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General thermodynamic relations and application to simple systems.

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Thermodynamic variables: The thermodynamic state of a substance can completely be described by some of its properties like P, V, T, S, U. These properties undergo a change when the system passes from one state to another. These variables are called thermodynamic variables or coordinates.

Extensive variables: An extensive variable of a system is a macroscopic parameter which describes a system in equilibrium and which has a value equal to the sum of its values in each part of the system. It depends on the mass or volume of the substance in the system.

For example: mass, Volume, entropy, internal energy, heat capacity etc.

Intensive variables: An intensive variable of a system is a macroscopic parameter which describes the system in equilibrium and has the same value in any part of the system. It is independent of mass or volume of the system.

For example: Pressure, temperature, density, viscosity, surface tension etc.

Thermodynamic functions:

The two laws of thermodynamics provide two relations given by $dU = dQ - dW$ and $dQ = TdS$. For complete knowledge of the system some other relation is necessary. Such a relation, for example, is provided by the equation of state of a fluid. But in general, when an equation of state is not available, certain functions of variables may be introduced for the purpose of simplifying the mathematical operations connected with a change in the condition of the system. These functions are called thermodynamic functions.

The major subsidiary terms are the four energetic quantities inner energy U, enthalpy H, Helmholtz energy A, and Gibbs energy G. The same quantity can serve different purpose depending on the variable chosen. The function $U(S, V, \dots)$ characterizes the system under consideration. The functions $U(T, V, \dots)$ and $H(T, P, \dots)$ serve to describe the heat exchanged between system and surroundings under different experimental conditions.



The functions $A(T, V, \dots)$ and $G(T, P, \dots)$ play a similar role. Both are used to calculate the energy released during the considered process.

Depending on how the system under consideration is controlled, one of the four thermodynamic functions of state, as opposed to any other, is advantageous to use:

* Internal energy, $U(S, V)$: The internal energy (U) is used when the entropy, the volume, and the composition of a system are controlled. The system is in equilibrium when its content of internal energy reaches the minimum value.

* Enthalpy, $H(P, S)$: The enthalpy (H) is used when the entropy, the pressure, and the composition of a system are controlled. The system is in equilibrium when its content of enthalpy reaches the minimum value. The enthalpy is related to the heat content of the system.

* Gibbs energy, $G(T, P)$: The Gibbs energy (G) is the most useful thermodynamic function of state and is used when the temperature, the pressure, and the composition of a system are controlled. The system is in equilibrium when its content of Gibbs energy reaches the minimum value.

* Helmholtz energy, $A(T, V)$: The Helmholtz energy (A) is used when the temperature, the volume, and the composition of a system are controlled. The system is in equilibrium when its content of Helmholtz energy reaches the minimum value.

Internal energy:

Let us recall the first law of thermodynamics which is given by,

$$dU = dQ + dW \quad \text{--- (1)}$$

Now, for a reversible change only, we have that

$$dQ = TdS, dW = -pdv \quad \text{--- (2)}$$

Therefore, changes in the internal energy U of a system are given by the first law of thermodynamics written in the form

$$dU = TdS - pdv \quad \text{--- (3)}$$

Constructing this equation, we have assumed that the change is reversible. However, since all the quantities in eqn. (3) are functions of state, and are therefore path independent, this equation holds for irreversible process as well! For an irreversible change, $dQ \leq TdS$ and also $dW \geq -pdv$, but with dQ being smaller than for the reversible case and dW being larger than for the reversible case so that dU is the same whether whether the change is reversible or irreversible.

This equation implies that the internal energy U changes when either S or V changes. Thus, the function U can be written in terms of the variables S and V which are its so-called natural variables.

Hence we write, $U = U(S, V)$

We also have that for isochoric process (V is constant)

$$dU = TdS \quad \text{--- (4)}$$

and for reversible isochoric process

$$dU = dQ = C_V dT \quad \text{--- (5)}$$

This relation can be used to define various other isochoric heat quantities such as integral and differential, molar and specific heats of reaction and the corresponding heat capacities.

Isochoric heat capacity,

$$C_V = \left(\frac{\partial U}{\partial T} \right)_V \quad \text{--- (6)}$$

Enthalpy:

Enthalpy (H) is defined as being derived from internal energy:

$$H = U + PV \quad \text{--- (1)}$$

In differential form,

$$\begin{aligned} dH &= d(U + PV) \\ &= dU + PDV + VdP \end{aligned} \quad \text{--- (2)}$$

According to first and second laws of thermodynamics,

$$dQ = dU + PDV, \quad dQ = TdS \quad \text{--- (3)}$$

$$\therefore dH = TdS + VdP \quad \text{--- (4)}$$

The natural variables for H are thus S and P , and we have that $H = H(S, P)$. We can therefore immediately write down that for a isobaric (i.e; constant P) process,

$$dH = TdS \quad \text{--- (5)}$$

and for a reversible isobaric process

$$dH = dQ = CpdT \quad \text{--- (6)}$$

so that,

$$\Delta H = \int_{T_1}^{T_2} CpdT \quad \text{--- (7)}$$

This shows the importance of H , that for reversible isobaric processes the enthalpy represents the heat absorbed by the system.

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Helmholtz Energy, F :

We define the Helmholtz function using,

$$F = U - TS \quad \text{--- (1)}$$

Hence we find that

$$dF = TdS - PdV - TdS - SdT \quad \text{--- (2)}$$

$$dF = -SdT - PdV \quad \text{--- (3)}$$

This implies that the natural variables for F are V, T and we can therefore write $F = F(T, V)$. For an isothermal process (constant T), we can simplify eqn. (3) further and write that,

$$dF = -PdV \quad \text{--- (4)}$$

and hence

$$\Delta F = - \int_{V_1}^{V_2} PdV \quad \text{--- (5)}$$

Hence a positive change in F represents reversible work done on the system by the surroundings, while a negative change in F represents reversible work done on the surroundings by the system.

