

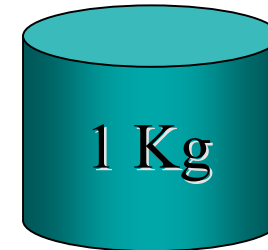
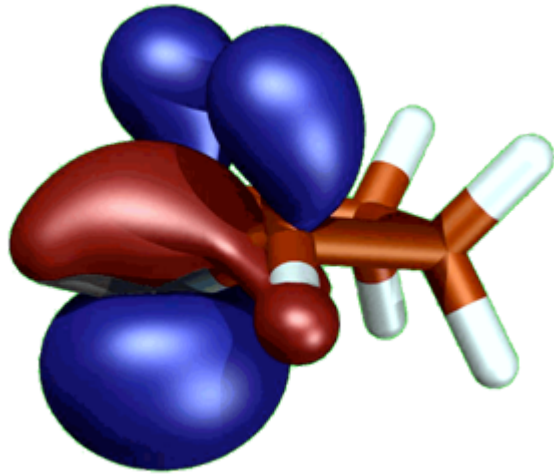
Classical Thermodynamics

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The background

- The field of Thermodynamics emerged as a consequence of the necessity to understand the processes associated with work production by means of steam engines.
- It deals with macroscopic systems, for which a molecular level description was either unconceivable (initially, no one knew about molecules) or considered extremely complicated (too large number of objects involved).
- It relies on experimental data to draw conclusions on the system under study.

The link between scientific fields



Statistical Mechanics predicts specific properties of compounds



Thermodynamics

Statistical Mechanics

Quantum Mechanics

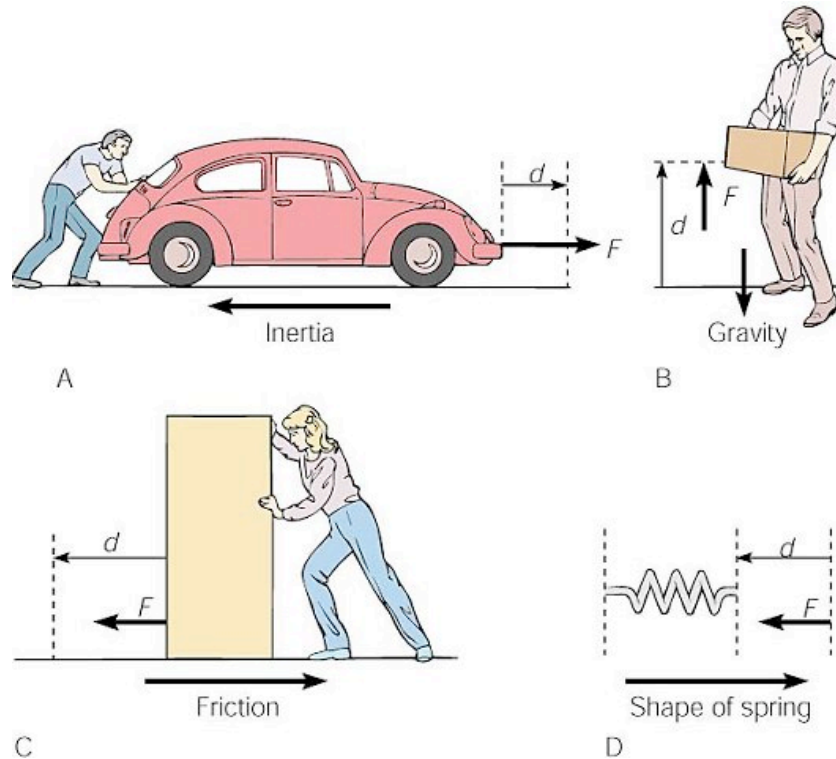


General Relationships between macroscopic variables (e.g. P, V, T, etc)



