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CC-VI

Thermal Physics

UNIT-II

Thermodynamic Potentials: Extensive and Intensive Thermodynamic Variables. Thermodynamic Potentials: Internal Energy, Enthalpy, Helmholtz Free Energy, Gibb's Free Energy. Their Definitions, Properties and Applications. Surface Films and Variation of Surface Tension with Temperature. Magnetic Work, Cooling due to adiabatic demagnetization, First and second order Phase Transitions with examples, Clausius-Clapeyron Equation and Ehrenfest equations **(6 Lectures)**

Maxwell's Thermodynamic Relations: Derivations and applications of Maxwell's Relations, Maxwell's Relations:(1) Clausius-Clapeyron equation, (2) Values of C_p-C_v , (3) TdS Equations, (4) Joule-Kelvin coefficient for Ideal and Van der Waals Gases, (5) Energy equations, (6) Change of Temperature during Adiabatic Process. **(6 Lectures)**

2.1.1 Thermodynamic Potentials

Extensive Thermodynamic Variables: Magnitude is dependent on size/amount and hence is additive for subsystems.

Examples: Mass, Volume, Entropy, energy, enthalpy, Gibbs potential, Helmholtz free energy, Internal energy, heat capacity etc.

Intensive Thermodynamic Variables: Magnitude is independent of the size/amount of the system. (Bulk property or Local physical property).

Examples: Temperature, Pressure, Chemical Potential, Density, Refractive index, Conductivity, viscosity, specific heat capacity etc.

Thermodynamic Potentials

A thermodynamic potential is a quantity that can be used to represent the state of a system and is important for the description of chemical thermodynamics of reactions and of non-cyclic processes.

There are four Thermodynamic potentials, each a function of two thermodynamic variables:

- 1) **Internal energy (U):** It is the primary one and is most easily understandable while the other three are derivable from it by Legendre transformations. From the first law of Thermodynamics:

$$\begin{aligned}dU &= dQ - dW + \sum_i \mu_i dN_i \\ \Rightarrow dU &= TdS - PdV + \sum_i \mu_i dN_i \\ \Rightarrow U &= \int \left(TdS - PdV + \sum_i \mu_i dN_i \right)\end{aligned}$$

It measures the capacity to do work plus capacity to release heat. Here, T = Temperature, S = Entropy, P = Pressure, V = Volume, μ_i = Chemical potential for i^{th} component, N_i = number of particles of i^{th} type in the system. The pairs (T, S) , (P, V) and (μ_i, N_i) are called conjugate pairs of variables. For closed systems, $U = U(S, V) \Rightarrow dU = TdS - PdV$.

- 2) **Helmholtz Free Energy (A or F):** It measures the capacity to do non-mechanical work in addition to the capacity for mechanical work.

$$\begin{aligned}F &= U - TS \\ dF &= -SdT - PdV + \sum_i \mu_i dN_i\end{aligned}$$

For a closed system, $F = F(T, V) \Rightarrow dF = -SdT - PdV$.

- 3) **Enthalpy (H):** It measures the capacity to do non-mechanical work plus the capacity to release heat.

$$H = U + PV$$

$$dH = TdS + VdP + \sum_i \mu_i dN_i$$

For a closed system, $H = H(S, P) \Rightarrow dH = TdS + VdP$.

- 4) **Gibbs Free Energy (G):** It measures the capacity for non-mechanical work.

$$G = H - TS = U + PV - TS$$

$$dG = -SdT + VdP + \sum_i \mu_i dN_i$$

For a closed system, $G = G(T, P) \Rightarrow dG = -SdT + VdP$.

Problem # 2.1: Show that:

$$dH - dU = dG - dF = d(PV)$$

$$dU - dF = dH - dG = d(TS)$$

Problem # 2.2: Derive the Euler Relation

$$U = TS - PV + \sum_i \mu_i N_i$$

And hence, the relations:

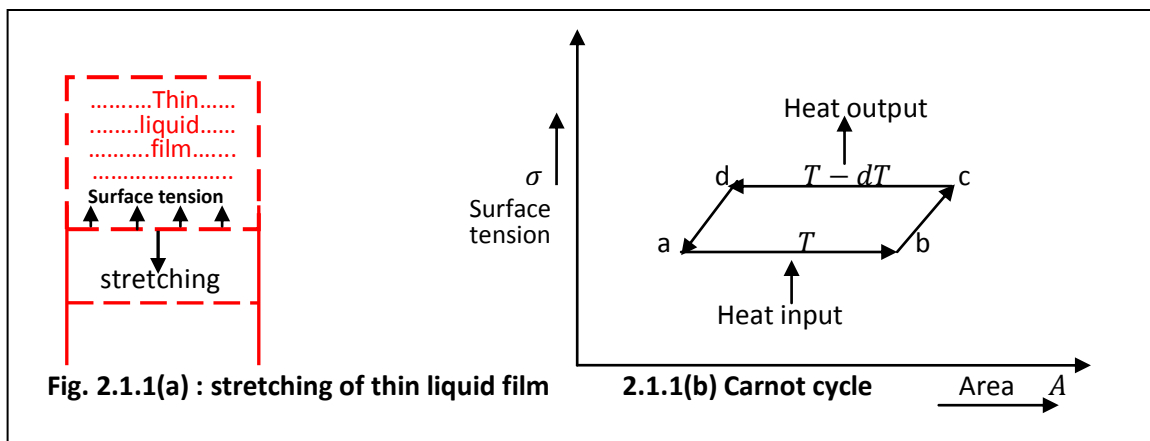
$$H = TS + \sum_i \mu_i N_i; \quad F = -PV + \sum_i \mu_i N_i; \quad G = \sum_i \mu_i N_i$$