Gibbs Energy, G

We define the Gibbs energy (sometimes called the Gibbs free energy) using

$$G = H - TS \quad \text{--- (1)}$$

Hence we find that

$$\begin{aligned} dG &= dH - TdS - SdT \\ &= TdS + Vdp - TdS - SdT \quad [dH = TdS + Vdp] \\ &= Vdp - SdT \quad \text{--- (2)} \end{aligned}$$

and hence the natural variables of G are T and p . Hence, $G = G(T, p)$. Having T and p as natural variables is particularly convenient as T and p are the easiest quantities to manipulate and control for most experimental systems.

Maxwell's relations:

In this section, we are going to derive four equations which are known as Maxwell's relations. The derivation proceeds along the following lines: a state function f is a function of variables x and y . A change in f can be written as

$$df = \left(\frac{\partial f}{\partial x}\right)_y dx + \left(\frac{\partial f}{\partial y}\right)_x dy \quad \text{--- (1)}$$

Because df is an exact differential, we have that

$$\frac{\partial^2 f}{\partial x \partial y} = \frac{\partial^2 f}{\partial y \partial x} \quad \text{--- (2)}$$

$$\text{Hence writing, } f_x = \left(\frac{\partial f}{\partial x}\right)_y \text{ and } f_y = \left(\frac{\partial f}{\partial y}\right)_x \quad \text{--- (3)}$$

We have that

$$\frac{\partial f_x}{\partial x} = \frac{\partial f_x}{\partial y} \quad \text{--- (4)}$$

We can now apply this idea to each of the state variables U, H, F and G in turn.

First equation:

The internal energy U is given by

$$dU = Tds - Pdv \quad \text{--- (1)}$$

The form of equ.(1) suggests that U may be written in terms of the independent pair of variables s and v as $U = U(s, v)$, where the notation $U(s, v)$ denotes a function of s and v . Hence,

$$dU = \left(\frac{\partial U}{\partial s}\right)_v ds + \left(\frac{\partial U}{\partial v}\right)_s dv \quad \text{--- (2)}$$

Comparing equ.(1) and (2),

$$T = \left(\frac{\partial U}{\partial s}\right)_v \text{ and } P = -\left(\frac{\partial U}{\partial v}\right)_s \quad \text{--- (3)}$$

U is a state function, dU is an exact differential. Using the condition for a differential to be exact,

$$\left(\frac{\partial T}{\partial v}\right)_s = -\left(\frac{\partial P}{\partial s}\right)_v \quad \text{--- (4)}$$

This is the first so-called Maxwell relation. The natural variables of U , namely s and v , are the quantities appearing outside the partial derivatives.

* Second equation:

The enthalpy H is given by,

$$dH = TdS + VdP \quad \text{--- (1)}$$

The natural variables for H are thus S and P . It is useful to write $H = H(S, P)$ and evaluate the exact differential:

$$dH = \left(\frac{\partial H}{\partial S}\right)_P dS + \left(\frac{\partial H}{\partial P}\right)_S dP \quad \text{--- (2)}$$

Comparing this equation with eqn. (1),

$$T = \left(\frac{\partial H}{\partial S}\right)_P \text{ and } V = \left(\frac{\partial H}{\partial P}\right)_S \quad \text{--- (3)}$$

This means that, if we know H in terms of its natural variables S and P , we can find both the temperature and the volume. Further, using the condition for dH in eqn. (1) to be an exact differential,

$$\left(\frac{\partial T}{\partial P}\right)_S = \left(\frac{\partial V}{\partial S}\right)_P \quad \text{--- (4)}$$

This is the second Maxwell relation, with the natural variables S and P appearing outside the partial derivatives.

* Third equation:

The helmholtz energy, F is given by,

$$dF = -pdV - SdT \quad \text{--- (1)}$$

The form of eqn. (1) suggests that the natural variables of F are V and T , so symbolically $F = F(V, T)$. Hence,

$$dF = \left(\frac{\partial F}{\partial V}\right)_T dV + \left(\frac{\partial F}{\partial T}\right)_V dT \quad \text{--- (2)}$$

Comparing co-efficients in equation (1) and (2);

$$P = -\left(\frac{\partial F}{\partial V}\right)_T \text{ and } S = -\left(\frac{\partial F}{\partial T}\right)_V \quad \text{--- (3)}$$

Because F is a function of state, dF is an exact differential. The condition for an exact differential in eqn. (1) given,

$$\left(\frac{\partial P}{\partial T}\right)_V = \left(\frac{\partial S}{\partial V}\right)_T \quad \text{--- (4)}$$

This is the third Maxwell relation, with the natural variables V and T appearing outside the derivatives.

④ Fourth relation:

The Gibbs energy ΔG is given by,

$$dQ = vdp - SdT \quad \text{---} \quad (1)$$

The form of equation (1) suggests that $A = h(\frac{P,T}{D,P})$. Hence,

$$dG = \left(\frac{\partial G}{\partial P}\right) dP + \left(\frac{\partial G}{\partial T}\right)_P dT \quad \text{--- (2)}$$

Comparing the coefficients in equation (1) and (2),

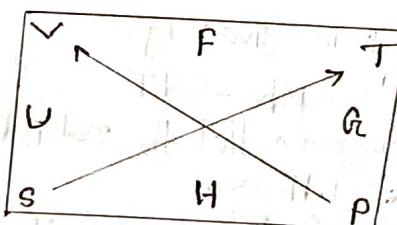
$$V = \left(\frac{\partial G}{\partial P}\right)_T \quad \text{and} \quad S = -\left(\frac{\partial G}{\partial T}\right)_P \quad \longleftarrow \text{Q3}$$

As G is a state function, dG is an exact differential. Using the condition for an exact differential in equ. (1),

$$\left(\frac{\partial V}{\partial T}\right)_P = - \left(\frac{\partial S}{\partial P}\right)_T \quad (4)$$

This is the fourth Maxwell relation, with the natural variables p and T appearing outside the partial derivatives.

