

Basic Thermodynamic Relations

Isolated system: this is a system that does not exchange energy with the surrounding media.

First Postulate (equilibrium theorem) : Isolated system always reaches the equilibrium state and never leaves it spontaneously.

Second Postulate (temperature)

Every equilibrium system is completely determined by the set of external variables (volume, pressure, magnetic field, etc.) plus one internal variable – **TEMPERATURE**.

At least one additional internal parameter is needed to describe a non-equilibrium system.

Equilibrium Process: This is a process that proceeds so slowly that the system is always in equilibrium state

The First Law of Thermodynamics

The First Law of Thermodynamics is a statement of conservation of energy in which the equivalence of work and heat flow is taken into account.

$$dU = dQ + dW$$

The internal energy of the system U depends only on the actual state of the system and not on the way the system is driven to it, i.e. it is a **function of state**.

The Second Law of Thermodynamics

Efficiency. This is a measure of how well the heat flow from the hotter thermal reservoir is converted to work. If the work done in one complete cycle is W , then efficiency h is defined as the ratio of the work done to the total heat flow Q

$$h \equiv \frac{W}{Q}$$

One of the main consequences of the Second Law of Thermodynamics is the existence of another function of state called entropy

$$dS \geq \frac{dQ}{T}$$

Processes in closed systems are always connected with an increase of entropy. In equilibrium the system has maximum of entropy.

$$TdS \geq dU + dW$$

$$\text{for } dW = pdV$$

$$TdS = dU + pdV$$

Free energy

For open systems

$$dW \leq -(dU - TdS)$$

$$F = U - TS \Rightarrow G = H - TS$$

$$W \leq (F_1 - F_2)_T$$

$$dF = dU - TdS - SdT - pdV - Vdp \quad (\text{for } T = \text{const})$$

$$dF = -SdT - pdV$$

Basic Thermodynamic Relations

First derivatives of Thermodynamic Potentials:

$$S = -\left(\frac{\partial F}{\partial T}\right)_V \quad p = -\left(\frac{\partial F}{\partial V}\right)_T$$

$$S = -\left(\frac{\partial G}{\partial T}\right)_p \quad V = -\left(\frac{\partial G}{\partial p}\right)_T$$

$$\mathbf{s} = \left(\frac{\partial F}{\partial O}\right)_{V,T} = \left(\frac{\partial G}{\partial O}\right)_{p,T}$$

$$\mathbf{m} = \left(\frac{\partial F}{\partial n}\right)_{V,T} = \left(\frac{\partial G}{\partial n}\right)_{p,T} = \left(\frac{\partial U}{\partial n}\right)_{V,T} = \left(\frac{\partial H}{\partial n}\right)_{p,S}$$

Second derivatives of Thermodynamic Potentials:

Heat capacity

$$c_v = -T \left(\frac{\partial^2 F}{\partial T^2} \right)_V$$

compressibility

$$k = -\frac{1}{V_o} \left(\frac{\partial V}{\partial P} \right)_T = \frac{1}{V_o \left(\frac{\partial^2 F}{\partial V^2} \right)_V}$$

$$c_p = -T \left(\frac{\partial^2 G}{\partial T^2} \right)_p = T \left(\frac{\partial S}{\partial T} \right)_p$$

$$k = -\frac{1}{V_o} \left(\frac{\partial V}{\partial P} \right)_T = \frac{1}{V_o \left(\frac{\partial^2 G}{\partial p^2} \right)_T}$$

Thermal expansion coefficient

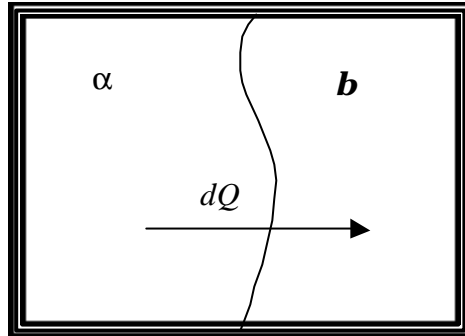
$$\mathbf{a} = \frac{1}{V_o} \left(\frac{\partial V}{\partial T} \right)_P$$

Thermodynamics of Phase Transitions

Every homogeneous part of a heterogeneous system is called PHASE. Phase is a macroscopic, homogeneous, quasi closed part of a system, separated from the other parts of the system by a separating surface.

