molecular interpretation of entropy, because $S = 0$ if there is only one way of arranging the molecules.

The Nernst heat theorem

The experimental observation consistent with the view that the entropy of a regular array of molecules is zero at $T = 0$, the **Nernst heat theorem**:

The entropy change accompanying any physical or chemical transformation approaches zero as the temperature approaches zero: $S \rightarrow 0$ as $T \rightarrow 0$ provided all the substances involved are perfectly ordered.

Example of the experimental evidence: consider the entropy of the transition between orthorhombic sulfur, $S(\alpha)$, and monoclinic sulfur, $S(\beta)$, which can be calculated from the transition enthalpy (-402 J mol^{-1}) and the transition temperature (369 K):

$$\Delta_{\text{trs}}S = S_{\text{m}}(\alpha) - S_{\text{m}}(\beta) = (-402 \text{ J mol}^{-1} / 369 \text{ K}) = -1.09 \text{ J K}^{-1} \text{ mol}^{-1}$$

The two individual entropies can also be determined by measuring the heat capacities from $T = 0$ up to $T = 369 \text{ K}$:

$$S_{\text{m}}(\alpha) = S_{\text{m}}(\alpha, 0) + 37 \text{ J K}^{-1} \text{ mol}^{-1}$$

$$S_{\text{m}}(\beta) = S_{\text{m}}(\beta, 0) + 38 \text{ J K}^{-1} \text{ mol}^{-1}$$

Therefore, at the transition temperature,

$$\Delta_{\text{trs}}S = S_{\text{m}}(\alpha, 0) - S_{\text{m}}(\beta, 0) - 1 \text{ J K}^{-1} \text{ mol}^{-1}$$

We can conclude that $S_{\text{m}}(\alpha, 0) - S_{\text{m}}(\beta, 0) \approx 0$

in accord with the theorem.

It follows from the Nernst theorem that, if we arbitrarily ascribe the value zero to the entropy of elements in their perfect crystalline form at $T = 0$, then all perfect crystalline compounds also have zero entropy at $T = 0$ (because the change in entropy that accompanies the formation of the compounds is zero).

Third Law of thermodynamics: The entropy of all perfect crystalline substances is zero at $T = 0$.

Third-Law entropies

Entropies reported on the basis that $S(0) = 0$ are called **Third-Law entropies**. When the substance is in its standard state at the temperature T , the **standard (Third-Law) entropy** is denoted $S^\ominus(T)$.

The standard reaction entropy

The difference in molar entropy between the products and the reactants in their standard states – the **standard reaction entropy**, $\Delta_r S^\ominus$:

$$\Delta_r S^\ominus = \sum \nu S_m^\ominus(\text{products}) - \sum \nu S_m^\ominus(\text{reactants})$$

ν - the stoichiometric coefficients in the chemical equation.

Concentrating on the system

Entropy is the basic concept for discussing the direction of natural change, but to use it we have to analyze changes in both the system and its surroundings. However, it is simple to calculate the entropy change in the surroundings, so it is possible to devise a simple method for taking that contribution into account automatically.

The Helmholtz and Gibbs energies

Consider a system in thermal equilibrium with its surroundings. When a change in the system occurs and there is a transfer of energy as heat between the system and the surroundings, according to the Clausius inequality,

$$dS - \frac{dq}{T} \geq 0$$

Criteria for spontaneity

Heat transfer at constant volume: $dq_V = dU$ and $dS - \frac{dU}{T} \geq 0$

$TdS \geq dU$ (constant volume, no additional, non-expansion work)

1) Constant internal energy, $dU = 0$ $TdS_{U,V} \geq 0$

2) Constant entropy, $dS = 0$ $dU_{S,V} \leq 0$

1) In a system at constant volume and constant internal energy (such as an isolated system), the entropy increases in a spontaneous change – the content of the Second Law.

2) If the entropy and volume of the system are constant, then the internal energy must decrease in a spontaneous change. If the entropy of the system is unchanged, then there must be an increase in entropy of the surroundings, which can be achieved only if the energy of the system decreases as energy flows out as heat.

