Lecture-22

# The Thermodynamic Web

* Thermodynamic state of a system can be characterized by its properties. our goal is to develop mathematical expressions through which we can relate the properties of a system to one another and to forms in which data are typically reported.

* Three distinct categories of thermodynamic properties:

→ Measured properties.
→ Fundamental properties.
→ Derived properties.

* **Measured properties:** are those properties that are directly accessible from measurements in the lab.
Pressure, volume, Temperature, composition

* **Fundamental properties:**
observations of nature led us to the two laws of thermodynamics. In formulating these laws, we introduced two new properties:

U (From conservation of energy)

S (from directionality of nature)

Since internal energy and entropy come from the two fundamental postulates of thermodynamics, we call them fundamental properties.

These properties can not be measured directly.

* ~~Dervied~~ Derived properties: These cannot be measured in the lab, nor are they properties directly fundamental to the postulates that govern thermodynamics; they are merely some specific combination of the above two types of properties that are defined out of convenience. Consider, for example, enthalpy:

$$H = U + PV$$

Helmholtz energy : $A = U - TS$

Gibbs energy : $G = H - TS$

We will develop a web of property relationships whereby we can relate the thermodynamic properties we need to solve problems to properties we can measure in the lab.

We want to relate fundamental and derived thermodynamic properties such as U, S, H, A and G, to things we can measure, such as measured properties P, V, T or to quantities for which measured data are typically reported, for example

$C_p$, $C_V$, $\beta$ and $K$.

We limit our present discussion to constant compositions systems. The state postulate says that for systems of constant composition, values of two independent, intensive properties completely constrain the state of the system.

Mathematically, the change in any intensive thermodynamic property of interest, z, can be written in terms of partial derivatives of the two independent intensive properties, x and y, as follows:

$$dz = \left(\frac{\partial z}{\partial x}\right)_y dx + \left(\frac{\partial z}{\partial y}\right)_x dy \longrightarrow (1)$$

## Fundamental Property Relations:

First law of thermodynamics,

$$dQ + dW = dU \longrightarrow (2)$$

Second law of thermodynamics,

$$dQ = Tds \longrightarrow (3)$$

[ closed system undergoing a reversible process]

From (2) & (3),

$$dU = Tds + dW$$

$$\Rightarrow \boxed{dU = Tds - PdV} \longrightarrow (4)$$

Enthalpy is defined as:

$$H = U + PV$$

$$\Rightarrow dH = dU + PdV + Vdp$$

Using eqn. (4),

$$dH = (Tds - PdV) + PdV + Vdp$$

$$\Rightarrow \boxed{dH = Tds + Vdp} \longrightarrow (5)$$

Helmholtz energy, $A = U - TS$

$$\Rightarrow \quad dA = dU - TdS - SdT$$

using eq$^n$. (4),

$$dA = (TdS - PdV) - TdS - SdT$$

$$\boxed{dA = -PdV - SdT} \longrightarrow (6)$$

Gibbs energy, $G = H - TS$

$$dG = dH - TdS - SdT$$

using eq$^n$. (5),

$$dG = (TdS + Vdp) - TdS - SdT$$

$$\boxed{dG = Vdp - SdT} \longrightarrow (7)$$

Equations (4), (5), (6) & (7) are known as the fundamental property relations. These equations can be applied to any process: reversible or irreversible.

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From eq$^n$. (1),

$$dz = \left(\frac{\partial z}{\partial x}\right)_y dx + \left(\frac{\partial z}{\partial y}\right)_x dy$$

or, $$\boxed{dz = M dx + N dy} \longrightarrow (8)$$

where, $M = \left(\frac{\partial z}{\partial x}\right)_y$ and $N = \left(\frac{\partial z}{\partial y}\right)_x$

Then, $\left(\frac{\partial M}{\partial y}\right)_x = \frac{\partial^2 z}{\partial y \partial x}$ and $\left(\frac{\partial N}{\partial x}\right)_y = \frac{\partial^2 z}{\partial x \partial y}$

The order of differentiation in mixed second derivatives is immaterial and thus,

$$\boxed{\left(\frac{\partial M}{\partial y}\right)_x = \left(\frac{\partial N}{\partial x}\right)_y} \longrightarrow (9)$$

Euler Relation

Therefore, using (8) and (9) with eq$^n$. (4),

$$\boxed{\left(\frac{\partial T}{\partial V}\right)_S = -\left(\frac{\partial P}{\partial S}\right)_V} \longrightarrow (10)$$

From eq$^n$. (5),

$$\boxed{\left(\frac{\partial T}{\partial P}\right)_S = \left(\frac{\partial V}{\partial S}\right)_P} \longrightarrow (11)$$

From eq$^n$. (6),

$$\boxed{\left(\frac{\partial P}{\partial T}\right)_V = \left(\frac{\partial S}{\partial V}\right)_T} \longrightarrow (12)$$

From eq$^n$. (7),

$$\boxed{\left(\frac{\partial V}{\partial T}\right)_P = -\left(\frac{\partial S}{\partial P}\right)_T} \longrightarrow (13)$$

Equations (10), (11), (12) & (13) are known as Maxwell's equations.