Quantum Mechanics allows one to compute the energy levels of atoms and molecules

The concepts of work and energy. I



When the state of a system (e.g. the height of a weight) is modified by an external process acting against a force (e.g. gravity) it is said that **WORK** is carried out.

$$W = \int \mathbf{F}(\mathbf{r}) d\mathbf{r}$$

(this integral is carried out over the curve representing the displacement of the system = **line integral**)

$$W = \int \mathbf{F}(\mathbf{r}) d\mathbf{r} = \int_0^d mg dh = mg \int_0^d dh = mgd$$

Work carried out against a constant force (gravitational, mg) along a straight line path (e.g. a crane lifting bricks on top of a building)

The concepts of work and energy. II

What would happen if we allow the weight to fall?

The gravitational force would accelerate the body with a constant acceleration and we can predict its velocity at $h=0$ using simple kinematics laws.

$$d = \frac{gt^2}{2} \Rightarrow t = \sqrt{\frac{2d}{g}} \Rightarrow v_f = gt = \sqrt{2gd}$$

With further elaboration, one gets:

$$W = mgd = mg \frac{gt^2}{2} = m \frac{v_f^2}{2} = E_{kin}$$

This tells us that:

- The work carried out lifting the weight can be converted into energy
- Kinetic energy can be used to change the height of a weight against the gravitational force (i.e. energy gives the capability of carrying out work), or

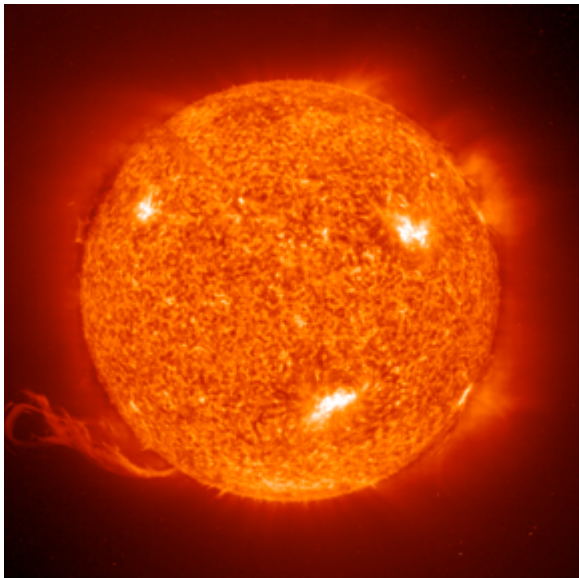
Work is a way of transferring energy between systems

The concept of heat

0th Law of Thermodynamics: if two closed systems in contact do not change their state it is said that they are in thermal equilibrium, no matter what is their composition. If A is in equilibrium with B, and B is in equilibrium with C, then A and C are in equilibrium.

The temperature of a system is defined on the basis of a macroscopic property of a reference system (height of mercury in a thermometer)

High temperature



Low temperature

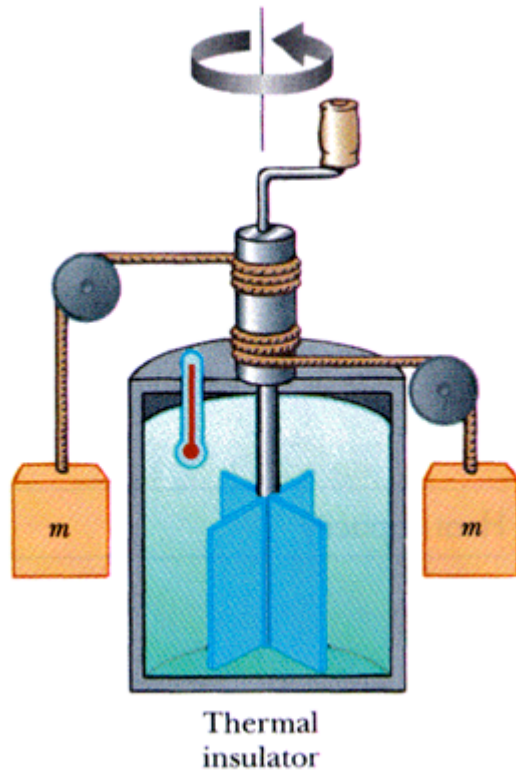


Heat flow



One witnesses a change in the temperature of both systems, decreasing the high T and increasing the low T. We speak about a **Heat Flow**.