According to the Classification of *Ehrenfest* the order of the phase transition is determined by the order of the derivative of thermodynamic potential that jumps at this point.

Thermal equilibrium

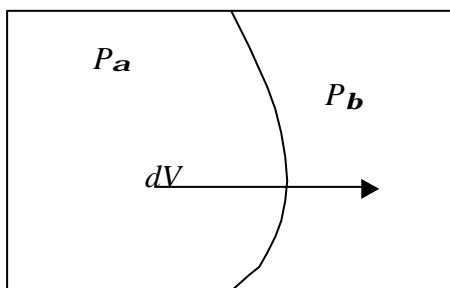


$$dS_a + dS_b \geq 0$$

$$-\frac{dQ}{T_a} + \frac{dQ}{T_b} \geq 0$$

$$T_a \geq T_b$$

Mechanical equilibrium (at $T_a = T_b$)



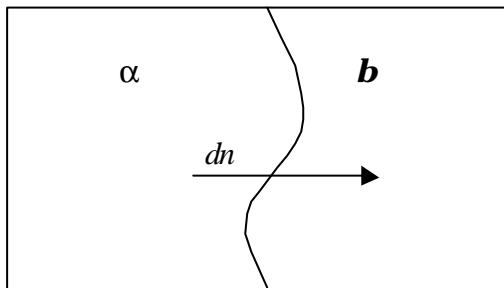
$$dF_a + dF_b \leq 0$$

$$dF = -pdV - SdT \quad (SdT=0)$$

$$-p_a dV + p_b dV \neq 0$$

$$p_a \neq p_b$$

Chemical equilibrium



At $T, P = \text{const}$ the two phases exchange material

$$dG_a + dG_b \neq 0$$

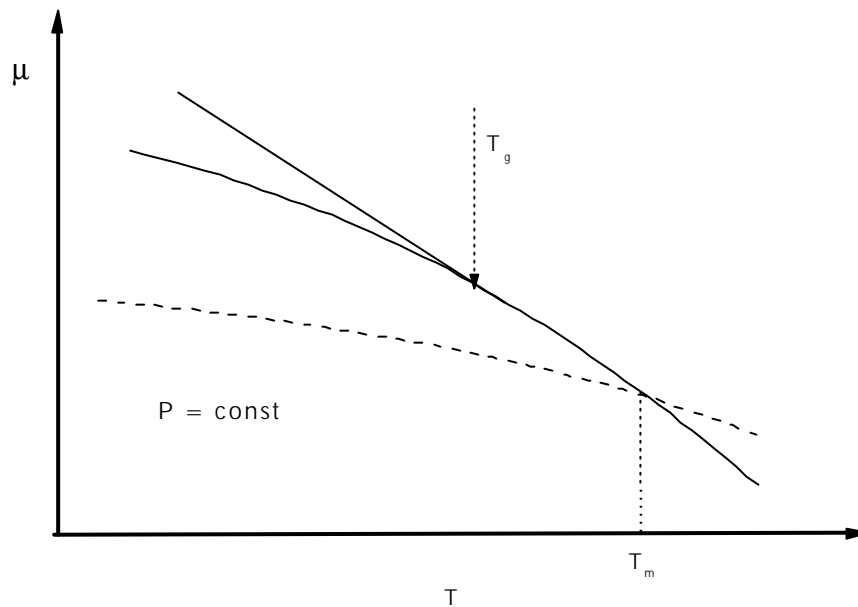
$$dG = v dp - S dT + \sum m_i dn_i$$

$$-m^a dn_i + m^b dn_i \neq 0$$

$$m^a \neq m^b$$

**For the first order phase transitions:
In the transition point the chemical potentials of
the two phases are equal**

$$\mu_1 = \mu_2$$



It is seen that *I* order phase transitions are accompanied by a heat transfer $DQ = T(S_2 - S_1)$. The heat of phase transition is the heat required to transfer substance from state 1 to state 2.