And also the Gibbs-Duhem relation:

$$0 = SdT - VdP + \sum_i N_i d\mu_i$$

2.1.2 Surface Film and Variation of Surface Tension with Temperature

A thin rectangular liquid film of area A and movable side of length L at temperature T is stretched adiabatically reversibly (*i.e.* slowly) to have the area increased by dA and temperature changed by dT (see fig. 2.1.1(a) and (b) below).



Here area A of the film plays the role of volume V , surface tension plays the role of (negative) pressure P . Internal energy of the film is given by:

$$U = U(A, T)$$

$$dU = \left(\frac{\partial U}{\partial T}\right)_A dT + \left(\frac{\partial U}{\partial A}\right)_T dA = CdT + EdA$$

where, $C = \left(\frac{\partial U}{\partial T}\right)_A$ is Specific Heat and $E = \left(\frac{\partial U}{\partial A}\right)_T$ is the surface energy (density).

Since dU is a perfect differential, $\left(\frac{\partial C}{\partial A}\right)_T = \left(\frac{\partial E}{\partial T}\right)_A$ (1)

If heat dQ is supplied to accomplish this change, then

$$dQ = dU + dW = dU - \sigma dA$$

where, σ is the surface tension (acting as negative pressure, against which external work is done to stretch the film. Thus we have,

$$dQ = CdT + (E - \sigma)dA$$

Or, $dS = \frac{dQ}{T} = \frac{C}{T}dT + \frac{E - \sigma}{T}dA$

Now since dS is a perfect differential, we must have,

$$\left(\frac{\partial}{\partial A}\left(\frac{C}{T}\right)\right)_T = \left(\frac{\partial}{\partial T}\left(\frac{E - \sigma}{T}\right)\right)_A$$

Or, $\left(\frac{\partial C}{\partial A}\right)_T = T\left(\frac{\partial}{\partial T}\left(\frac{E - \sigma}{T}\right)\right)_A$ (2)

From (1) and (2): $\left(\frac{\partial E}{\partial T}\right)_A = T\left(\frac{\partial}{\partial T}\left(\frac{E - \sigma}{T}\right)\right)_A$

On simplifying we get,

$$E = \sigma - T\left(\frac{\partial \sigma}{\partial T}\right)_A$$
 (3)

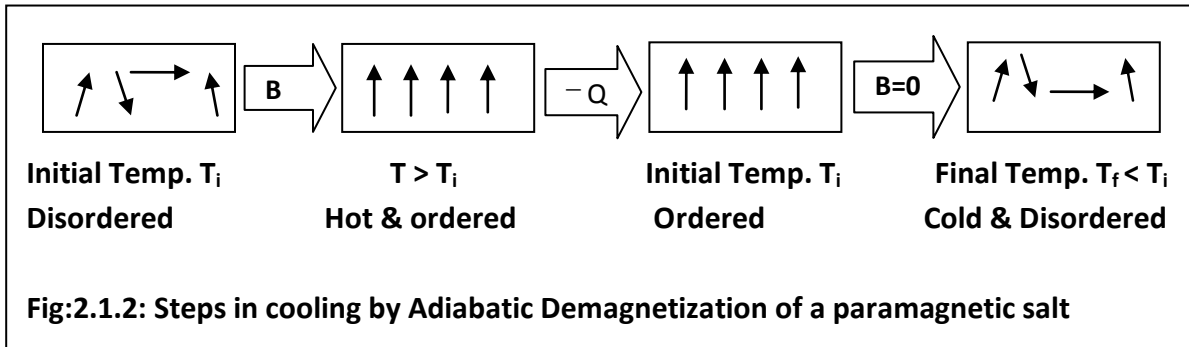
This is the required expression for surface energy in terms of temperature dependence of surface tension. The surface tension decreases with increase of temperature and hence the surface energy increases upon stretching.

