Glossary

Thermodynamics - the science that is concerned with **energy**, particularly **'energy-in-transit'** in the forms of **heat** (Q) and **work** (W), and those **properties** of **systems** that are related to energy.

Energy – the ability to do work. **All energy is *relative*!** Energy-in-transit is not relative.

Three kinds of energy:

1) Potential (E_p): energy due to *relative* position,
2) Kinetic (E_k): energy due to *relative* velocity,
3) Internal (U): the sum of all potential and kinetic energies of constituent parts [atoms, molecules, etc.] of a system.

So, the total energy will be:

$$E = E_p + E_k + U$$

In the absence of motion and gravity

$$E = U$$

1 and 2 are partially macroscopic, and 3 is partially microscopic.

Two kinds of 'energy-in-transit':

1) Heat (Q): energy transferred between system and surroundings because of a temperature difference, or gradient. Or, a way to change internal energy, besides work. (Energy in transit.)
2) Work (W): energy transferred between system and surroundings because of a pressure difference, or gradient.

Thermodynamic System – just "the thing" that we are talking about!

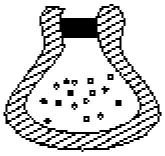
- ☞ ***System*** some portion of the physical world (e.g. a piece of metal, a magnet, etc)
- ☞ ***Surroundings are*** everything else.

The sum of the **system and the surroundings** is the **universe**.

Universe = system (interior) + surrounding (exterior).

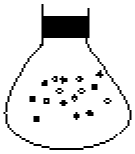
Three kinds of systems:

1) Isolated system (not an important concept): neither energy nor mass may cross the system boundaries, e.g. a thermos.
2) Closed system : System with fixed quantity of material; energy can cross the system boundaries but mass cannot, e.g. a sealed beaker.
3) Open system : a particular region of space; both mass and energy may cross the system boundaries, e.g. an open beaker.



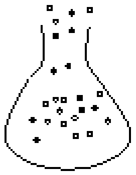
micro-canonical

Isolated



canonical

Closed



grand-canonical

Open

In elementary thermodynamics all systems consist only of atoms and molecules where the net electric charge of the system is zero. In addition, all electrical and magnetic and surface forces are generally neglected.

☞ ***Ensembles*** I have a set of 1000 systems. I want to predict *average* values for this set. This is *the right question* for Stat Thermo! Which we will talk about in the future. The set is called *ensemble*.

- ***Macroscopic state variables*** such as volume V, pressure P, temperature T, mole numbers n.

Five basic thermodynamic properties:

1) Temperature [T] (thermal potential) - a measure of the relative hotness or coldness of a material. Or, a measure of the internal energy of a system.
2) Pressure [P] (mechanical potential) - the normal (perpendicular) component of force per unit area.
3) Volume [V] (mechanical displacement) - the quantity of space possessed by a material.
4) Entropy [S] (thermal displacement) - the quantity of disorder possessed by a material. The change of entropy is equal to the heat added or removed divided by the temperature.
5) Internal energy [U] - the energy of a material which is due to the kinetic and potential energies of its constituent parts (atoms and molecules, usually). Or, the energy of atoms or molecules that does not give macroscopic motion.

Two secondary thermodynamic properties:

[1] Enthalpy [H] - internal energy plus the pressure-volume product.

[2] Heat capacity [Cp or Cv] (specific heat) - the amount of energy required to increase the temperature of one unit quantity of material by one degree, under specific conditions.

(a) constant pressure Cp = dh/dT
(b) constant volume Cv = du/dT

☞ Unlike gases, liquids and solids are nearly incompressible, and it is almost impossible to change their temperature while holding their volumes constant. The specific heats of liquids and solids almost always imply their constant pressure heat capacity (usually on a unit mass basis), so that, in general, for liquids and solids we used Cp.

The variables of state can be divided into two types:

1) **Intensive variables**: do not depend on the amount of substance present. Examples include: the temperature T, pressure P, density (mass/volume) ρ, and the external magnetic field $\vec{\mathrm{H}}$.
2) **Extensive variables**: depend on the amount of matter in the system (e.g. mass). Examples include: the volume V, internal energy U, enthalpy H, entropy S, and heat capacity C, total magnetic moment $\vec{M}$.

Notes:

- ➢ When we put two identical systems together, the intensive quantities, such as the temperature, would be unchanged but the extensive quantities, such as the entropy, would be doubled. This is possible only when the surface energy of the system is neglected. Such condition is justified since we are considering a macroscopic system which can be assumed arbitrarily large and the surface effect can be made arbitrarily small.
- ➢ Any extensive variable can be converted to an intensive variable by dividing it by the moles or the mass.