Thermodynamic relations:



From the square;

$$U = (S, V) \quad dU = \cancel{\partial S/\partial p} T dS - p dV \quad \left(\frac{\partial U}{\partial V}\right)_S = -\left(\frac{\partial p}{\partial T}\right)$$

$$H = (s, p) \quad dH = TdS + Vdp \quad \left(\frac{\partial T}{\partial p}\right)_S = \left(\frac{\partial V}{\partial S}\right)_p$$

$$Q = (P, T) \quad dQ = V dP - S dT \quad \left(\frac{\partial S}{\partial T}\right)_P = \left(\frac{\partial S}{\partial P}\right)_T$$

$$f = (v, T) \quad df = -pdv - SdT \quad \left(\frac{\partial p}{\partial T}\right)_v = -\left(\frac{\partial S}{\partial T}\right)_v$$

Difference in heat capacity, $C_p - C_v$?

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We know that for an ideal gas,

$$C_p = C_v + nR \quad (1)$$

This result can be generalized for any system with the state variables P, V , and T . The starting point comes from either of the two basic relations for the principal heat capacities

$$C_v = T \left(\frac{\partial S}{\partial T} \right)_V \quad (2)$$

$$\text{and, } C_p = T \left(\frac{\partial S}{\partial T} \right)_P \quad (3)$$

The form of equ. (2) suggests writing $S = S(T, V)$, so that

$$dS = \left(\frac{\partial S}{\partial T} \right)_V dT + \left(\frac{\partial S}{\partial V} \right)_T dV \quad (4)$$

In order to obtain C_p , divide both sides of equ. (4) by dT at constant pressure and multiply by T . This gives C_p on the left side and C_v on the right side.

$$T \left(\frac{\partial S}{\partial T} \right)_P = T \left(\frac{\partial S}{\partial T} \right)_V + T \left(\frac{\partial S}{\partial V} \right)_T \left(\frac{\partial V}{\partial T} \right)_P \quad (5)$$

$$\Rightarrow C_p = C_v + T \left(\frac{\partial S}{\partial V} \right)_T \left(\frac{\partial V}{\partial T} \right)_P \quad (6) \quad \begin{matrix} \text{From equ. (2)} \\ \text{and (5)} \end{matrix}$$

The aim is to produce a relation between C_p and C_v in terms of quantities that can be measured. In this case, the appropriate quantities are the thermal expansion coefficient β and bulk modulus B , where

$$\beta = \frac{1}{V} \left(\frac{\partial V}{\partial T} \right)_P \quad (7)$$

$$\text{and, } B = -V \left(\frac{\partial P}{\partial V} \right)_T = \frac{1}{k} \quad (8)$$

In equation (6) $\left(\frac{\partial V}{\partial T} \right)_P$ is therefore equal to βV . $\left(\frac{\partial S}{\partial V} \right)_T$ is not recognizable, but it can be made so by applying a Maxwell relation. The appropriate one is,

$$\left(\frac{\partial P}{\partial T} \right)_V = \left(\frac{\partial S}{\partial V} \right)_T \quad (9)$$

Hence, equation (6) becomes,

$$C_p = C_v + T \left(\frac{\partial P}{\partial T} \right)_V \cdot \left(\frac{\partial V}{\partial T} \right)_P \quad (10) \quad \begin{matrix} \text{From equ. (9)} \end{matrix}$$

The first partial derivatives in equ. (10) has P, V, T in the wrong order to use to or β directly, but this can be repaired by using

Cyclic rule,

$$\left(\frac{\partial P}{\partial T}\right)_V \cdot \left(\frac{\partial V}{\partial P}\right)_T \cdot \left(\frac{\partial T}{\partial V}\right)_P = -1$$

$$\Rightarrow \left(\frac{\partial P}{\partial T}\right)_V = -\left(\frac{\partial P}{\partial V}\right)_T \cdot \left(\frac{\partial V}{\partial T}\right)_P \quad \xrightarrow{\text{---}} \textcircled{11}$$

Hence, the eqn. $\textcircled{10}$ becomes,

$$C_p = C_V - T \left(\frac{\partial V}{\partial T}\right)_P^2 \cdot \left(\frac{\partial P}{\partial V}\right)_T$$

Now, the results in eqn. $\textcircled{7}$ and $\textcircled{8}$ can be substituted to find

$$C_p = C_V - T (\beta V)^2 \cdot \left(-\frac{B}{V}\right) \quad \begin{bmatrix} \left(\frac{\partial V}{\partial T}\right)_P = \beta V \text{ and} \\ \left(\frac{\partial P}{\partial V}\right)_T = -\frac{B}{V} \end{bmatrix}$$
$$\Rightarrow C_p = C_V + T \beta^2 B V. \quad \xrightarrow{\text{---}} \textcircled{12}$$

Ratio of heat Capacities, $\frac{C_p}{C_v}$:

$$\frac{C_p}{C_v} = \frac{\kappa_T}{\kappa_s}$$

where, κ_T is the usual isothermal compressibility and κ_s is the adiabatic compressibility.

$$\kappa_T = -\frac{1}{V} \left(\frac{\partial V}{\partial P}\right)_T$$

$$\kappa_s = -\frac{1}{V} \left(\frac{\partial V}{\partial P}\right)_S$$

Joule-kelvin coefficient for the Joule-kelvin effect / throttling process:

Joule-kelvin effect is an important effect, because it is widely used for refrigerator and in the liquefaction of gases.