Problem #2.3: Derive eq. (3) without using the concept of thermodynamic potentials by using a Carnot cycle with the surface film having steps (1) isothermal stretching at temp T and surface tension σ (2) adiabatic expansion to cool to temperature $T - dT$ with rise of surface tension to $\sigma + d\sigma$ (3) isothermal contraction at $T - dT$ and (4) adiabatic contraction to regain initial temperature T and surface tension σ .

2.1.3 Magnetic Work and Cooling due to adiabatic demagnetization

Debye, in 1926, suggested that much lower temperatures can be obtained by adiabatic demagnetization of a paramagnetic salt using what is known as **magneto-caloric effect**: Paramagnetic substances (rare-earths like gadolinium or Cerium and their alloys such as $Gd_5Si_2Ge_2$ and $CeMgNO_3$) heat up when placed in magnetic field and cool down when the field is removed.

Applied magnetic field does work on the randomly oriented magnetic moments in a paramagnetic salt and aligns them along the field. This external work heats up the system. This heat can be taken away using a heat exchanger, leaving the specimen in an ordered state in the magnetic field, but now at the initial temperature. Next, suddenly the magnetic field is removed (or reduced to very low values), so that the moments become disordered again by breaking away from the diminishing field and in the process doing work against it. In doing this work to become randomly oriented again they expend internal energy and hence the temperature falls drastically. Thus we now have a disordered state now at a temperature below the initial temperature. The cycle can be repeated again and again to attain any desirable low temperature of the order of millikelvins.



The operational procedure thus involves the following four steps:

- (1) Adiabatic Magnetization
- (2) Isomagnetic enthalpic transfer
- (3) Adiabatic demagnetization
- (4) Isomagnetic entropic heat transfer.

To apply first law of thermodynamics to magnetic systems, we note that for them we have an additional conjugate pair (\mathbf{B}, \mathbf{M}) consisting of the magnetic field \mathbf{B} and the magnetization \mathbf{M} . The magnetic work done on the system by the applied field \mathbf{B} in increasing the magnetization of the system from \mathbf{M} to $\mathbf{M}+d\mathbf{M}$ is $dW_{mag} = -\mathbf{B} \cdot d\mathbf{M} = -BdM$, where we have used the $-ve$ sign for the work done on the system and the fact that the change in magnetization $d\mathbf{M}$ is along the magnetic field \mathbf{B} .

Thus we write the first law as:

$$dQ = dU + PdV - BdM = dU - BdM$$

where, we have used the fact that there is negligible or no change in volume ($dV=0$) of a solid specimen during the process.

Now using second law $dQ = TdS$, we get:

$$dU = TdS + BdM$$

We now define an enthalpy-like potential for the system:

$$J = U - BM$$

We then have dJ as a perfect differential:

$$dJ = TdS - MdB$$

This gives us the definitions:

$$M = -\left(\frac{\partial J}{\partial B}\right)_S \text{ and } T = \left(\frac{\partial J}{\partial S}\right)_B$$

$$\text{And also } \left(\frac{\partial T}{\partial B}\right)_S = -\left(\frac{\partial M}{\partial S}\right)_B$$

$$\text{Using, } \left(\frac{\partial M}{\partial S}\right)_B = \left(\frac{\partial M}{\partial T}\right)_B \left(\frac{\partial T}{\partial S}\right)_B = \frac{\left(\frac{\partial M}{\partial T}\right)_B}{\left(\frac{\partial S}{\partial T}\right)_B} = \frac{T}{C_B} \left(\frac{\partial M}{\partial T}\right)_B$$

Where, $C_B = \left(\frac{dQ}{dT}\right)_B = T \left(\frac{\partial S}{\partial T}\right)_B$ is the specific heat at constant applied field.

$$\text{We get: } \left(\frac{\partial T}{\partial B}\right)_S = -\frac{T}{C_B} \left(\frac{\partial M}{\partial T}\right)_B$$

This gives the expression for change of temperature due to magnetization/ demagnetization brought about by applied field or its removal. This is precisely the magneto-caloric effect. The change of temperature can be obtained by integration:

$$T_f - T_i = - \int_{T_i}^{T_f} \frac{T}{C_B} \left(\frac{\partial M}{\partial T}\right)_B dB$$

If χ is the susceptibility per unit volume, then magnetization is given by:

$$M = \chi V B = \frac{c}{T} V B$$

where we used Curie's law for paramagnetism: $\chi = \frac{c}{T}$, where c is Curie constant.

Differentiating with respect to temperature at constant B,

$$\left(\frac{\partial M}{\partial T}\right)_B = -\frac{cVB}{T^2}$$

Using this and completing the integral:

$$T_f - T_i = \Delta T = \frac{cV}{2\bar{C}_B T_i} (B_f^2 - B_i^2)$$

Where \bar{C}_B is the average value of $T \left(\frac{\partial S}{\partial T}\right)_B$ for the entire range of integration and T is approximated by T_i in the denominator assuming its variations to be small compared to other quantities in the integrand.