The link between work and heat



Joules proved the equivalence between heat and mechanical work

The work carried out to move the paddles increases the temperature of water, making the process equivalent to heat exchange

- ✓ Joules also showed that the amount of heat was proportional to the amount of work carried out

Work and heat are both ways of transferring energy

The first law of Thermodynamics. I

Thermodynamics variable: a macroscopic observable that characterizes the state of a system (e.g. pressure, volume, etc) and that it is, within limits, under external control.

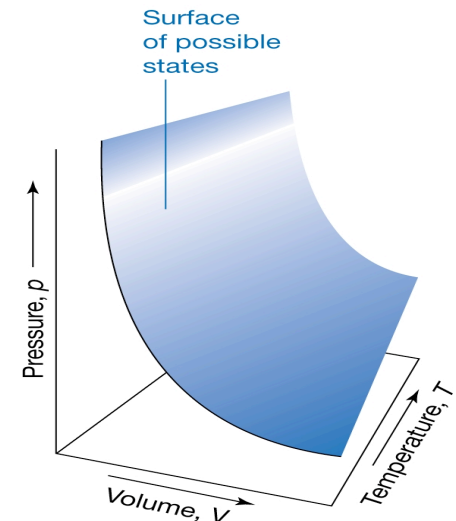
N.B.: not all thermodynamics variables of a system may be varied independently, they are connected through the **State Law**.

$$pV = nRT \quad \text{Ideal gas state law}$$

Thermodynamics function: a macroscopic quantity that depends only on the state of a system but not on the process (or path) that has been used to reach the state itself (e.g. height). Changing the value of a thermodynamics variable changes the value of state functions. Notice that

$$\int_{l_1} \mathbf{n}_z ds = \int_{l_2} \mathbf{n}_z ds = h$$

$$\oint \mathbf{n}_z ds = 0$$



The first law of Thermodynamics. II

Let's rewrite the previous two equations, assuming that there is no friction along any path and that the gravitational force does not change with height:

$$W = mg \int_{l_1} \mathbf{n}_z ds = mg \int_{l_2} \mathbf{n}_z ds = mgh = \Delta E_{pot}$$

$$mg \oint \mathbf{n}_z ds = 0$$



The change in energy does not depend on the path but only on the initial and final states.