Heat transfer at constant pressure: $dq_p = dH$ and $dS - \frac{dH}{T} \geq 0$

$TdS \geq dH$ (constant pressure, no additional, non-expansion work)

1) Constant enthalpy, $dH = 0$ $TdS_{H,p} \geq 0$

2) Constant entropy, $dS = 0$ $dH_{S,p} \leq 0$

1) The entropy of the system at constant pressure must increase if its enthalpy remains constant.

2) The enthalpy must decrease if the entropy of the system is constant.

The spontaneity inequalities can be rearranged as

$$dU - TdS \leq 0 \qquad dH - TdS \leq 0$$

We can introduce two more thermodynamic quantities:

$A = U - TS$ **Helmholtz energy**

$G = H - TS$ **Gibbs energy**

All the symbols refer to the system. At constant temperature,

$$dA = dU - TdS \qquad dG = dH - TdS$$

Then, the criteria of spontaneity become

$$dA_{T,V} \leq 0 \qquad dG_{T,p} \leq 0$$

The Helmholtz energy

A change in a system at constant T and V is spontaneous if $dA_{T,V} \leq 0$. A change at these conditions is spontaneous if it corresponds to a decrease in the Helmholtz energy. Such systems move spontaneously towards states of lower A if a path is available. The criterion of equilibrium, when neither the forward nor reverse process has a tendency to occur, is $dA_{T,V} = 0$

Maximum work

The change in the Helmholtz function is equal to the maximum work accompanying a process: $dw_{\max} = dA$

A is sometimes called the ‘maximum work function’ or the ‘work function’. First we prove that a system does maximum work when it is working reversibly. We combine the Clausius inequality $dS \geq dq/T$ in the form $dq \leq TdS$ with the First Law, $dU = dq + dw$:

$$dU \leq TdS + dw \qquad dw \geq dU - TdS$$

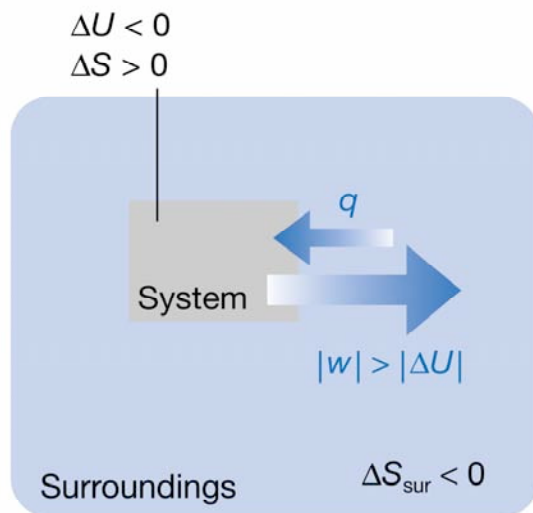
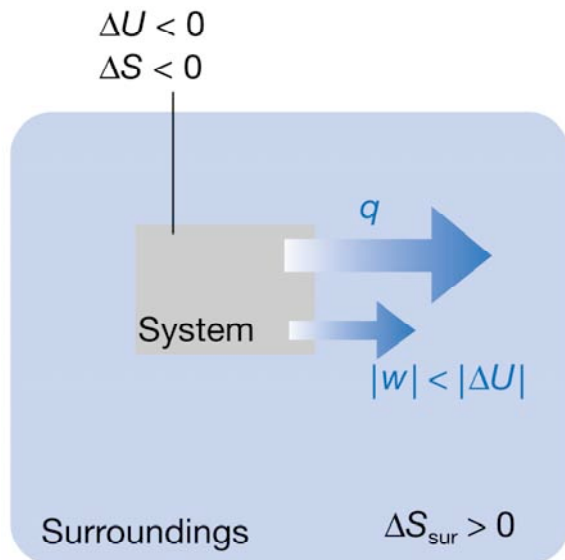
It follows that the most negative value of dw and therefore the maximum energy that can be obtained from the system as work, is

$$dw_{\max} = dU - TdS \qquad dw_{\max} = dA$$

When a macroscopic isothermal change takes place in the system,

$$\Delta w_{\max} = \Delta A \quad \text{with} \quad \Delta A = \Delta U - T\Delta S$$

This shows that in some cases, depending on the sign of $T\Delta S$, not all the change in internal energy may be available for doing work.