- Thermodynamic limit, i. e. in the limit where

$$V \to \infty, \quad N_i \to \infty, \quad \text{at fixed intensive variables.}$$

Reasons :

- ➢ For finite systems the thermodynamic quantities are always **analytic functions** of their variables. Singular behavior as required for phase transitions does not occur. Because of the finite volume **the correlation length is finite**.
- ➢ **Spontaneous symmetry breaking** exists only in the thermodynamic limit. In finite systems the breaking is explicit by an external field or by the boundary conditions.
- ➢ In the thermodynamic limit the different ensembles are equivalent.
- ➢ In the thermodynamic limit there is no boundary (surface) dependence.

☞ The usual extensive variables become infinite in the thermodynamic limit. We therefore use densities:

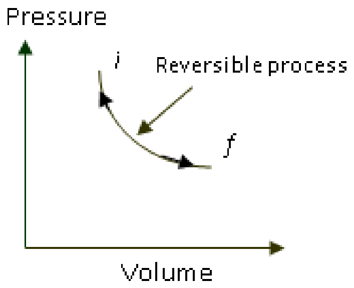
$$\epsilon = U/V \quad \text{energy density}$$
$$\vec{M} = \vec{\mathcal{M}}/V \quad \text{magnetization}$$
$$s = S/V \quad \text{entropy density}$$
$$f = F/V = \epsilon - Ts \quad \text{free energy density}$$

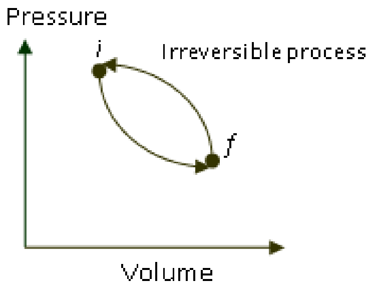
- ***Path*** is a series of states through which a system passes.

- ***A process*** is a change of state expressed in terms of a path along the equation of state surface. i.e. it is any succession of events.
- ***A quasi-static process*** is a process in which, at each instant, the system is only departs infinitesimally from an equilibrium state.

- ***A reversible process*** is a process whose direction can be reversed by an infinitesimal change in some of its property. It is a quasi-static process in which no dissipative forces such as friction are present. In another words, if the process happens slow enough to be reversed.

- ***Irreversible***: if the process cannot be reversed (like most processes).





***Some more definitions, regarding the process, are as follows*:**

1) **isobaric:** process done at constant pressure, ($\Delta P = 0$).
2) **isochoric:** process done at constant volume, ($\Delta V = 0$).
3) **isothermal:** process done at constant temperature, ($\Delta T = 0$).
4) **adiabatic:** process where, ($\Delta Q = 0$).
5) **cyclic:** process where initial state = final state

Reversible process – an *idealized* process in which the deviation from thermodynamic equilibrium is infinitesimal at any particular instant during the process. All of the states through which a system passes during a reversible process may be considered to be equilibrium states. This is an *idealized* situation that would require infinite time and/or equipment size to be realized. The concept of a reversible process serves to set a maximum for the efficiency of a given process. Note that an *isentropic* process is an adiabatic-*reversible* process, so that real *isentropic* processes are not possible.
thermodynamic cycle - a process for which the final and initial states are the same.

Thermodynamic Processes and Cycles

1) Chemical process - a chemical or physical operation, or series of operations, which transforms raw materials into products.
2) Thermodynamic process - the path of succession of states through which the system passes in moving from an initial state to a final state.
3) Polytropic process - a thermodynamic process for which [PV^n] is constant. These processes are usually associated only to systems for which the ideal gas assumption holds.

Four special polytropic processes:

1) Isobaric - - - - - - - constant pressure [$n = 0$]
2) Isothermal - - - - - - constant temperature [$n = 1$]
3) Isentropic - - - - - - constant entropy [$n = \gamma = C_p / C_V$]
4) Isochoric (isometric) - constant volume [$n = \infty$]

Two other important processes:

1) adiabatic - no heat transfer.
2) isenthalpic - constant enthalpy. This is the same as isothermal for an ideal gas system.

Equilibrium state is one in which the properties of the system are uniform throughout and do not change with time unless the system is acted upon by external influences (e.g. magnetic or electric fields)

***A system is said to be in thermodynamic equilibrium if it attains*:**

1) Thermal equilibrium ($\Delta T = 0$).
2) Mechanical equilibrium ($\Delta P = 0$), which means that all forces of interaction between the system and surroundings are in equilibrium.
3) Chemical equilibrium ($\Delta \mu_i = 0$), i.e. no change in structure takes place.

- ***Non-Equilibrium*** characterizes a systemin which gradients exist and whose properties vary with time (e.g. the atmosphere and the oceans)

- ***Equation of state*** is a functional relationship among the state variables for a system in equilibrium, e.g. $PV = nRT$.