Energy is a state function

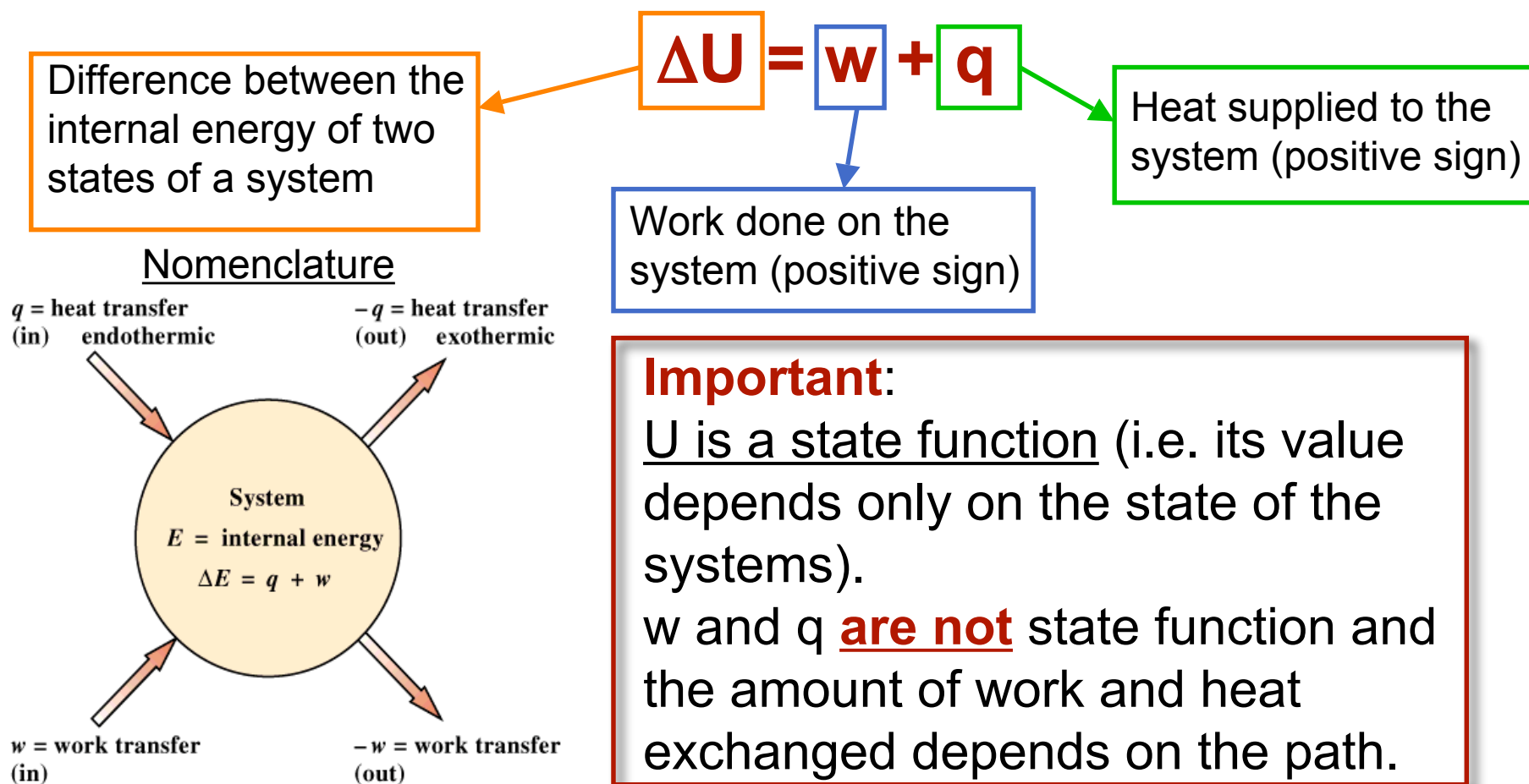
In presence of friction, an additional force is present, so that

$$W = \int_{l_1} (\mathbf{F}_{frict} + mg\mathbf{n}_z) ds = \int_{l_2} \mathbf{F}_{frict} ds + mgh = q + \Delta E_{pot}$$

Where q represents the amount of work which has been dissipated due to friction and has not been used to change the energy of the system (mechanical definition of heat).

The first law of Thermodynamics. III

The first law of Thermodynamics is a conservation law, equivalent to the conservation of the total energy (kinetic plus potential) in classical mechanics.



Processes: reversible and irreversible

One distinguishes two different kind of changes:

- Reversible: the direction of the process can be reversed by an infinitesimal modification of a variable (e.g. p). It is a process during which the system is in equilibrium with its surrounding (e.g. $T_{\text{sys}} = T_{\text{env}}$; $p_{\text{int}} = p_{\text{ex}}$) and it is quasi-static (i.e. the change happens infinitely slowly) with no dissipation due to friction.
- Irreversible: processes in which an infinitesimal modification of a variable does not reverse the direction (e.g. expansion of a compressed gas against the atmospheric pressure). Notice that **all** spontaneous processes are irreversible.