Problem # 2.4: Show that the difference between specific heats at constant magnetic field and at constant magnetization is given by:

$$C_B - C_M = \frac{\chi V B^2}{T}$$

(Hint: Use the analogous formula for this difference from the formula:

$$C_P - C_V = T \left(\frac{\partial P}{\partial T}\right)_V \left(\frac{\partial V}{\partial T}\right)_P \text{ to get } C_B - C_M = -T \left(\frac{\partial B}{\partial T}\right)_M \left(\frac{\partial M}{\partial T}\right)_B \text{ and proceed}$$

2.1.4 Phase Transitions

Phase: A distinct, physically homogeneous, mechanically separable part of a system having a boundary for itself.

Examples: petrol and water in a bottle; ice and salt in a jar; water, ice and vapor together in a box at $\sim 4^\circ\text{C}$; Magnetic/electric ordering of dipoles in a substance etc.

Phase transition: When a parameter like pressure or temperature is varied, a substance may undergo change of phase as happens, for example, in case of water as temperature is lowered or raised to $\sim 4^\circ\text{C}$.

The quantity of interest in phase transitions is the Gibbs potential:

$$G = U + PV - TS$$

Its first derivatives: $S = -\left(\frac{\partial G}{\partial T}\right)_P$; $V = \left(\frac{\partial G}{\partial P}\right)_T$ and second derivatives: Sp. Heat $C_P = T \left(\frac{\partial S}{\partial T}\right)_P = -T \left(\frac{\partial}{\partial T} \left(\frac{\partial G}{\partial T}\right)_P\right) = -T \left(\frac{\partial^2 G}{\partial T^2}\right)_P$; Volume coefficient of expansion $\alpha = \frac{1}{V} \left(\frac{\partial}{\partial T} \left(\frac{\partial G}{\partial P}\right)_T\right)_P = \frac{1}{V} \left(\frac{\partial V}{\partial T}\right)_P$;

isothermal compressibility $\kappa = -\frac{1}{V} \left(\frac{\partial^2 G}{\partial P^2}\right)_T$ determine the order of phase transitions. In fact, the nomenclatures- first and second order phase transitions *etc.*- are based on the lowest order of derivative of G that is discontinuous at the transition point. For an n th order phase transitions the derivatives of G up to the $(n - 1)$ th order would be continuous and discontinuity would occur only at the n th derivative.

2.1.5 First Order Phase Transitions: Phase change at constant temp and pressure, with corresponding change in volume and entropy by exchange of heat. This heat is called the Latent heat for the transition. For example, conversion of water into steam or melting of ice into water at constant temperature and pressure is a first order phase transition. The Gibbs potential G is continuous but its first derivatives are discontinuous at the transition point between the phases 1 and 2:

$$G_2 - G_1 = 0$$

$$S_2 - S_1 = \left(\frac{\partial G_2}{\partial T}\right)_P - \left(\frac{\partial G_1}{\partial T}\right)_P = \frac{L}{T}; \quad (L = \text{Latent heat of the transition})$$

$$V_2 - V_1 = \left(\frac{\partial G_2}{\partial P}\right)_T - \left(\frac{\partial G_1}{\partial P}\right)_T \neq 0$$

In addition, $C_P = -T \left(\frac{\partial^2 G}{\partial T^2}\right)_P$, the second derivative of G w.r.t. T , is discontinuous too at the transition.

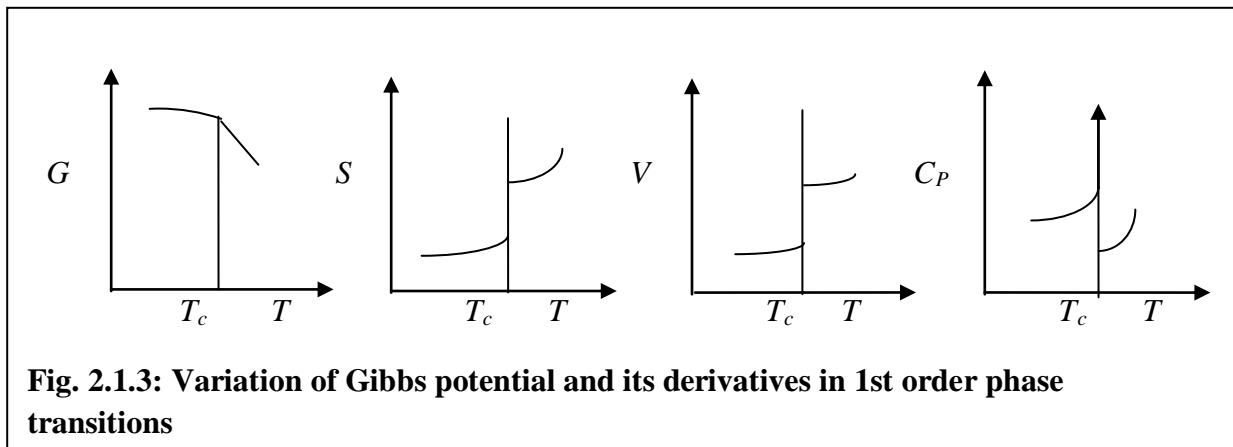


Fig. 2.1.3: Variation of Gibbs potential and its derivatives in 1st order phase transitions