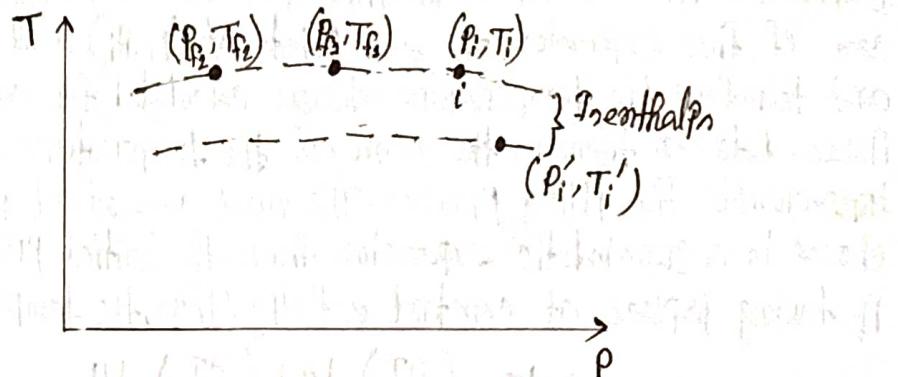


Fig. 1: Inenthalps of a Joule-kelvin effect.

The most convenient way to represent the effect is on a temperature-pressure plot, as in fig. 1. Suppose that the initial equilibrium state before throttling is the point i at (T_i, P_i) . The gas can be throttled to the lower pressure P_{f_1} , where it reaches final temperature T_{f_1} so that the gas ends up in the final equilibrium state (T_{f_1}, P_{f_1}) . This state will have the same enthalpy as i. If instead the gas were throttled from the same initial state i to a lower final pressure P_{f_2} , it would then be in the final equilibrium state (T_{f_2}, P_{f_2}) , again with the same enthalpy as i. By repeating this experiment many times, we could obtain a series of points representing the different final equilibrium points, all starting from the same initial equilibrium point i and all with the same enthalpy as i. The curve joining the i is called an inenthalp, as shown in fig. 1.

If now a second initial point (T'_i, P'_i) is chosen, a second inenthalp may be drawn. This is shown as the lower curve in fig. 1. In a similar way, we can draw a whole series of experimentally determined inenthalps, and the results would appear as in fig. 2 for a typical gas.

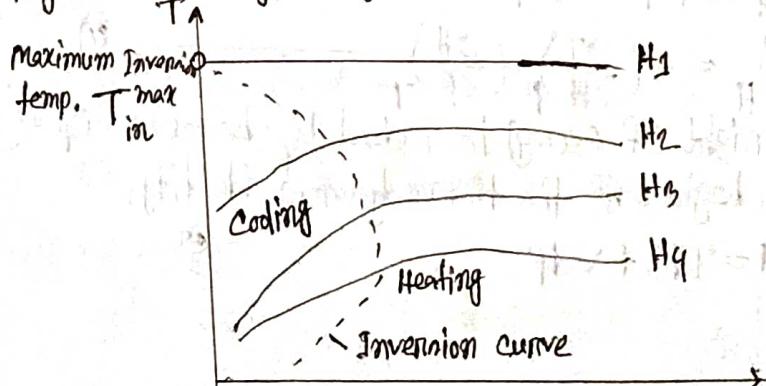


Fig. 2. Inversion curve for a throttling process.

The maxima of the different isenthalps lie on the inversion curve. The inversion curve separates the region of heating from the region of cooling. The point of the throttling process is to reduce temperature. It is possible to find a general expression for ΔT for a throttling process in terms of P, V , and T . As for the case of free expansion, the end points at (P_i, H_i) and (P_f, H_f) are equilibrium states, and therefore the temperature change calculated for an imaginary reversible process between them is the same as the temperature change in the actual irreversible throttling process. The most convenient reversible process to choose is a quasi-static expansion from the initial pressure P_i to the final pressure P_f taking place at constant enthalpy. Thus, the temperature is $T = T(P, H)$, so that

$$dT = \left(\frac{\partial T}{\partial P}\right)_H dP + \left(\frac{\partial T}{\partial H}\right)_P dH \quad \rightarrow ①$$

As the enthalpy H is constant in the process,

$$dT = \left(\frac{\partial T}{\partial P}\right)_H dP$$

$$\text{Integrating, } \int_{T_i}^{T_f} dT = \int_{P_i}^{P_f} \left(\frac{\partial T}{\partial P}\right)_H dP$$

$$\Rightarrow T_f - T_i = \left(\frac{\partial T}{\partial P}\right)_H (P_f - P_i)$$

$$\Rightarrow \frac{\Delta T}{\Delta P} = \left(\frac{\partial T}{\partial P}\right)_H \quad \rightarrow ②$$

$\frac{\partial T}{\partial P}$ is defined to be the Joule-Kelvin coefficient α_{JK} . Thus,

$$\alpha_{JK} = \left(\frac{\partial T}{\partial P}\right)_H \quad \rightarrow ③$$

The difficulty with equ. ③ is the constant H outside the partial derivative. It can be brought inside using the cyclic rule.

$$\left(\frac{\partial T}{\partial P}\right)_H \left(\frac{\partial H}{\partial T}\right)_P \left(\frac{\partial P}{\partial H}\right)_T = -1$$

$$\Rightarrow \left(\frac{\partial T}{\partial P}\right)_H = - \left(\frac{\partial T}{\partial H}\right)_P \left(\frac{\partial H}{\partial P}\right)_T \quad \rightarrow ④$$

The first factor on the right of equ. ④ is indeed $\frac{1}{C_p}$; because $C_p = \left(\frac{\partial H}{\partial T}\right)_P$. To solve the second factor, begin with the thermodynamic identity,

$$dH = TdS + Vdp \quad \rightarrow ⑤$$

Taking the Partial derivative with respect to p at constant temperature,

$$\left(\frac{\partial H}{\partial p}\right)_T = T \left(\frac{\partial S}{\partial p}\right)_T + V \quad \text{---} \quad (6)$$

This can be simplified by using the Maxwell relation, (3rd relation)

$$\left(\frac{\partial V}{\partial T}\right)_p = - \left(\frac{\partial S}{\partial p}\right)_T \quad \text{---} \quad (7)$$

Substituting eqn (7) into eqn. (6)

$$\left(\frac{\partial H}{\partial p}\right)_T = V - T \left(\frac{\partial V}{\partial T}\right)_p \quad \text{---} \quad (8)$$

Hence eqn. (8) becomes,

$$\gamma_{jk} = \frac{1}{C_p} \left[T \left(\frac{\partial V}{\partial T}\right)_p - V \right] \quad \text{---} \quad (9)$$

This is the desired result for the Joule-Kelvin coefficient.