A reversible change is an idealization that allows us to eliminate the concept of time in Thermodynamics and that frees us from many complications in deriving general statements.

The first law of Thermodynamics. IV

How does U depend on the thermodynamics variables V , T ?

Let us consider a gas in a rigid container of volume V ; heating the gas is equivalent to increase its internal energy ($w=0$) and raises the gas temperature. We defined therefore

$$C_v = \left(\frac{\partial U}{\partial T} \right)_v \quad \text{Heat capacity at constant volume}$$

In the case mechanical work is carried out reversibly on the system with no heat exchange, one has

$$dU = \delta w = -p_{\text{int}} dV$$

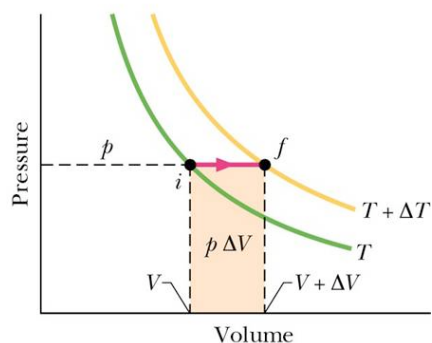
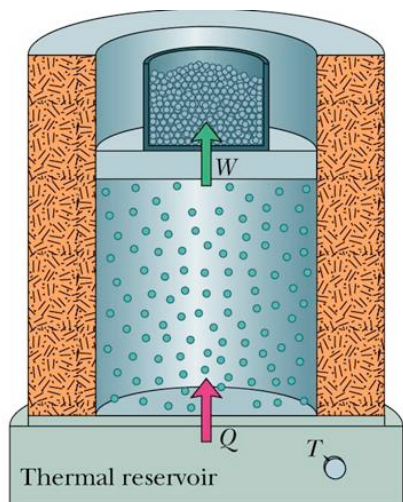
However, Joule proved that an **ideal gas** (i.e. non-interacting point particles) during a free expansion at constant T did not absorb any heat, so that

$$\left(\frac{\partial U}{\partial V} \right)_T = 0 \quad \longrightarrow$$

For an ideal gas, U is only function of T
 $T=\text{const} \longrightarrow U=\text{const}$

Processes at constant p_{ext} : enthalpy

In chemistry, very often changes happen with the system (e.g. the reaction vessel) being able to change its volume against a constant pressure applied by environment (isobaric). This indicates that mechanical work is exchanged between the two and suggests that an alternative state function may be better suited than U to describe the system.



Work done by the system against constant p_{ex} :

$$F_{\text{ex}} = Ap_{\text{ex}}$$

$$W_{p_{\text{ex}}} = -\int F_{\text{ex}} dh = -Ap_{\text{ex}} \int dh = -Ap_{\text{ex}} h = -p_{\text{ex}} \Delta V$$

Notice that the amount of work carried out depends only on the change of the thermodynamics variable V of the system; this allows us to define

$H=U+pV$ (enthalpy), which is a state function.

The heat exchanged with a thermal bath is given by:

$$q_p = \Delta U - w_p = \Delta U + p \Delta V = \Delta H$$

so that the change in enthalpy is equal to the amount of heat exchanged at constant pressure when no other work than expansion is done.

Thermochemistry and Born-Haber cycle. I

Often, it is useful to know in advance how much heat is released during a chemical process (e.g. combustion in a furnace) at constant p_{ex} . To do this, we can exploit the state function property of enthalpy (i.e. it depends only on the state of the system) and define the reaction enthalpy

$$\sum_i c_i^r R_i \rightarrow \sum_j c_j^p P_j \quad \Delta_r H = \sum_j c_j^p H_{P_j} - \sum_i c_i^r H_{R_i}$$