If the change occurs with a decrease in entropy of the system, $T\Delta S \leq 0$, then $\Delta U - T\Delta S$ is not as negative as ΔU itself, and the maximum work is less than ΔU . For the change to be spontaneous, some of the energy must escape as heat in order to generate enough entropy in the surroundings to overcome the reduction in entropy in the system.

A – ‘Helmholtz free energy’, because ΔA is that part of the change in internal energy that we are free to use to do work. Recall that work is energy transferred to the surroundings as the uniform motion of atoms. $A = U - TS$ means that A is the total internal energy of the system, U , less a contribution that is stored in a disordered manner, TS . Because energy stored in a disordered manner cannot be used to achieve uniform motion in the surroundings, only the part of U that is not stored in a disordered way, $U - TS$, is available for conversion into work.

If the change occurs with an increase of entropy of the system, $T\Delta S \geq 0$, then $\Delta U - T\Delta S$ is more negative than ΔU and the maximum work that can be obtained from the system is greater than ΔU . The explanation of this apparent paradox is that the system is not isolated and energy may flow in as heat as work is done. Because the entropy of the system increases, we can afford a reduction of S_{sur} and still have a spontaneous process.

Example. Calculating the maximum available work.

When 1.00 mol $\text{C}_6\text{H}_{12}\text{O}_6$ (glucose) is oxidized to carbon dioxide and water at 25°C according to the equation $\text{C}_6\text{H}_{12}\text{O}_6(\text{s}) + 6 \text{O}_2(\text{g}) \rightarrow 6 \text{CO}_2(\text{g}) + 6 \text{H}_2\text{O}(\text{l})$, calorimetric measurements give $\Delta_r U^\ominus = -2808 \text{ kJ mol}^{-1}$ and $\Delta_r S^\ominus = +182.4 \text{ J K}^{-1} \text{ mol}^{-1}$. How much of this energy change can be extracted as (a) heat at constant pressure, (b) work?

The heat released at constant pressure is equal to the value of ΔH , so we need to relate $\Delta_r H^\ominus$ to $\Delta_r U^\ominus$. $\Delta_r H^\ominus = \Delta_r U^\ominus + \Delta \nu_g RT$

For the maximum work available, $\Delta_r A^\ominus = \Delta_r U^\ominus - T\Delta_r S^\ominus$

$$\Delta \nu_g = 0 \quad \Delta_r H^\ominus = \Delta_r U^\ominus = -2808 \text{ kJ mol}^{-1}$$

$$\begin{aligned} \Delta_r A^\ominus &= -2808 \text{ kJ mol}^{-1} - (298 \text{ K}) \times (182.4 \text{ J K}^{-1} \text{ mol}^{-1}) \\ &= -2862 \text{ kJ mol}^{-1} \end{aligned}$$

The Gibbs energy

The Gibbs energy (the ‘free energy’) – more common in chemistry because we are usually more interested in changes occurring at constant pressure. $dG_{T,p} \leq 0$ – *at constant temperature and pressure, chemical reactions are spontaneous in the direction of decreasing Gibbs energy.* If G decreases as the reaction proceeds, then the reaction has a spontaneous tendency to convert the reactants into products. If G increases, then the reverse reaction is spontaneous.

The existence of spontaneous endothermic reactions illustrates the role of G . In such reactions, H increases, $dH > 0$. Because the reaction is spontaneous we know that $dG < 0$ despite $dH > 0$. Therefore, the entropy of the system increases so much that TdS is strongly positive and overweighs dH in $dG = dH - TdS$. Endothermic reactions are driven by the increase of entropy of the system, and this entropy change overcomes the reduction of entropy brought about in the surroundings by the inflow of heat into the system ($dS_{\text{sur}} = -dH/T$ at constant pressure).