For ideal gas:

The equation for the state of an ideal gas,

$$\begin{aligned} PV &= RT \\ \Rightarrow V &= \frac{RT}{P} \end{aligned} \quad \therefore \left(\frac{\partial V}{\partial T}\right)_P = \frac{\partial}{\partial T} \left(\frac{RT}{P} \right) = \frac{R}{P}$$

Hence, the Joule-Kelvin coefficient,

$$\begin{aligned} \gamma_{jk} &= \frac{1}{C_p} \left[T \left(\frac{\partial V}{\partial T}\right)_p - V \right] \\ &= \frac{1}{C_p} \left[\frac{RT}{P} - \frac{RT}{P} \right] \\ &= 0. \end{aligned}$$

So, there is no temperature change when an ideal gas undergoes a throttling process.

For real gas:

$$\left(P + \frac{a}{V^2}\right)(V - b) = RT \quad \text{---} \quad (1)$$

$$\text{or, } \left(P + \frac{a}{V^2}\right) = \frac{RT}{V-b} \quad \text{---} \quad (2)$$

Differentiating eqn. (1):

$$\left(P + \frac{a}{V^2}\right) \left(\frac{\partial V}{\partial T}\right)_P + (V-b) \left[-\frac{2a}{V^3} \left(\frac{\partial V}{\partial T}\right)_P\right] = R$$

$$\Rightarrow \frac{RT}{v-b} \left(\frac{\partial v}{\partial T} \right)_P - \frac{2a(v-b)}{v^3} \left(\frac{\partial v}{\partial T} \right)_P = R \quad \left[P + \frac{a}{v^2} = \frac{RT}{v-b} \right]$$

$$\Rightarrow \left(\frac{RT}{v-b} - \frac{2a(v-b)}{v^3} \right) \left(\frac{\partial v}{\partial T} \right)_P = R$$

$$\Rightarrow T \cdot \left(\frac{\partial v}{\partial T} \right)_P = \frac{RT}{\frac{RT}{v-b} - \frac{2a(v-b)}{v^3}} \quad \text{[Multiplying by } T \text{]}$$

$$\Rightarrow T \cdot \left(\frac{\partial v}{\partial T} \right)_P - v = \frac{RT}{\frac{RT}{v-b} - \frac{2a(v-b)}{v^3}} - v$$

$$\Rightarrow T \cdot \left(\frac{\partial v}{\partial T} \right)_P - v = \frac{\frac{2a}{RT} \left(1 - \frac{b}{v} \right)^2 - b}{1 - \frac{2a}{vRT} \left(1 - \frac{b}{v} \right)^2} \quad \text{③}$$

We know that, the Joule-Kelvin coefficient;

$$U_{JK} = \frac{1}{C_P} \left[T \cdot \left(\frac{\partial v}{\partial T} \right)_P - v \right] \quad \text{④}$$

Substituting eqn. ③ into eqn. ④;

$$U_{JK} = \frac{1}{C_P} \left[\frac{\frac{2a}{RT} \left(1 - \frac{b}{v} \right)^2 - b}{1 - \frac{2a}{vRT} \left(1 - \frac{b}{v} \right)^2} \right]$$

$$\Rightarrow U_{JK} = \frac{1}{C_P} \left[\frac{\frac{2a}{RT} \left(1 - \frac{b}{v} \right)^2 - b}{1 - \frac{2a}{vRT} \left(1 - \frac{b}{v} \right)^2} \right] \quad \left[\text{because, } \frac{2a}{vRT} \left(1 - \frac{b}{v} \right)^2 \approx 0 \right]$$

$$\text{Now; } \frac{2a}{RT} \left(1 - \frac{b}{v} \right)^2 > b$$

$$\Rightarrow \frac{2a}{RT} > b \quad \left[\text{because; } \left(1 - \frac{b}{v} \right)^2 \neq 1 \right]$$

$$\Rightarrow \frac{1}{T} > \frac{b \cdot R}{2a}$$

$\therefore T < \frac{bR}{2a}$ that is the inversion temperature, T_1

another temperature;

$$T > \frac{bR}{2a}$$

Application of Joule-Kelvin on throttling process:

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1. The throttling process is of enormous importance, especially in the liquefaction of gases.
 2. Gases might also be cooled by allowing them to expand adiabatically in an engine.
 3. Throttling process is also used in mechanical refrigeration for attaining low temperatures.
 4. This process is also used in the liquefaction of nitrogen or helium.
 5. The effect is applied in the Linde technique in the petrochemical industry, where the cooling effect is used to liquefy gases.

Joule effect of cooling or physics behind the Joule-Kelvin coefficient:

We know,

$$J_{JK} = \frac{1}{C_p} \left[T \left(\frac{\partial v}{\partial T} \right)_p - v \right]$$

$$\Rightarrow C_p \frac{\Delta T}{\Delta p} = T \left(\frac{\partial v}{\partial T} \right)_p - v \quad [J_{JK} = \frac{\Delta T}{\Delta p}] \quad \text{--- (1)}$$

Again, $T dS = dU + PdV$

Differentiating, $T \left(\frac{\partial S}{\partial P} \right)_T = \left(\frac{\partial U}{\partial P} \right)_T + P \left(\frac{\partial V}{\partial P} \right)_T \quad \text{--- (2)}$

with r.t. P and keeping T

constant; Maxwell third relation,

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

Applying this Maxwell relation in equ. (2)

$$-T \left(\frac{\partial V}{\partial T} \right)_P = \left(\frac{\partial U}{\partial P} \right)_T + P \left(\frac{\partial V}{\partial P} \right)_T \quad \text{--- (3)}$$

Substituting equ. (3) into equ. (1);

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

$$= - \left(\frac{\partial U}{\partial P} \right)_T - \frac{\partial}{\partial P} (PV)$$

Hence, $- \left(\frac{\partial U}{\partial P} \right)_T$ is the Joule effect of cooling.