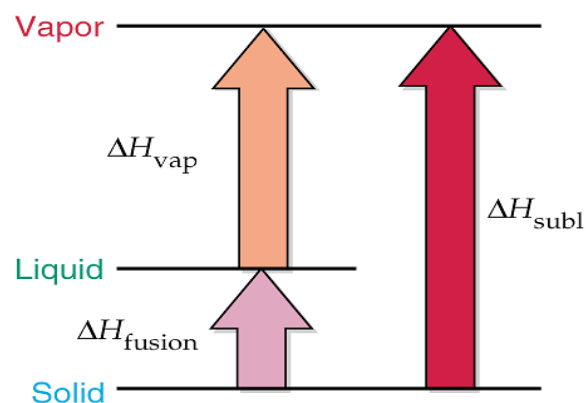
$\Delta H > 0$ endothermic
 $\Delta H < 0$ exothermic

If ΔH is measured at 1 bar and 298.15 K with P and R in their most stable form in those conditions, it is called **standard reaction enthalpy** ($\Delta_r H^\circ$). In these conditions, if the reaction has only pure elements as R and only a P, it is called **formation reaction** and its change of enthalpy is called **standard formation enthalpy** ($\Delta_f H^\circ$). By definition, all $\Delta_f H^\circ$ for pure elements in their standard phase are zero.

Hess's Law: the standard reaction enthalpy is the sum of the standard enthalpies of the reaction (or formation) into which the overall reaction may be formally divided.

Thermochemistry and Born-Haber cycle. II

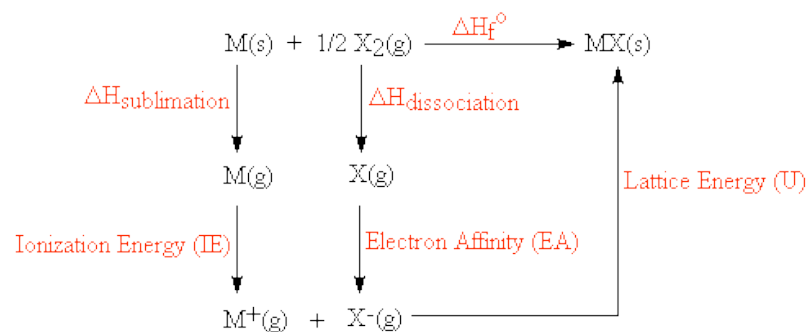
The state function property of H can also be used to estimate unknown enthalpy changes, provided there are alternative path to go from R's to P's.



Suppose we would like to know the standard vaporization enthalpy for water (l→v). We can think about this process as taking place in two step, namely crystallization and sublimation. Since the system moves between the same initial and final states, ΔH for the two step process is the same as vaporization: $\Delta H_{\text{vap}} = \Delta H_{\text{subl}} - \Delta H_{\text{fusion}}$.

Similarly to the case above where two phases of water are connected via different paths, the cycle for the formation of ionic salts from elements is indicated with the name of **Born-Haber cycle**.

Born - Haber Cycle



$$\Delta H_f^\circ = \Delta H_{\text{sub}} + \text{IE} + \Delta H_{\text{diss}} + \text{EA} + U$$

Entropy: the disorder of a system

We still cannot predict if a possible process is spontaneous or not, even with all the concepts introduced so far. However, we can extract useful insights by considering a very simple case, namely the free expansion of a gas in an isolated vessel.



For this spontaneous process, neither work is done nor heat is exchanged, so that the energy is constant. Thus, U is not the driving force.

However, we can easily understand that the total number of states available to any particle in the gas is doubled by the process (think about filling the volume with molecule-size boxes). In this case, a more disordered system is created at the end of the expansion. As a way of measuring the total number of states available to the system, one can define the **entropy** as

$$S = k_B \ln(\Omega)$$

where Ω indicates the number of state available to a system for a given energy U . In our example, $\Delta S > 0$, the signature of spontaneity.