- ***State function*** depends only on the initial and final positions. For example: Energy (U), Entropy (S). Work (W) and heat (Q) are not state functions because they are depending on their path.

- ***Exact differentials*** e.g. dV, dP, dT, and dU. Exact differentials may be integrated since we are only concerned with the initial and final states, not with the path taken as dW. Usually the state function is an exact differential.

- ***Inexact differentials*** e.g. dW and dQ, cannot integrated unless we know the path taken by the system in passing from state to another.

- ***Systems wall*** is the boundary between a system and its surroundings through which changes may be imposed.

We have two kinds of separation walls:

1) ***Adiabatic wall*** is a boundary that permits no heat interaction between the system and its surroundings.
2) ***Diathermal wall*** is a boundary that freely allows heat to be exchanged.

Four common '*idealized*' thermodynamic cycles:

1) Carnot cycle - isothermal and isentropic compressions followed by isothermal and isentropic expansions.
2) Rankine cycle - isobaric and isentropic compressions followed by isobaric and isentropic expansions.
3) Otto cycle - isentropic and isochoric compressions followed by isentropic and isochoric expansions.
4) Diesel cycle - isentropic compression followed by isobaric, isentropic and isochoric expansions

Thermodynamic Laws

A physical law is a simple statement of an observable physical phenomenon that has no underlying, more-basic reason for being except that the most accurate observations have always proved it to be true.

Laws of Thermodynamics

Zeroth: It is the concept of temperate; and states that:

"*If objects A and B are separately in **thermal equilibrium** with a third object, C, then A and B are in thermal equilibrium with each other* ".

(This "Law" simply states that 'thermometers work'.)

First:

A Simple Statement:

"*Heat and work are both forms of energy in transit, and energy is always conserved.*"

or

A Classical Statement:

"*During any cyclic process on a closed system the cyclic integral of heat is always equal to the cyclic integral of work*".

Second: Simple Statement #1:

"*Spontaneous fluxes always take place down their corresponding potential gradients.*"

or

Simple Statement #2:

"*Heat and work are both forms of energy in transit, but they are not qualitatively equal forms of energy because work can always be converted entirely into heat, but heat can never be converted entirely into work.*"

or

Kelvin-Plank Statement:

"*It is impossible to construct a device which operates in a cycle and produces no effect other than the raising of a weight and the exchange of heat with a single reservoir.*"

or

Clausius Statement:

“*It is impossible to construct a device which operates in a cycle and produces no effect other than the transfer of heat from a cooler body to a hotter body.*”

Albert Einstein considered the Second Law of Thermodynamics to be the **only** real physical law.

The Third Law of Thermodynamics

Nerst’sstatement:

“All reactions in a ***pureliquid or solid*** *in thermal equilibrium take place with no change of entropy in the neighborhood of absolute zero“.*

$$\lim_{T\to 0}\left(S_i - S_f\right) = 0$$

where the subscripts i and f refer to the initial and final states, respectively.

Planck’sstatement:

“The entropy of a true equilibrium state of a system at absolute zero is zero. It is applicable to all condensed phases, including solutions.“

$$\lim_{T\to 0} S = 0$$

Unattainability statement:

“It is impossible to reduce the temperature of a system to absolute zero using a finite number of processes.“

Important notes:

1) As the entropy of a substance is a measure of randomness or disorder, $S_o = 0$ implies a highly order (maximum order) state of matter.
2) This law applies to perfect crystalline substance only. Unfortunately, perfect crystalline substances are difficult to identify.
3) A glass or amorphous substance is not completely ordered even at the absolute zero of temperature. Therefore, any disorder remaining at the absolute zero of temperature gives a finite value of S_o.

Consequences of the third law:

1) For all known solids, the expansivity approaches zero as the temperature approaches absolute zero.

$$\lim_{T\to 0} \beta = 0 .$$

2) The slope of the boundary between two phases is zero at absolute zero.

$$\lim_{T\to 0} \frac{dP}{dT} = 0 .$$

3) The heat capacities approach zero as the temperature approaches absolute zero.

$$\lim_{T\to 0} C_P = 0, \quad \lim_{T\to 0} C_V = 0\,.$$

Other Laws of Importance in Thermodynamics

Conservation of Matter: Matter can be neither created nor destroyed but only changed from one form to another. Note that Albert Einstein showed that matter could be ‘destroyed’ by converting it into energy.
Joule's “Law”: The internal energy of an ideal gas is a function of temperature only.
Avagadro's “Law”: Equal volumes of different ideal gases at the same temperature and pressure contain the same number of molecules.

Critical Relationships

Zero'th law of Thermodynamics

Two bodies which are in thermal equilibrium with a third body are in thermal equilibrium with each other.