Clausius-Clapeyron equation: From the equality of the Gibbs potentials ($G_1 = G_2$) in the two phases we can derive the Clausius-Clapeyron equation (also called the first Latent heat equation) which expresses the variation of melting point or Boiling point with pressure.

$$\begin{aligned} dG_1 &= dG_2 \\ \Rightarrow V_1 dP - S_1 dT &= V_2 dP - S_2 dT \\ \Rightarrow \frac{dP}{dT} &= \frac{S_2 - S_1}{V_2 - V_1} = \frac{\Delta S}{\Delta V} = \frac{\Delta Q}{T\Delta V} = \frac{L}{T\Delta V} \end{aligned}$$

where L is the latent heat of fusion or vaporization as the case may be, and we have used the second law.

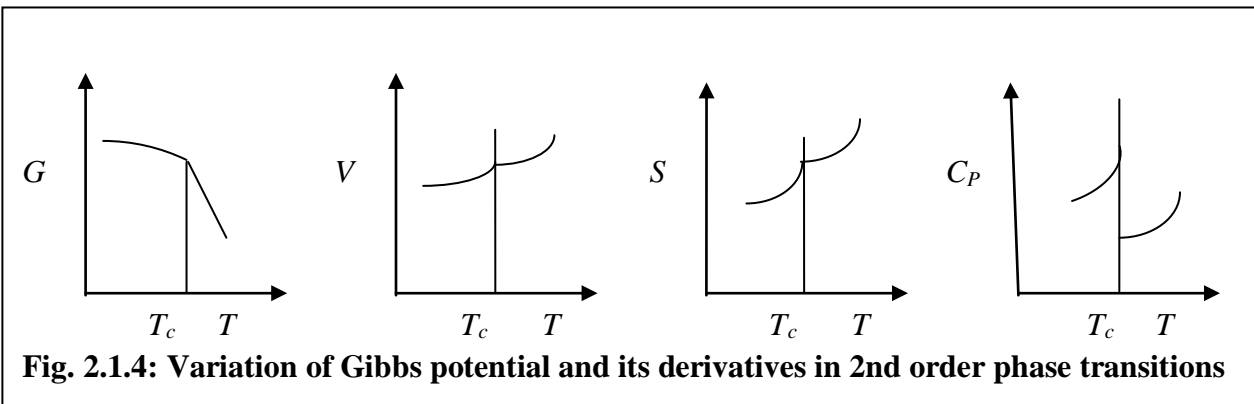
Problem # 2.5 Using Clausius-Clapeyron equation explain the rise/fall of boiling point of a liquid with increase/decrease of pressure and also the rise/fall of melting point with increase of pressure corresponding to increase/decrease of volume upon phase transition to liquid state. (For example, water boils at lower temperatures on hilltops and ice melts at lower temperatures than 0°C at higher than 1 atm pressure.)

2.1.6 Second Order Phase Transitions

A phase transition where the second derivatives of the Gibbs potential are discontinuous at the transition point, but the first derivatives are continuous is called a second order phase transition. Here no latent heat is required for the transition.

- Examples:** (1) Lambda transition from liquid He- I to He- II at λ -point : $T_\lambda = 2.19\text{K}$
 (2) Ferromagnetic to paramagnetic order at Curie point
 (3) Normal metal to superconductor at zero magnetic field ($\mathbf{B} = \mathbf{0}$)

As mentioned earlier, 2nd order phase transitions have continuous G and its 1st derivatives but discontinuous second derivatives, as shown in fig. 2.1.4.



Ehrenfest equations: Like the Clausius-Clapeyron equation for first order transitions, the two Ehrenfest equations for $\frac{dP}{dT}$ describe the discontinuities in the second order transitions. The equation connecting the discontinuities in C_p and volume coefficient of expansion α is obtained

from the equality of entropies in the two phases, while that connecting discontinuities in the isothermal compressibility κ and α is obtained from the equality of volumes in the two phases.