Entropy in action: the second law

A more general analysis of spontaneous processes would also conclude that for these the entropy of a system and its environment cannot decrease. More directly:

Second Law: the entropy of an isolated system increases in the course of a spontaneous change. $\Delta S_{sys} + \Delta S_{env} \geq 0$

The same analysis would also conclude that, for a reversible process, the infinitesimal change of entropy dS of the system at any stage of the process is given by

$$dS = \frac{\delta q}{T}$$

where δq is the infinitesimal amount of heat exchanged at temperature T . Notice that, whereas δq is not a state function, dividing by T makes it so.

Focusing on the system: free energy

Let us suppose that a system is in equilibrium with its surroundings, the latter acting as thermal bath with temperature T . During an infinitesimal change, the variation of entropy of the surroundings is simply $\delta q_{\text{sys}}/T$ due to heat exchange. This allows us to write the Second Law inequality as

$$dS_{\text{sys}} - \delta q_{\text{sys}}/T \geq 0$$

which focuses only on the system. Can we give an expression for the amount of heat exchanged as a function of the process?

At constant V , the mechanical δw is zero, so from the First Law

$$\delta q_v = dU$$

At constant p , instead, we have already shown that

$$\delta q_p = dH$$

$$dU - TdS_{\text{sys}} = dA \leq 0$$

$$A = U - TS$$

Helmholtz function

Indicate the direction
of a spontaneous
process

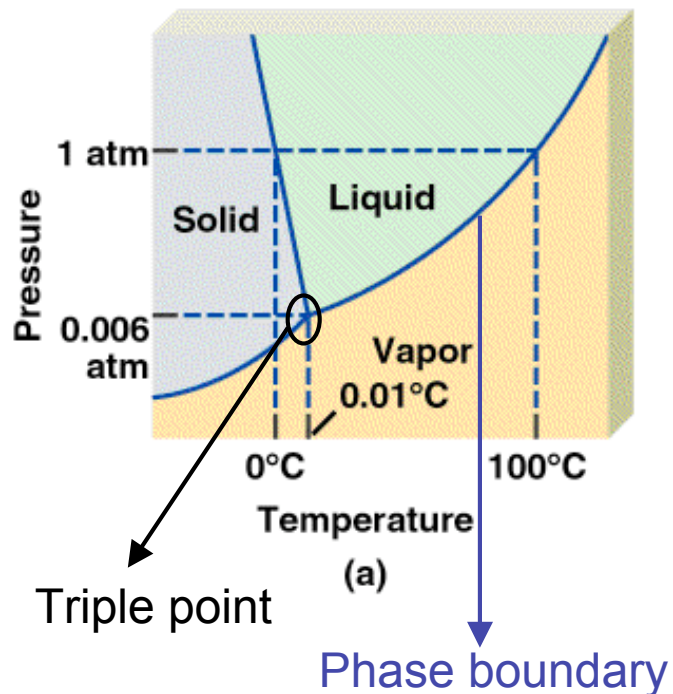
$$dH - TdS_{\text{sys}} = dG \leq 0$$

$$G = H - TS$$

Gibbs function

Phase diagrams and phase transitions. I

Matter can present itself in different forms (phases) with properties that strongly depend on the specific form. A phase diagram gives the conditions in which the different phases of a compound (e.g. water) can be found (are stable) as a function of the thermodynamics variables.



Along the phase boundaries, two or more phases are present and in equilibrium. It is said that a phase transition takes place at the value of p and T defined by the boundaries. At equilibrium, the direction is set by infinitesimal displacements of the variables. Depending on how the behavior of state variables and functions varies, one can distinguish two different kind of phase transitions:

First order: involves the exchange of latent heat

Second order: proceeds without heat exchange

Phase diagrams and phase transitions. II

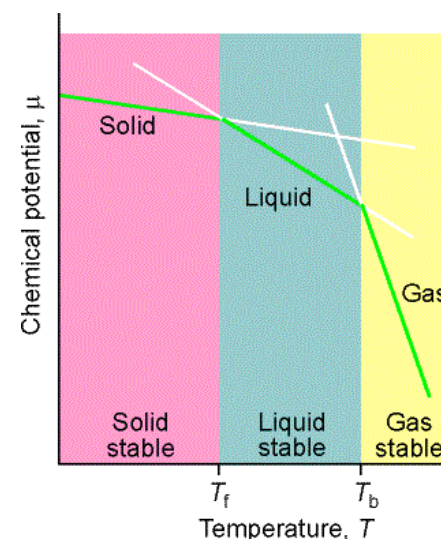
From the practical point of view, it would be useful to predict phase boundaries. We start with realizing that for two phases in equilibrium, moving one molecule from one phase to the other should make no difference with respect to the free energy of the system. To discuss this, let us introduce the **chemical potential** for phase 1

$$\mu_1 = \left(\frac{\partial G}{\partial n_1} \right)_{p,T,n_2,etc}$$

which tells us the change of G for the system when a molecule is added to phase 1. The condition of equilibrium between two phases is therefore

$$\left(\frac{\partial G}{\partial n_1} \right)_{p,T,n_2,etc} = \mu_1 = \mu_2 = \left(\frac{\partial G}{\partial n_2} \right)_{p,T,n_1,etc}$$

On the other hand, if the two chemical potentials were different, the system would prefer to have molecules in the phase with lower chemical potential to decrease its free energy. These ideas can be used to predict the location of phase boundaries.



Phase diagrams and phase transitions. III

From general arguments, one can show that

$$\left(\frac{\partial \mu}{\partial T}\right) = -S_m, \quad \left(\frac{\partial \mu}{\partial p}\right) = V_m$$

The subscript m indicates molar quantities

$$d\mu = -S_m dT + V_m dp$$

Changes in T e p that leave the system on the phase boundary must be such that

$$d\mu_1 = -S_{m,1}dT + V_{m,1}dp = d\mu_2 = -S_{m,2}dT + V_{m,2}dp$$

$$\frac{dp}{dT} = \frac{V_{m,2} - V_{m,1}}{S_{m,2} - S_{m,1}} = \frac{\Delta S_m}{\Delta V_m} = \frac{\Delta H_m}{T\Delta V_m}$$

Clapeyron equation

Notice that the previous equation does imply that p and T cannot vary independently if we want the two phases to coexist. Gibbs proved a general theorem that relates the number of independent variables (F) whose value could be changed still maintaining unchanged the number of components (C) and the number of phases (P) in the system (**phase rule**)

$$F = C - P + 2$$

Chemical equilibrium

Similar arguments can be used for a chemical transformation in the gas phase, i.e. to predict the equilibrium conditions for the reaction

$$\sum_i c_i^r R_i \rightarrow \sum_j c_j^p P_j \quad dG = \sum_j c_j^p \mu_{P_j} d\xi - \sum_i c_i^r \mu_{R_i} d\xi$$

where $d\xi$ is an infinitesimal advancement of the reaction. At equilibrium, $dG=0$ and one gets

$$0 = \sum_j c_j^p \mu_{P_j} - \sum_i c_i^r \mu_{R_i}$$

For an ideal gas, $\mu = \mu^\ominus + RT \ln \left(\frac{p}{p^\ominus} \right)$ where the superscript indicates standard quantities ($p=1$ bar).

Substituting into the equilibrium conditions, one obtains

$$0 = \boxed{\sum_j c_j^p \mu_{P_j}^\ominus - \sum_i c_i^r \mu_{R_i}^\ominus} + RT \ln \left(\frac{\prod_j p_{P_j}^{c_j^p}}{\prod_i p_{R_i}^{c_i^r}} \right) \rightarrow -\boxed{\frac{\Delta G^\ominus}{RT}} = \ln \left(\frac{\prod_j p_{P_j}^{c_j^p}}{\prod_i p_{R_i}^{c_i^r}} (p^\ominus)^{-\sum_j c_j^p + \sum_i c_i^r} \right)$$