First law of Thermodynamics

The total energy of an isolated system must remain constant, although there may be changes from one form of energy to another. If we designate the total or internal energy of an isolated or closed system as E, heat as Q and work as W , then the circular integral involving no change in net internal energy is:

$$\oint (dQ - dW) = 0 \tag{1}$$

If the system is closed to the input of matter, but not of energy, then

$$dE = dQ - dW \tag{2}$$

Mechanical work is, of course only the product of force times distance, and force is pressure P time surface area, so mechanical work is simply the product of pressure times surface area times distance, or PV. At constant pressure:

$$dW = PdV \tag{3}$$

Substituting in Eq. 2 yields the most common form of the first law of thermodynamics:

$$dE = dQ - PdV \tag{4}$$

In other words, you can't win -- energy cannot be created, only converted from one form to another.

Enthalpy

The enthalpy or heat content is defined as:

$$H = E + PV \tag{5}$$

It's clear from this relationship that enthalpy is the sum of two energy terms. Differentiating (5) at constant pressure:

$$dH=dE+PdV \tag{6}$$

and from (4) $dE=dQ-PdV$, we have

$$dH = dQ \tag{7}$$

which shows that at constant pressure, the change in enthalpy is governed by the added work performed on the system.

Heat Capacity

Heat capacity is defined as the heat added to the system divided by the rise in temperature. While the heat capacity is not strictly speaking constant, it remains a nearly constant material property over wide temperature ranges. Heat capacity is either considered at constant pressure:

$$C_P = \left(\frac{\partial Q}{\partial T}\right)_P \tag{8}$$

or constant volume

$$C_V = \left(\frac{\partial Q}{\partial T}\right)_V \tag{9}$$

Heat capacity normally has the units W/kg ^{o}C and is physically defined as the amount of heat required to raise 1 kg of a material $1\,^{\circ}\mathrm{C}$. Closely related is the **Specific Heat**, which has the same units, and is the ratio of the heat capacity of a substance to that of water at $15\,^{\circ}\mathrm{C}$.

Second Law of Thermodynamics

A succinct statement of the second law: "Things break down", or "You can't even break even". Entropy, S is the measure of the disorder in the system and is a single-valued function of the state of the system. Like the internal energy, it is dependent on the mass of the system. Under equilibrium conditions:

$$dS = \left(\frac{dQ}{T}\right)_{rev} \tag{10}$$

meaning that the process is reversible. for a spontaneous, disequilibrium process:

$$dS > \left(\frac{dQ}{T}\right)_{irr} \tag{11}$$

That is, irreversible processes increase the entropy of the system.

Third Law of Thermodynamics

There is such a thing as absolute zero, a temperature below which there is no more entropy in the system. Knowing this entropy allows us to use the second law to calculate the isobaric entropy within a phase at any temperature. From Eq. 8, the definition of isobaric heat capacity, we have:

$$dQ = C_P\, dT \tag{12}$$

which can be substituted into Eq. 10 to yield

$$dS = \frac{C_p dT}{T} \tag{13}$$

The entropy at some fixed pressure and any temperature T is then

$$S_T = S_0 + \int_0^T \frac{C_p dT}{T} + \sum \frac{\Delta H_{trans}}{T} \tag{14}$$

or

$$S_T = S_0 + \int_0^T C_p d\ln T + \sum \frac{\Delta H_{trans}}{T} \tag{15}$$

where the second term accounts for the heat of transition for any phase transformation that may have occurred along the way.

Gibbs Free Energy $G(P,T)$

The energy available to drive reactions in a system is less than the total energy, because some is tied up in entropy and some is tied up in the PV term. The remaining energy is called the Gibbs free energy, and is defined as:

$$G = E + PV - TS = H - TS \tag{16}$$

at constant P and T:

However, for the more general case, let us differentiate Eq. 16:

$$dG = dE + PdV + VdP - TdS - SdT \tag{18}$$

Substituting the expressions for the first and second laws (Eqs. 4 and 5) gives:

$$G = VdP - SdT \qquad (19).$$

Two important relationships from this equation lie in its partial derivatives with respect to pressure and temperature:

$$\left(\frac{\partial G}{\partial T}\right)_P = -S \tag{20}$$

and

$$\left(\frac{\partial G}{\partial P}\right)_T = V \tag{21}$$

Reversible equilibrium reactions take place with no change in G, whereas spontaneous reactions involve a decrease in G.