Ehrenfest equation for C_p discontinuity:

Since entropy $S = S(P, T)$ does not change in second order phase transitions:

$$S_1(P, T) = S_2(P, T) \\ \Rightarrow dS_1(P, T) = dS_2(P, T)$$

Expanding the differentials in terms of dP and dT , using $\left(\frac{\partial S}{\partial T}\right)_P = \frac{C_p}{T}$

$$\frac{C_{p1}}{T} + \left(\frac{\partial S_1}{\partial P}\right)_T \frac{dP}{dT} = \frac{C_{p2}}{T} + \left(\frac{\partial S_2}{\partial P}\right)_T \frac{dP}{dT}$$

From perfect differential nature of $dG = VdP - SdT$, we have: $\left(\frac{\partial S}{\partial P}\right)_T = -\left(\frac{\partial V}{\partial T}\right)_P$. Using this:

$$\frac{dP}{dT} = \frac{C_{p2} - C_{p1}}{TV(\alpha_2 - \alpha_1)}$$

where, $\alpha = \frac{1}{V} \left(\frac{\partial V}{\partial T}\right)_P$ is the volume coefficient of expansion.

Ehrenfest equation for α and κ discontinuity:

Using equality of molar volume ($v = V/n$) in the two phases: $v_1 = v_2$; $dv_1 = dv_2$

Taking $v = v(T, p)$, where $p = P/n$ is molar pressure at temp T: $dv = \left(\frac{\partial v}{\partial T}\right)_p dT + \left(\frac{\partial v}{\partial p}\right)_T dp$

Using the definitions: $\left(\frac{\partial v}{\partial T}\right)_p = v\alpha$ and $\left(\frac{\partial v}{\partial p}\right)_T = -\kappa v$:

$$: dv_1 = \alpha_1 v dT - \kappa_1 v dp \quad \text{and} \quad dv_2 = \alpha_2 v dT - \kappa_2 v dp$$

Thus, we get finally,

$$\frac{dp}{dT} = \frac{\alpha_2 - \alpha_1}{\kappa_2 - \kappa_1}$$

This is the second Ehrenfest equation for second order phase transitions.

2.2 Maxwell's Thermodynamic Relations

For a closed system, there are four thermodynamic variables (P, V, T, S) and only one equation *viz.* the equation of state $f(P, V, T) = 0$ connecting three of them. Thus there is one variable superfluous since thermodynamic state description requires only two variables. Further, there are four thermodynamic potentials (U, H, F, G) each depending on two of the four variables. This leads us to look for more relations connecting the variables. There are four thermodynamic relations derivable from the perfect differential nature of each of dF, dG, dH and dU . These four relations among the mutual derivatives of P, V, T and S are called the Maxwell Thermodynamic Relations (MTR).

We have: $dU = TdS - PdV$; $dH = TdS + VdP$;
 $dF = -SdT - PdV$; $dG = -SdT + VdP$.

(i) From dU we get the definitions: $T = \left(\frac{\partial U}{\partial S}\right)_V$ and $P = -\left(\frac{\partial U}{\partial V}\right)_S$

Equating the second derivatives of U we get the 1st relation: $\left(\frac{\partial T}{\partial V}\right)_S = -\left(\frac{\partial P}{\partial S}\right)_V$

(ii) From dH , we get the definitions: $T = \left(\frac{\partial H}{\partial S}\right)_P$ and $V = \left(\frac{\partial H}{\partial P}\right)_S$

Equating the second derivatives of H we get the 2nd relation: $\left(\frac{\partial T}{\partial P}\right)_S = \left(\frac{\partial V}{\partial S}\right)_P$

(iii) From dF , we get the definitions: $S = -\left(\frac{\partial F}{\partial T}\right)_V$ and $P = -\left(\frac{\partial F}{\partial V}\right)_T$

Equating the second derivatives of F we get the 3rd relation: $\left(\frac{\partial S}{\partial V}\right)_T = \left(\frac{\partial P}{\partial T}\right)_V$

(iv) From dG , we get the definitions: $S = -\left(\frac{\partial G}{\partial T}\right)_P$ and $V = \left(\frac{\partial G}{\partial P}\right)_T$

Equating the second derivatives of G we get the 4th relation: $\left(\frac{\partial S}{\partial P}\right)_T = -\left(\frac{\partial V}{\partial T}\right)_P$

These four Maxwell Thermodynamic Relations prove very handy for very simple and almost magical derivations of many important thermodynamic formulae some of which we will illustrate below. You can try to have a mnemonic for convenient remembrance of the four relations, as we usually get confused when the number of similar things to be remembered becomes more than three.

2.2.1 Applications of Maxwell's Thermodynamic Relations

(a) Clausius-Clapeyron Equation

Taking MTR $\left(\frac{\partial S}{\partial V}\right)_T = \left(\frac{\partial P}{\partial T}\right)_V$, multiplying by T and using $TdS = dQ$, we have $\left(\frac{\partial Q}{\partial V}\right)_T = T\left(\frac{\partial P}{\partial T}\right)_V$ which on using $dQ = L$ =latent heat of phase transition, and $dV = V_2 - V_1$ = associated change in volume, we get the Clausius-Clapeyron equation which is also called the first latent heat equation.