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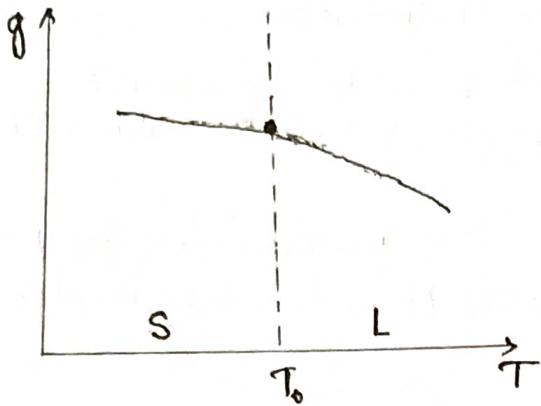


Fig. 2(a): The variation of g with T along the section XY of Fig. 1(b).

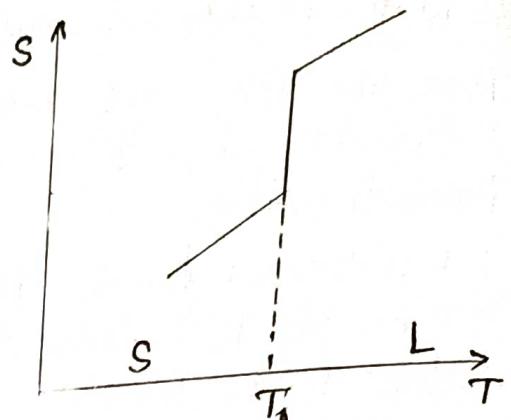


Fig. 2(b): The corresponding behaviour of the entropy.

Ehrenfest equations for second-order phase changes:

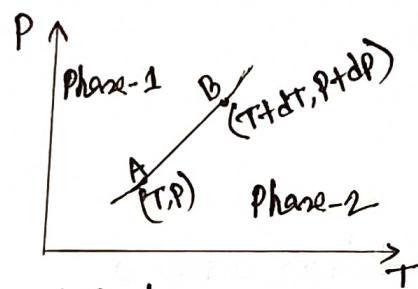


Fig. 1: A portion of a phase boundary.

Consider Fig. 1, where there is a second-order phase change between the two phases, and the solid line is the phase boundary for this transition.

Consider the two neighbouring points A and B on the phase boundary at (T, P) and $(T + dT, P + dP)$. In a second order phase change there is no change in either S or V in going from one phase to another. Therefore,

$$\text{At } A, \quad S_1(T, P) = S_2(T, P) \quad \text{--- (1)}$$

$$\text{At } B, \quad S_1(T + dT, P + dP) = S_2(T + dT, P + dP) \quad \text{--- (2)}$$

Using Taylor's theorem and keeping only first-order derivatives for small changes, equation (2) becomes,

$$S_1(T, P) + \left(\frac{\partial S_1}{\partial T}\right)_P dT + \left(\frac{\partial S_1}{\partial P}\right)_T dP = S_2(T, P) + \left(\frac{\partial S_2}{\partial T}\right)_P dT + \left(\frac{\partial S_2}{\partial P}\right)_T dP$$

This can be simplified using eqn. (1)

$$\left(\frac{\partial S_1}{\partial T}\right)_P dT + \left(\frac{\partial S_1}{\partial P}\right)_T dP = \left(\frac{\partial S_2}{\partial T}\right)_P dT + \left(\frac{\partial S_2}{\partial P}\right)_T dP \quad \text{--- (3)}$$

Multiplying eqn. (3) through by T and remembering that

$$C_p = T \left(\frac{\partial S}{\partial T} \right)_p, \beta = \frac{1}{V} \left(\frac{\partial V}{\partial T} \right)_p = \frac{1}{V} \left(\frac{\partial v}{\partial T} \right)_p, \text{ and } V_1 = V_2$$

and the Maxwell relation,

$$\left(\frac{\partial S}{\partial P} \right)_T = - \left(\frac{\partial V}{\partial T} \right)_P \quad \text{--- (4)}$$

Equation (3) reduces to,

$$C_{p_1} dT - TV \beta_1 dP = C_{p_2} dT - TV \beta_2 dP \quad \text{--- (5)}$$

Where the subscripts on C_p and β refer to the two phases. Solving for dP/dT in equation (5),

$$\frac{dP}{dT} = \frac{C_{p_1} - C_{p_2}}{TV(\beta_1 - \beta_2)} \quad \text{--- (6)}$$

This is the first Ehrenfest equation. As in the case of the Clausius-Clapeyron equation, the extensive quantities (here C_p and V) must refer to the same mass of the substance in each phase.