Chemical Potential

The Gibbs free energy is only a function of P, T and the quantities of phases in the system. It is necessary to extend G to also describe compositional changes in the phases. In phases showing chemical variation, it is useful to establish another quantity, the chemical potential μ , which is the partial molar free energy of a component in a phase, and is defined as:

$$\mu_i = \left(\frac{\partial G}{\partial n_i}\right)_{T,P,n_1,n_2,\dots n_{i-1}} \tag{22}$$

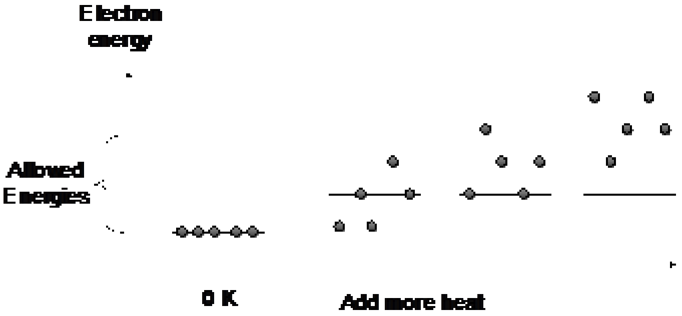
where ni are the numbers of moles of each component in each phase in the system. The more general form of the Gibbs free energy equation then becomes:

$$dG = \left(\frac{\partial G}{\partial T}\right)_{T,P,n_1,n_2,\dots n_{i-1}} dT + \left(\frac{\partial G}{\partial P}\right)_{T,P,n_1,n_2,\dots n_{i-1}} dP + \sum\left(\frac{\partial G}{\partial n_i}\right)_{T,P,n_1,n_2,\dots n_{i-1}} dn_i \tag{23}$$

So not only must the Gibbs free energy of both reactant and product in a single component system be equal, at equilibrium (as we saw in the previous section) but the chemical potentials of each component must be equal between the phases. The chemical potentials will be different from each other within each given phase, of course. The minimization of the Gibbs free energy of a system is the basis of almost all petrology and geochemistry.

Brief Review of Thermodynamics

Discussion on statistical mechanics (SM) often begins with thermodynamics. Thermal energy (heat) transferred to a molecule does not change the nature of the available energy levels, but it does change which energy levels are occupied by the electrons:



Within a macroscopic material sample (made up of Avogadro's number of atoms), the total internal energy is still theoretically quantized, though the energy levels may be very close together (so close that we cannot really measure the quantization). At finite temperature, each atom's electrons are excited to some distribution among the available energy levels; with increasing thermal energy in the system, the electrons are able to access higher and higher energy levels. One of the main objectives of statistical mechanics is to predict how the energy levels are occupied for a given model of how a system responds to thermal energy.

The reason is that SM provides a microscopic basis of thermodynamics and meaning to such terms as entropy and free energy which is otherwise rather hard to understand. Another important reason, not often emphasized enough, is that thermodynamics by itself is not very useful because it does not have the capacity to generate numbers needed to understand experiments. For example, the first two laws define all sorts of relations between thermodynamic variables and functions, but do not tell you how to calculate them. This deficiency partly the reason for the third law which tells that entropy of a perfectly crystalline solid is zero. Remember that this law is used to obtain entropy and enthalpy and then free energy, by integrating temperature dependent specific heat all the way from zero Kelvin.

Let us go through the three laws quickly. The *first law* has to do with conservation of energy. But in practical terms in gives a relation between energy, work and heat.

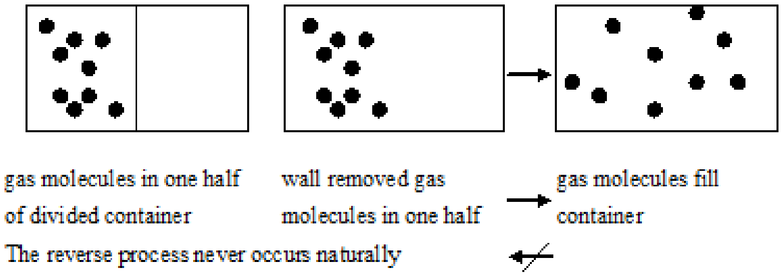
$$\text{đ}Q = \text{đ}W + dU = PdV + dU \Rightarrow \quad C_V = \left(\frac{\partial U}{\partial T}\right)_V$$

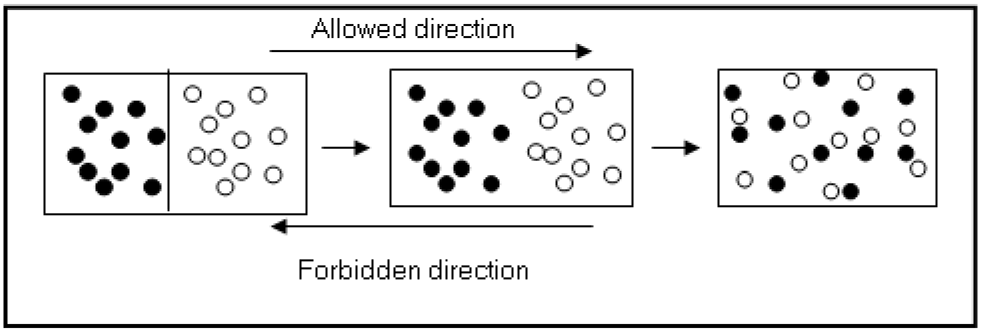
where work and heat are not exact differentials because they depend on path and are not state functions.