Problem# 2.6: Derive the second latent heat equation obtainable from the entropy changes *e.g.* in a liquid (phase 1) to vapour (phase 2) transition: $C_v - C_l = T \frac{d}{dT} \left(\frac{L}{T}\right)$ where C_v and C_l are respectively the specific heats of saturated vapour and liquid respectively.

(b) $C_p - C_v$ Relations

Taking $S = S(T, V) \Rightarrow dS = \left(\frac{\partial S}{\partial T}\right)_V dT + \left(\frac{\partial S}{\partial V}\right)_T dV$ in $C_p = \left(\frac{dQ}{dT}\right)_P = T \left(\frac{\partial S}{\partial T}\right)_P$

We get, $C_p = C_v + T \left(\frac{\partial S}{\partial V}\right)_T \left(\frac{\partial V}{\partial T}\right)_P$

On using the MTR $\left(\frac{\partial S}{\partial V}\right)_T = \left(\frac{\partial P}{\partial T}\right)_V$ we get the desired relation:

$$C_p - C_v = T \left(\frac{\partial P}{\partial T}\right)_V \left(\frac{\partial V}{\partial T}\right)_P$$

Problem# 2.7: Show that for one mole of (i) an ideal gas ($PV = RT$) it gives, $C_p - C_v = R$ and (ii) Van der Waals gas obeying the Van der Waals equation of state $\left(P + \frac{a}{V^2}\right)(V - b) = RT$ it gives $C_p - C_v \cong R \left(1 + \frac{2a}{VRT}\right)$, where a and b are the Van der Waals constants of the gas.

Problem # 2.8: Using the definitions of κ and α re-express $C_p - C_v$ to obtain $C_p - C_v = T\kappa\alpha^2V$

Problem # 2.9: Show using appropriate MTRs that the pressure derivative of C_p and volume derivative of C_v are given by: $\left(\frac{dC_p}{dP}\right)_T = -T\left(\frac{d^2V}{dT^2}\right)_P$ and $\left(\frac{dC_v}{dV}\right)_T = T\left(\frac{d^2P}{dT^2}\right)_V$.

(c) TdS equations

The pair of equations expressing first law ($dQ = dU + dW$) in terms of second law ($dQ = TdS$) and one of the specific heats are called TdS equations.

$$\text{Taking } S = S(V, T) \Rightarrow dS = \left(\frac{\partial S}{\partial T}\right)_V dT + \left(\frac{\partial S}{\partial V}\right)_T dV$$

Multiplying by T and using $C_v = T\left(\frac{\partial S}{\partial T}\right)_V$ and MTR $\left(\frac{\partial S}{\partial V}\right)_T = \left(\frac{\partial P}{\partial T}\right)_V$ we get the **first TdS equation:** $TdS = C_v dT + T\left(\frac{\partial P}{\partial T}\right)_V dV$

Problem # 2.10: Following exactly similar steps starting with $S = S(P, T)$ and using appropriate MTR, derive the **second TdS equation:** $TdS = C_p dT - T\left(\frac{\partial V}{\partial T}\right)_P dP$

One readily sees why $C_p > C_v$ from the two TdS equations.

(d) Joule-Kelvin Coefficient

Joule-Kelvin effect (also called Joule-Thomson coefficient, since the earlier name of Aussie physicist Lord Kelvin was William Thomson) is the change of temperature of a gas isenthalpically throttled across a porous substance to a low pressure region and the effect is measured by a quantity called the Joule-Kelvin coefficient $\mu = \left(\frac{\partial T}{\partial P}\right)_H$. Details of the effect will be discussed later.

For an isenthalpic process, $dH = 0 \Rightarrow TdS + VdP = 0$

Using second TdS equation: $C_p dT - T\left(\frac{\partial V}{\partial T}\right)_P dP + VdP = 0 \Rightarrow C_p dT = T\left(\frac{\partial V}{\partial T}\right)_P dP - VdP$

This gives: $\mu = \left(\frac{\partial T}{\partial P}\right)_H = \frac{1}{C_p} \left[T\left(\frac{\partial V}{\partial T}\right)_P - V \right]$

One can see that for an ideal gas μ vanishes while it is nonvanishing for a real gas described by the Van der Waals equation. Since initial pressure is higher than the final pressure after throttling, a positive coefficient for the VdW gas means there will be cooling, while negative coefficient means heating and vanishing value implies no effect on temperature. The temperature

$T_i = V \left(\frac{\partial T}{\partial V} \right)_P$ is called the inversion temperature since the heating effect changes to cooling effect at that temperature (We will come back to it later).

Problem # 2.11: Using the smallness of the Van der Waals constants a and b , show that the J-K coefficient for VdW gas is given by $\mu = \frac{1}{C_p} \left[\frac{2a}{RT} - b \right]$.