The maximal work is

$$W_{max} = (DF)_T = DQ - (DU)_T$$

$$\left(\frac{\partial DQ}{\partial T} \right)_p = DC_p$$

The Kirhoff equation gives the temperature dependence of the heat of phase transition in differential form

Equation of Clausius-Clapeyron

$$\mathbf{m}(T, p) = \mathbf{m}_2(T, p) \Rightarrow p=p(T)$$

$$d\mathbf{m}(p, T) = d\mathbf{m}(p, T)$$

or

$$\left(\frac{\partial \mathbf{m}}{\partial T}\right)_p dT + \left(\frac{\partial \mathbf{m}}{\partial p}\right)_T dp = \left(\frac{\partial \mathbf{m}_2}{\partial T}\right)_p dT + \left(\frac{\partial \mathbf{m}_2}{\partial p}\right)_T dp$$

So that

$$\frac{dp}{dT} = \frac{s_2 - s_1}{v_2 - v_1} = \frac{DQ}{T(v_2 - v_1)} \text{ Equation of Clausius-Clapeyron}$$

For the second order phase transitions: In the transition point the molar enthalpies, the second order derivatives of thermodynamic potentials of the two phases are equal

$$\frac{dp}{dT} = \frac{s_2 - s_1}{v_2 - v_1} = \frac{0}{0} = ?$$

L'Hopital

$$\frac{dp}{dT} = \frac{\left(\frac{ds_2}{dT}\right)_p - \left(\frac{ds_1}{dT}\right)_p}{\left(\frac{dv_2}{dT}\right)_p - \left(\frac{dv_1}{dT}\right)_p} = \frac{Dc_p}{TD\left(\frac{dv}{dT}\right)_p}$$

$$\frac{dp}{dT} = \frac{\left(\frac{ds_2}{dp}\right)_T - \left(\frac{ds_1}{dp}\right)_T}{\left(\frac{dv_2}{dp}\right)_T - \left(\frac{dv_1}{dp}\right)_T} = - \frac{\mathbf{D}\left(\frac{dv}{dT}\right)_p}{\mathbf{D}\left(\frac{dv}{dp}\right)_T}$$

because $\frac{\partial v}{\partial T} = \frac{\partial^2 \mathbf{m}}{\partial T \partial P} = - \frac{\partial s}{\partial p}$

Ehrenfest Equation

$$\frac{\mathbf{D}k\mathbf{D}C_p}{TV\mathbf{D}a^2} = 1$$

SUPERSATURATION \mathbf{Dm}

$$S = - \left(\frac{\partial G}{\partial T} \right)_p \Rightarrow \Delta \mathbf{m} = \int_T^{T_m} \Delta S(T) dT$$

$$\Delta S = \int_0^T \frac{\Delta C_p}{T} dT = \Delta S_m - \int_T^{T_m} \frac{\Delta C_p}{T} dT$$

$$\mathbf{Dm} = \mathbf{D}S_m \mathbf{D}T - \int_T^{T_m} dT \int_T^{T_m} \frac{\mathbf{D}C_p}{T} dT$$

note:

$$\int_T^{T_m} \frac{\mathbf{D}C_p}{T} dT = \mathbf{D}S_m - \mathbf{D}S(T)$$

Therefore

$$Dm = \int_T^{T_m} DS(T) dT$$

A truncated Taylor expansion of $DS(T)$ in the vicinity of T_m gives:

$$DS(T) = DS_m + \left(\frac{\partial DS}{\partial T} \right)_{T_m} (T - T_m) = DS_m - DC_{p,m} \frac{T_m - T}{T_m}$$

So that supersaturation becomes

$$Dm = DS_m DT - DC_{p,m} \frac{DT^2}{2T_m}$$

$$Dm = DH_m \frac{DT}{T_m} \left(1 - \frac{DC_{p,m}}{2DS_m} \frac{DT}{T_m} \right)$$

example: for $DC_p = const$

$$\Delta m = (\Delta H_m - \Delta C_p T_m) \frac{\Delta T}{T_m} + \Delta C_p T_m \frac{T}{T_m} \ln \frac{T}{T_m}$$

Nature of Glass Transition: experimental evidence