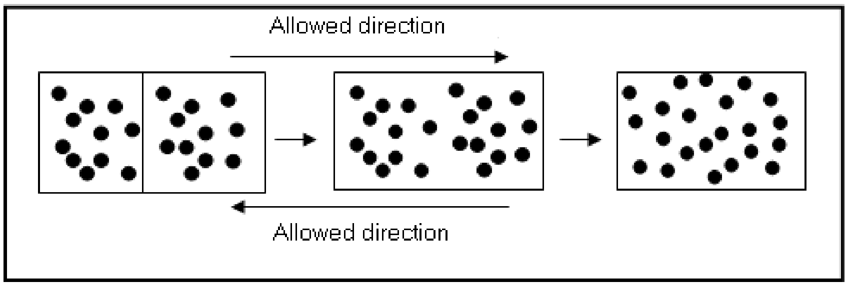
There are several nearly equivalent statements of *the second law* but ultimately all boil down to statements about entropy. The extensive state function entropy is an increasing function of energy. Entropy obeys Clausius Inequality in the form

$$dS \geq \frac{\text{đ}Q}{T}$$

where the equality is sign is for a reversible process. The success of second law of thermodynamics is of course in the introduction of free energies







Internal Energy

$$dU = TdS - PdV \Rightarrow T = \left(\frac{\partial U}{\partial S}\right)_{N,V}, \qquad P = -\left(\frac{\partial U}{\partial V}\right)_{N,S}, \qquad \frac{P}{T} = \left(\frac{\partial S}{\partial V}\right)_{N,E}$$

Enthalpy

$$H = U + PV$$

$$dH = dU + PdV = dQ \quad \text{at constant } P \text{ and } T \Rightarrow \quad C_P = \left(\frac{\partial H}{\partial T}\right)_P$$

It is a state function.

Helmholtz free energy

$$F = U - TS \Rightarrow \quad dF = dU - TdS - SdT = -PdV - SdT, \quad S = \left(\frac{dF}{dT}\right)_V$$

and the important variational statement that for a system at equilibrium, the free energy of the system is minimum. That is, any change will increase the free energy of the system. It measures the useful work obtainable for a closed thermodynamic system at a constant temperature and volume.

Gibb's function

$$G = F + PV \Rightarrow \quad dG = VdP - SdT = 0 \text{ at constant } P \text{ and } T$$

(e.g. in phase transition such as melting)

Maxwell's relations

$$\begin{aligned} dU &= -PdV + TdS, \\ dH &= VdP + TdS, \\ dF &= -PdV - SdT, \\ dG &= VdP - SdT \end{aligned}$$

$$\left(\frac{\partial T}{\partial V}\right)_S = -\left(\frac{\partial P}{\partial S}\right)_V, \quad \left(\frac{\partial V}{\partial S}\right)_P = \left(\frac{\partial T}{\partial P}\right)_S, \quad \left(\frac{\partial S}{\partial P}\right)_V = -\left(\frac{\partial V}{\partial T}\right)_P, \quad \left(\frac{\partial P}{\partial T}\right)_V = \left(\frac{\partial S}{\partial V}\right)_T$$

For different components

$$\begin{aligned} dU &= -PdV + TdS + \sum \mu_i dn_i, \\ dH &= VdP + TdS + \sum \mu_i dn_i, \\ dF &= -PdV - SdT + \sum \mu_i dn_i, \\ dG &= VdP - SdT + \sum \mu_i dn_i \end{aligned}$$

Where the chemical potential μ_i is given by:

$$\mu_i = \left(\frac{\partial U}{\partial n_i}\right)_{S,V} = \left(\frac{\partial H}{\partial n_i}\right)_{S,P} = \left(\frac{\partial F}{\partial n_i}\right)_{T,V} = \left(\frac{\partial G}{\partial n_i}\right)_{T,P}$$

Students are encouraged to read the article by Frank Lambert in Chemical Education, available in a more recent form in the site http://www.entropysite.com/students_approach.html for a shorter approach to understanding the second law and entropy.

The *third law* is simple : Entropy of a perfectly crystalline substance is zero ate absolute zero.

However, it is the third law that allows calculation of entropy

$$\Delta S = \int_0^T (C_P / T) dT$$

We can find temperature dependence of the specific heat in the form of a series in T in many handbooks and these expansions are widely used by Geologists, Metallurgists and Chemical Thermodynamics researchers in the evaluation of free energy.