(e) Energy equations:

These equations give the changes in internal energy with volume and pressure. The first energy equation can be derived as follows:

$$dU = TdS - PdV \Rightarrow \left(\frac{\partial U}{\partial V} \right)_T = T \left(\frac{\partial S}{\partial V} \right)_T - P$$

which on using MTR gives: $\left(\frac{\partial U}{\partial V} \right)_T = T \left(\frac{\partial P}{\partial T} \right)_V - P$

This is the **first energy equation**. As an application one can check that the internal energy of an ideal gas is independent of its volume.

Problem # 2.12: Using appropriate MTR, derive the **second energy equation**:

$$\left(\frac{\partial U}{\partial P} \right)_T = -T \left(\frac{\partial V}{\partial T} \right)_P - P \left(\frac{\partial V}{\partial P} \right)_T$$

It is easy to show that for an ideal gas, the internal energy is independent of pressure as well. Recall our experience from kinetic theory which gave the energy of ideal gas to be directly proportional to T only and that the ideal gas molecules have no potential energy among them which could presumably have led to a volume-dependence.

Problem # 2.13: Using the first energy equation show that the internal energy of a Van der Waals gas is given by: $U = \int C_V dT - \frac{a}{V^2} + U_0$ where U_0 is a constant energy.

(f) Change of temperature during adiabatic process

Using the MTR $\left(\frac{\partial T}{\partial V} \right)_S = - \left(\frac{\partial P}{\partial S} \right)_V$ we may rewrite it as $\left(\frac{\partial T}{\partial V} \right)_S = -T \left(\frac{dP}{dQ} \right)_V$.

We see that if on supply of heat at constant volume there is increase of pressure (as happens, for example, in case of an ideal gas), then $\left(\frac{dP}{dQ} \right)_V > 0$ which means $\left(\frac{\partial T}{\partial V} \right)_S < 0$. This last inequality has entropy fixed and hence is isentropic *i.e.* adiabatic. Thus, it implies a fall of temperature in an adiabatic expansion. Similarly, in situations where $\left(\frac{dP}{dQ} \right)_V < 0$, there would be a rise of temperature with adiabatic expansion of the system to larger volumes.

Next, rewriting the MTR $\left(\frac{\partial T}{\partial P} \right)_S = \left(\frac{\partial V}{\partial S} \right)_P$ as $\left(\frac{\partial T}{\partial P} \right)_S = T \left(\frac{dV}{dQ} \right)_P$ we get $\left(\frac{\partial T}{\partial P} \right)_S > 0$ when $\left(\frac{dV}{dQ} \right)_P > 0$ which means that in an adiabatic compression of the system (such as an ideal gas) there will be a rise of temperature.

Exercise-2

2.1 Using thermodynamic potentials deduce the Gibbs-Helmholtz relation

$$U = -T^2 \left[\frac{d}{dT} \left(\frac{F}{T} \right) \right]_V = F - T \left(\frac{\partial F}{\partial T} \right)_V.$$

2.2 Show that enthalpy and Gibbs potential are related by

$$H = -T^2 \left[\frac{d}{dT} \left(\frac{G}{T} \right) \right]_P = G - T \left(\frac{\partial G}{\partial T} \right)_P.$$

2.3 Prove that Gibbs potential and Helmholtz free energy are related by

$$G = -V^2 \left[\frac{d}{dV} \left(\frac{F}{V} \right) \right]_T = F - V \left(\frac{\partial F}{\partial V} \right)_T.$$

2.4 Using MTR prove the following:

(a) $\left(\frac{\partial H}{\partial P} \right)_T = V - T \left(\frac{\partial V}{\partial T} \right)_P.$

(b) $\left(\frac{\partial T}{\partial P} \right)_S = \frac{TV\alpha}{C_P}.$

(c) $\left(\frac{\partial V}{\partial T} \right)_S = -\frac{C_V}{C_P - C_V} \left(\frac{\partial V}{\partial T} \right)_P$ and $\left(\frac{\partial P}{\partial T} \right)_S = \frac{C_P}{C_P - C_V} \left(\frac{\partial P}{\partial T} \right)_V.$

(d) $\left(\frac{\partial P}{\partial S} \right)_T \left(\frac{\partial S}{\partial T} \right)_P = -\left(\frac{\partial P}{\partial T} \right)_S$ and $\left(\frac{\partial P}{\partial V} \right)_T \left(\frac{\partial V}{\partial T} \right)_P \left(\frac{\partial T}{\partial P} \right)_V = -1.$

(e) $\left(\frac{dQ}{dP} \right)_T = -TV\alpha$

2.5 Prove that $C_P - C_V = -T \left(\frac{\partial P}{\partial T} \right)_V \left[\left(\frac{\partial V}{\partial T} \right)_P \right]^2.$

2.6 Show that $P = T \left(\frac{\partial S}{\partial V} \right)_T - \left(\frac{\partial U}{\partial V} \right)_T.$