Now consider the continuity of V in a second-order transition

$$\text{At A, } V_1(T, P) = V_2(T, P) \quad \text{--- (7)}$$

$$\text{At B, } V_1(T+dT, P+dP) = V_2(T+dT, P+dP) \quad \text{--- (8)}$$

Following the same procedure as above, applying Taylor's theorem of eqn. (2) and keeping only first-order derivatives given,

$$V_1(T, P) + \left(\frac{\partial V_1}{\partial T} \right)_P dT + \left(\frac{\partial V_1}{\partial P} \right)_T dP = V_2(T, P) + \left(\frac{\partial V_2}{\partial T} \right)_P dT + \left(\frac{\partial V_2}{\partial P} \right)_T dP$$

Using eqn. (7), this simplifies to,

$$\left(\frac{\partial V_1}{\partial T} \right)_P dT + \left(\frac{\partial V_1}{\partial P} \right)_T dP = \left(\frac{\partial V_2}{\partial T} \right)_P dT + \left(\frac{\partial V_2}{\partial P} \right)_T dP \quad \text{--- (9)}$$

Remembering that

$$\beta = \frac{1}{V} \left(\frac{\partial V}{\partial T} \right)_P = \frac{1}{V} \left(\frac{\partial v}{\partial T} \right)_P \text{ and } k' = - \frac{1}{V} \left(\frac{\partial v}{\partial P} \right)_T$$

Equation (9) becomes,

$$\beta_1 V_1 dT - k' V_1 dP = \beta_2 V_2 dT - k' V_2 dP \quad \text{--- (10)}$$

Collecting terms and remembering that $V_1 = V_2$,

$$\frac{dP}{dT} = \frac{\beta_2 - \beta_1}{k'_2 - k'_1} \quad \text{--- (11)}$$

This is the second Ehrenfest equation.

Chemical Potential: The Chemical Potential of a species in a mixture is defined as the rate of change of free energy of a thermodynamic system with respect to the change in the number of atoms or molecules of the species that are added to the system.

Chemical potential and internal energy U:

For a variable-mass system such as the gas-filled ^{Chamber} with a hole in wall, it is necessary to modify the thermodynamic identity

$$dU = TdS - PdV \quad \text{--- (1)}$$

to allow for the extra energy brought into the system by the additional particles. [The extra energy is clearly of importance if it can be released to the rest of the system, and this could be the case if the particles were involved in, say, a chemical reaction of some form]. Suppose, for a moment that the system consists of only one type of particles, and dn particles are added. Then eqn.(1) can be modified as,

$$dU = TdS - PdV + \mu dn \quad \text{--- (2)}$$

where, μ is called the Chemical Potential, defined as the increase in the internal energy per particle added under conditions of constant S and V .

That is, $\mu = \left(\frac{\partial U}{\partial n}\right)_{S,V} \quad \text{--- (3)}$

Chemical Potential and helmholtz function F:

$$\text{Helmholtz function, } F = U - TS \quad \text{--- (1)}$$

$$\Rightarrow dF = dU - TdS - SdT$$

$$\Rightarrow dF = TdS - PdV - TdS - SdT \quad \boxed{dU = TdS - PdV + \mu dn} \\ TdS - PdV + \mu dn - TdS - SdT$$

$$\Rightarrow dF = -PdV - SdT + \mu dn \quad \text{--- (2)}$$

Therefore,

$$\mu = \left(\frac{\partial F}{\partial n}\right)_{V,T} \quad \text{--- (3)}$$

That is, μ is the increase of the Helmholtz free energy upon the addition of one particle under conditions of constant T and V .

Chemical Potential and Gibb's function G :

Gibb's function, $G = H - TS$

$$= U + PV - TS$$

where the second equality uses the fact that $H = U + PV$. Differentiating,

$$dG = dU + pdv + vdp - Tds - SdT$$

$$\Rightarrow dG = Tds - pdv + \cancel{pdn} + pdv + vdp - SdT - Tds \quad [dU = Tds - pdv + \cancel{pdn}]$$

$$\Rightarrow dG = vdp - SdT + \cancel{pdn} \quad \text{--- (1)}$$

Therefore,

$$\cancel{dU} = \left(\frac{\partial G}{\partial n} \right)_{T,P} \quad \text{--- (2)}$$

Thus, \cancel{dU} is the increase of the Gibb free energy upon the addition of one particle under condition of constant T and P .

(*) we know,

$$dU = Tds - pdv + \cancel{pdn}$$

$$\Rightarrow \frac{dU}{T} = ds - \frac{P}{T}dv + \cancel{\frac{P}{T}dn} \quad [\text{Dividing by } T]$$

$$\Rightarrow ds = \frac{dU}{T} + \frac{P}{T}dv - \frac{\cancel{P}}{T}dn$$

$$\therefore \cancel{dU} = \cancel{T} - T \left(\frac{\partial S}{\partial n} \right)_{U,V}$$

Phase equilibrium:

The internal energy of phase is,

$$U = U(S, V, n_1, n_2, \dots, n_k) \quad \text{--- (1)}$$

Where, n_i is the number of moles of the i th constituent present in the phase. Then,

$$dU = \left(\frac{\partial U}{\partial S} \right)_{V,n} ds + \left(\frac{\partial U}{\partial V} \right)_{S,n} dv + \left(\frac{\partial U}{\partial n_i} \right)_{S,V,n'} dn_i + \cdots + \left(\frac{\partial U}{\partial n_k} \right)_{S,V,n'} dn_k \quad \text{--- (2)}$$

Where, the subscript n' signifies that the number of moles of all constituents is constant except for the constituent appearing in the derivative. We know the equation $dU = Tds - pdv + \cancel{pdn}$ which can be written as,

$$dU = Tds - pdv + \cancel{pdn} + \cdots + \cancel{n_k dn_k} \quad \text{--- (3)}$$

Where,

$$\cancel{n_i} = \left(\frac{\partial U}{\partial n_i} \right)_{P,T,n'} \quad \text{--- (4)}$$

The last equation defines the chemical potential of the i th constituent in the phase.