FORMULA SHEET FOR STATISITICAL THERMODYNAMICS

Thermodynamic potential	Independent variables	Reciprocity relations	Maxwell relations
Internal energy U	S,V $dU = TdS - PdV$	$T = \left(\frac{\partial U}{\partial S}\right)_V, -P = \left(\frac{\partial U}{\partial V}\right)_S$	$\left(\frac{\partial T}{\partial V}\right)_S = -\left(\frac{\partial P}{\partial S}\right)_V = \frac{\partial^2 U}{\partial V \partial S}$
Enthalpy $H = U+PV$	S,P $dH = TdS + VdP$	$T = \left(\frac{\partial H}{\partial S}\right)_P, V = \left(\frac{\partial H}{\partial P}\right)_S$	$\left(\frac{\partial T}{\partial P}\right)_S = \left(\frac{\partial v}{\partial S}\right)_P = \frac{\partial^2 H}{\partial P \partial S}$
Helmholtz function $F = U - TS$	T,V $dF = -SdT - PdV$	$S = -\left(\frac{\partial F}{\partial T}\right)_V, -P = \left(\frac{\partial F}{\partial V}\right)_T$	$\left(\frac{\partial S}{\partial V}\right)_T = \left(\frac{\partial P}{\partial T}\right)_V = \frac{\partial^2 F}{\partial V \partial T}$
Gibbs function $G = U - TS+PV$ $=H - TS=F+PV$	T,P $dG = -SdT + VdP$	$S = -\left(\frac{\partial G}{\partial T}\right)_P, V = \left(\frac{\partial G}{\partial P}\right)_T$	$\left(\frac{\partial S}{\partial P}\right)_T = -\left(\frac{\partial V}{\partial T}\right)_P = \frac{\partial^2 G}{\partial P \partial T}$
First Td equation	$Tds = C_V dT + T\left(\frac{\partial P}{\partial T}\right)_V dV$	$Tds = C_V dT + T\frac{\beta}{\kappa} dV$	
Second Td equation	$Tds = C_P dT - T\left(\frac{\partial V}{\partial T}\right)_P dP$	$Tds = C_P - T\beta dP$	
Third Td equation	$Tds = C_V\left(\frac{\partial T}{\partial P}\right)_V dP + C_P\left(\frac{\partial T}{\partial V}\right)_P dV$		
S,V are constant.	$dS = dV = 0$	$dU \le 0$	*Minimum U*
S,P are constant.	$dS = dP = 0$	$dH \le 0$	*Minimum H*
T,V are constant.	$dT = dV = 0$	$dF \le 0$	*Minimum F*
T,P are constant.	$dT = dP = 0$	$dG \le 0$	*Minimum G*
Adiabatic	$dQ = dU + PdV = 0$	$dS \ge 0$	*Maximum S*

Theromdynamic functions	Notation	Independent variables	Differential
Internal energy	U	S,V,N	$TdS - PdV + \mu dN$
Heat function (enthalpy)	H	S,P,N	$TdS + VdP + \mu dN$
Helholtz free energy	F	T,V,N	$-SdT - PdV + \mu dN$
Gibbs free energy	G	T,P,N	$-SdT + VdP + \mu dN$
Landau free energy	Ω	T,V,μ	$-SdT - PdV - Nd\mu$

Thermodynamic potentials (summary)

$\beta = \frac{1}{V}\left(\frac{\partial V}{\partial T}\right)_P$	$\kappa = -\frac{1}{V}\left(\frac{\partial V}{\partial P}\right)_T$	$PV = NRT$	$R = C_P - C_V$
$dQ = dU + dW$	$dQ = Tds$	$C_P = \left(\frac{\partial U}{\partial T}\right)_P$	$C_V = \left(\frac{\partial U}{\partial T}\right)_V$
$\frac{\beta}{\kappa} = \left(\frac{\partial P}{\partial T}\right)_V$	$\frac{C_V}{T} = \left(\frac{\partial S}{\partial T}\right)_V$	$\left(\frac{\partial X}{\partial Y}\right)_Z \left(\frac{\partial Y}{\partial Z}\right)_X \left(\frac{\partial Z}{\partial X}\right)_Y = -1$	$\bar{K} = \frac{3}{2}KT$
$Q = mc\Delta T$	$P = \frac{W}{t}$	$\eta = \frac{W}{Q_h} = \frac{Q_h - Q_c}{Q_h}$	$\eta = 1 - \frac{T_c}{T_h} \quad (carnot)$
$n(number\ of\ mole) = \frac{M_{sample}}{mN_A}$	$m(mass\ of\ atom) = \frac{M_{sample}}{N_A}$	$PV^{\gamma} =$ constant, $PV =$ nRT	R = 8.31 J/mol K
$T(R) = T(F) + 459.67$	$T(F) = \frac{9}{5}T + 32$	1Bar $= 10^5$ Pascal	1atm $= 1.01 \times 10^5$ pascal
1 Liter = 10^{-3} m^3	1 calorie = 4.186 Joule	k = 1.38 x 10^{-23} J/K	NA = 6.02 x 10^{23} molecules/mole