Maximum non-expansion work

At constant temperature and pressure, the maximum additional (non-expansion) work, $w_{\text{add,max}}$, is given by the change in Gibbs energy: $dw_{\text{add,max}} = dG$ $\Delta w_{\text{add,max}} = \Delta G$

This expression is useful for assessing the electrical work produced by fuel cells and electrochemical cells.

$$H = U + pV \quad dH = dq + dw + d(pV) \quad G = H - TS$$

$$dG = dH - TdS - SdT = dq + dw + d(pV) - TdS - SdT$$

When the change is isothermal,

$$dG = dq + dw + d(pV) - TdS$$

When the change is reversible, $dw = dw_{\text{rev}}$ and $dq = dq_{\text{rev}} = TdS$

So, for a reversible isothermal process we have

$$dG = TdS + dw_{\text{rev}} + d(pV) - TdS = dw_{\text{rev}} + d(pV)$$

The work consists of expansion work, $-pdV$ for a reversible change, and possibly some other kind of work (the electrical work of pushing electrons through a circuit), $dw_{\text{add,rev}}$.

$$d(pV) = pdV + Vdp$$

$$dG = (-pdV + dw_{\text{add,rev}}) + pdV + Vdp = dw_{\text{add,rev}} + Vdp$$

At constant pressure, $dG = dw_{\text{add,rev}}$ and, because the process is reversible, the work done must have its maximum value:

$$dw_{\text{add,max}} = dG$$

Example. Calculating the maximum non-expansion work of a reaction.

How much energy is available for sustaining muscular and nervous activity from the combustion of 1.00 mol of glucose molecules under standard conditions at 37°C (blood temperature)? The standard reaction entropy is $+182.4 \text{ J K}^{-1} \text{ mol}^{-1}$.

The non-expansion work available from the reaction is equal to the change in standard Gibbs energy, $\Delta_r G^\ominus$. Approximately we can ignore the temperature dependence of the reaction enthalpy and use the tabulated value $\Delta_r H^\ominus = -2808 \text{ kJ mol}^{-1}$ at 25°C.

$$\Delta_r G^\ominus = \Delta_r H^\ominus - T\Delta_r S^\ominus = -2808 \text{ kJ mol}^{-1} - (310 \text{ K}) \times (+182.4 \text{ J K}^{-1} \text{ mol}^{-1}) = -2865 \text{ kJ mol}^{-1}$$

$w_{\text{add,max}} = -2865 \text{ kJ}$ for the combustion of 1 mol glucose molecules.

A person of mass 70 kg would need to do 2.1 kJ of work to climb vertically through 3.0 m; at least 0.13 g of glucose is needed to complete the task (and in practice significantly more).

Standard molar Gibbs energies

The **standard Gibbs energy of reaction**:

$$\Delta_r G^\ominus = \Delta_r H^\ominus - T\Delta_r S^\ominus$$

The standard Gibbs energy of reaction is the difference in standard molar Gibbs energies of the products and reactants in their standard states. It is convenient to define the **standard Gibbs energy of formation**, $\Delta_f G^\ominus$, the standard reaction Gibbs energy for the formation of a compound from its elements in their reference states. Standard free energies of formation of the elements in their reference states are zero, because their formation is a ‘null’ reaction. $\Delta_r G^\ominus$ can be easily obtained from $\Delta_f G^\ominus$ of the products and reactants:

$$\Delta_r G^\ominus = \sum \nu \Delta_f G^\ominus(\text{products}) - \sum \nu \Delta_f G^\ominus(\text{reactants})$$

Calorimetry (for ΔH directly and for S via heat capacities) is only one of several ways to determine Gibbs energies. They may also be obtained from equilibrium constants and electrochemical measurements, and calculated using data from spectroscopic observations and theoretically, using quantum mechanics.