Gibbs Phase rule:

The difference in the Gibbs function between two states at the same temperature and pressure for an open system of K constituents is,

$$d\Delta G = dU - TdS + PdV$$

$$\Rightarrow dG_i = TdS - PdV + U_i dm_i + \dots + U_K dm_K - TdS + PdV$$

$$\Rightarrow dG_i = U_i dm_i + \dots + U_K dm_K . \quad \text{--- (1)}$$

And,

$$U_i = \left(\frac{\partial G}{\partial n_i} \right)_{P,T,m'} \quad \text{--- (2)}$$

The chemical potential of a constituent is not dependent on the size of the phase, but is specified by the relative composition, the pressure, and the temperature. Consider the phase to consist of two parts which are equal in every respect. If Δn_i moles of constituent i are added to each half of the phase without changing the pressure or the temperature of either half, the pressure and the temperature of the whole phase do not change and we can write for each half,

$$\delta U_i = \frac{\Delta G}{\Delta n_i}$$

For the two halves, we get

$$\delta U_i = \frac{2\Delta G}{2\Delta n_i} = \frac{\Delta G}{\Delta n_i}.$$

(*)

Hence, the chemical potential U_i is independent of the size of the phase.

[The specific Gibbs function has the same value in phase for equilibrium both phase of a single constituent requires modification when more than one constituent is present in the system.] We consider a closed system consisting of π phases and K constituents in equilibrium at constant temperature and pressure. As before, a constituent will be designated by subscript $i = 1, 2, 3, \dots, K$ and a phase by a superscript $(j) = 1, 2, 3, \dots, \pi$. Thus, the symbol $U_i^{(j)}$ means the chemical potential of constituent i in phase j .

The Gibbs function of constituent i in phase j is the product of the chemical potential $U_i^{(j)}$ of that constituent in phase j , and the number of moles $n_i^{(j)}$ of the constituent in phase j . The total Gibbs function of phase j is the sum of all such products over all constituents, that is, it equals

$$\sum_{i=1}^{i=K} U_i^{(j)} \cdot n_i^{(j)}$$

Finally, the total Gibbs function of the entire system is the sum of all such sums over all phases of the system, and can be written,

$$G = \sum_{j=1}^{J=\pi} \sum_{i=1}^{i=k} \mu_i^{(j)} n_i^{(j)} \quad (3)$$

When we compare the equilibrium state with a second state at the same temperature and pressure, but differing slightly from the equilibrium state, the first variation in the Gibbs function is zero: $dG_{T,p} = 0$.

[In the second state, the numbers of moles $n_i^{(j)}$ of each constituent in each phase are slightly different from their equilibrium values. Then since the chemical potentials are constants at constant temperature and pressure, we have from eqn.(3):]

$$dG_{T,p} = \sum_{j=1}^{J=\pi} \sum_{i=1}^{i=k} \mu_i^{(j)} \cdot n_i^{(j)} = 0 \quad (4)$$

If the number of variables is one greater than the number of equations, an arbitrary value can be assigned to one of the variables and the remainder are completely determined. The system is then called monovariant and is said to have a variance of 1.

In general, the variance f is defined as the excess of the number of variables over the number of equations, and

$$f = [\pi(k-1) + 2] - [k(\pi-1)] \\ \Rightarrow f = K - \pi + 2. \text{ (no chemical reactions)} \quad (5)$$

This equation is called the Gibbs phase rule.

Example: (H_2O).

Consider liquid water in equilibrium with its vapor. There is only one constituent (H_2O) and $K=1$. There are two phases, $\pi=2$

\therefore The number of equations of phase equilibrium is: $K(\pi-1)$
 $\qquad\qquad\qquad \simeq 1(2-1) = 1$.

This single equation simply states, the chemical potential has the same value in both phases.

\therefore The number of variables is: $\pi(k-1) + 2 = 2(1-1) + 2 = 2$.

\therefore The variance f is therefore, $f = K - \pi + 2$

$$\Rightarrow f = 1 - 2 + 2$$

$$\therefore f = 1$$

At the triple point of water, all three phases are equilibrium and $\pi=3$. Then $K(\pi-1) = 1(3-1) = 2$, and there are two equations of phase equilibrium stating that the chemical potential in any one phase is equal to its value in each of the other phases. The number of variables in $\pi(\pi-1)+2 = 3(1-1)+2 = 2$, which is equal to the number of equations. The variance is,

$$f = K - \pi + 2$$

$$\Rightarrow f = 1 - 3 + 2$$

$\therefore f = 0$. and the system is therefore invariant.

Third law of thermodynamics: The third law of thermodynamics is often stated as: "The entropy of a system must approach zero in the limit of zero temperature."

The Nernst heat theorem: (statements of 3rd law)

The third law of thermodynamics is concerned with the entropy of a system as the temperature is reduced toward absolute zero.

Integrating entropy equation from absolute zero to temperature T ,

$$S = \int_0^T \frac{dQ}{T} + S_0 \quad \text{--- (1)}$$

In this case S_0 , the entropy at absolute zero, can not be determined from the second law. This is where the third law becomes meaningful, providing a value for S_0 .

The original statement of the third law was given by Walther Nernst in 1906. Nernst noticed that, in many chemical reactions occurring with no change in the end point temperatures, the value of ΔH decreased while that of ΔS increased. Nernst postulated an heat theorem that not only do these two quantities become equal at $T=0$, but they also approach each other asymptotically, as shown in Fig.1.

Consider what this means in terms of entropy:

$$\Delta G = \Delta H - T \Delta S. \quad \text{--- (2)}$$

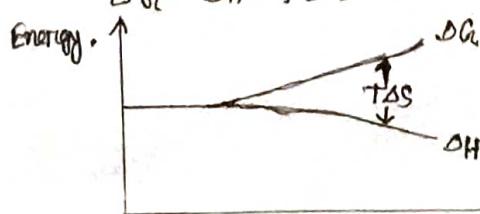


Fig.1: Nernst postulated that the curves for ΔH and ΔG in a chemical reaction approach each other asymptotically as $T \rightarrow 0$.

Statement of the Nernst heat theorem:

"The entropy change in a process that occurs between the pair of equilibrium states, associated with a change in an external parameter, tend to zero as the temperature approaches absolute zero."

Planck formulation of the third law:

A particular useful statement of the third law was given by Planck in 1911. It is a more powerful statement than the earlier statement of Nernst and is,

"The entropy of all perfect crystals in the state of absolute zero, and may be taken as zero."