Define $v = V/N$,

Thermal expansivity $= \beta(T,P) = \frac{1}{v}\left(\frac{\partial v}{\partial T}\right)_P$,

Isothermal comprisibility $= \kappa(T,P) = -\frac{1}{v}\left(\frac{\partial v}{\partial P}\right)_T$

$and \quad \left(\frac{\partial P}{\partial T}\right)_v = \frac{\beta}{\kappa}$

prove the following:

(i) $\left(\frac{\partial U}{\partial P}\right)_T = Pv\kappa - Tv\beta$,

(ii) $\left(\frac{\partial U}{\partial v}\right)_T = \frac{T\beta}{\kappa} - P$,

(iii) $\left(\frac{\partial U}{\partial v}\right)_T = \frac{T\beta}{\kappa} - P$

(iv) $\mu = \frac{v}{c_P}(\beta T - 1)$

Answer:

(i) To Prove that $\left(\frac{\partial U}{\partial P}\right)_T = Pv\kappa - Tv\beta$,

use $dU = Tds - Pdv$ which implies $\left(\frac{\partial U}{\partial P}\right)_T = T\left(\frac{\partial S}{\partial P}\right)_T - P\left(\frac{\partial V}{\partial P}\right)_T$,

and use Maxwell's equation $\left(\frac{\partial S}{\partial P}\right)_T = -\left(\frac{\partial v}{\partial T}\right)_P$, one can gets

$$\left(\frac{\partial U}{\partial P}\right)_T = -T\left(\frac{\partial v}{\partial T}\right)_P - P\left(\frac{\partial v}{\partial P}\right)_T = -Tv\beta + Pv\kappa$$

(ii) To Prove that $\left(\frac{\partial U}{\partial v}\right)_T = \frac{T\beta}{\kappa} - P$, use $dU = Tds - Pdv$ which implies $\left(\frac{\partial U}{\partial v}\right)_T = T\left(\frac{\partial S}{\partial v}\right)_T - P$, and use Maxwell's equation $\left(\frac{\partial S}{\partial v}\right)_T = -\left(\frac{\partial P}{\partial T}\right)_v$, one can gets

$$\left(\frac{\partial U}{\partial v}\right)_T = T\left(\frac{\partial P}{\partial T}\right)_v - P = \frac{T\beta}{\kappa} - P$$

(iii) To Prove $dh = c_P dT + v(1 - T\beta)dP$ use $dh = Tds + vdP$ which implies

$$\left(\frac{\partial h}{\partial P}\right)_T = T\left(\frac{\partial S}{\partial P}\right)_T + v = v - T\left(\frac{\partial v}{\partial T}\right)_P = v(1 - T\beta),$$

then

$$dh = \left(\frac{\partial h}{\partial T}\right)_P dT + \left(\frac{\partial h}{\partial P}\right)_T dP = c_P dT + v(1 - T\beta)dP$$

(iv) To Prove $\mu = \frac{v}{c_P}(\beta T - 1)$ use $dh = Tds + vdP$ which implies

$$\left(\frac{\partial h}{\partial T}\right)_P = T\left(\frac{\partial S}{\partial T}\right)_P = c_P$$

$$\left(\frac{\partial h}{\partial P}\right)_T = T\left(\frac{\partial S}{\partial P}\right)_T + v = v - T\left(\frac{\partial v}{\partial T}\right)_P = v - Tv\beta,$$

then

$$\mu = \left(\frac{\partial T}{\partial P}\right)_h = -\left(\frac{\partial h}{\partial P}\right)_T \left(\frac{\partial T}{\partial H}\right)_T = \frac{v}{c_P}(\beta T - 1)$$

To calculate

$$\left(\frac{\partial h}{\partial V}\right)_T = T\left(\frac{\partial P}{\partial T}\right)_v + v\left(\frac{\partial P}{\partial v}\right)_T = T\left(\frac{\partial P}{\partial T}\right)_v - \frac{1}{\kappa} = T\frac{\beta}{\kappa} - \frac{1}{\kappa}$$

$$= \frac{1}{\kappa}(T\beta - 1) = \frac{\mu c_P}{v\kappa}$$

To calculate

$$\left(\frac{\partial h}{\partial T}\right)_v = c_v + v\left(\frac{\partial P}{\partial v}\right)_v = c_P - \frac{Tv\beta^2}{\kappa} + v\frac{v\beta}{\kappa} = c_P[1 - \frac{v\beta}{c_P\kappa}(T\beta - 1)]$$

$$= c_P[1 - \frac{\mu\beta}{\kappa}]$$