Other useful Mathematical Relations:

$$\left(\frac{\partial z}{\partial x}\right)_a = \left(\frac{\partial z}{\partial y}\right)_a \left(\frac{\partial y}{\partial x}\right)_a \longrightarrow (14)$$

↳ chain Rule.

~~Derivative inversion allows us to flip partial derivatives~~

$$\cancel{\left(\frac{\partial x}{\partial z}\right)_y = \frac{1}{\quad}}$$

Again, $dz = \left(\frac{\partial z}{\partial x}\right)_y dx + \left(\frac{\partial z}{\partial y}\right)_x dy$

Taking partial derivative of each term with respect to x ~~and~~ at constant z, we get:

$$\left(\frac{\partial z}{\partial x}\right)_z = \left(\frac{\partial z}{\partial x}\right)_y \underset{\downarrow(1)}{\left(\frac{\partial x}{\partial x}\right)_z} + \left(\frac{\partial z}{\partial y}\right)_x \left(\frac{\partial y}{\partial x}\right)_z$$

$$0 = \left(\frac{\partial z}{\partial x}\right)_y + \left(\frac{\partial z}{\partial y}\right)_x \left(\frac{\partial y}{\partial x}\right)_z$$

$$\Rightarrow \left(\frac{\partial z}{\partial y}\right)_x \left(\frac{\partial y}{\partial x}\right)_z = -\left(\frac{\partial z}{\partial x}\right)_y$$

$$\Rightarrow \boxed{\left(\frac{\partial x}{\partial z}\right)_y \left(\frac{\partial y}{\partial x}\right)_z \left(\frac{\partial z}{\partial y}\right)_x = -1} \longrightarrow (15)$$

$\downarrow$

Cyclic Relation

Heat capacity at constant volume,

$$C_V = \left(\frac{\partial U}{\partial T}\right)_V$$

using $dU = TdS - PdV$, we get-

$$C_V = \frac{\partial}{\partial T}(T\partial S - P\partial V)_V$$

$$= T\left(\frac{\partial S}{\partial T}\right)_V - \underset{\substack{\downarrow \\ 0}}{P\left(\frac{\partial V}{\partial T}\right)_V}$$

$$\Rightarrow C_V = T\left(\frac{\partial S}{\partial T}\right)_V$$

$$\Rightarrow \boxed{\left(\frac{\partial S}{\partial T}\right)_V = \frac{C_V}{T}} \longrightarrow (16)$$

Heat capacity at constant pressure,

$$C_p = \left(\frac{\partial H}{\partial T}\right)_p$$

using, $dH = TdS + Vdp$

$$\Rightarrow \quad C_p = T\left(\frac{\partial S}{\partial T}\right)_p + \underset{\overset{\downarrow}{0}}{V\left(\frac{\partial P}{\partial T}\right)_p}$$

$$\Rightarrow \quad C_p = T\left(\frac{\partial S}{\partial T}\right)_p$$

$$\Rightarrow \quad \boxed{\left(\frac{\partial S}{\partial T}\right)_p = \frac{C_p}{T}} \longrightarrow (17)$$

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$$x = x(y,z)$$

$$dx = \left(\frac{\partial x}{\partial y}\right)_z dy + \left(\frac{\partial x}{\partial z}\right)_y dz$$

$$z = z(x,y)$$

similarly, $dz = \left(\frac{\partial z}{\partial x}\right)_y dx + \left(\frac{\partial z}{\partial y}\right)_x dy$

$$dx = \left(\frac{\partial x}{\partial y}\right)_z dy + \left(\frac{\partial x}{\partial z}\right)_y \left[\left(\frac{\partial z}{\partial x}\right)_y dx + \left(\frac{\partial z}{\partial y}\right)_x dy\right]$$

$$= \left(\frac{\partial x}{\partial y}\right)_z dy + \cancel{\left(\frac{\partial x}{\partial z}\right)_y}\cancel{\left(\frac{\partial z}{\partial x}\right)_y} dx + \left(\frac{\partial x}{\partial z}\right)_y \left(\frac{\partial z}{\partial y}\right)_x dy$$

$$\cancel{dx} = \left(\frac{\partial x}{\partial y}\right)_z dy + \cancel{dx} + \left(\frac{\partial x}{\partial z}\right)_y \left(\frac{\partial z}{\partial y}\right)_x dy$$

$$\Rightarrow \left(\frac{\partial x}{\partial y}\right)_z + \left(\frac{\partial x}{\partial z}\right)_y \left(\frac{\partial z}{\partial y}\right)_x = 0$$

$$\Rightarrow \left(\frac{\partial x}{\partial y}\right)_z = -\left(\frac{\partial x}{\partial z}\right)_y \left(\frac{\partial z}{\partial y}\right)_x$$

$$\Rightarrow \boxed{\left(\frac{\partial x}{\partial y}\right)_z \left(\frac{\partial y}{\partial z}\right)_x \left(\frac{\partial z}{\partial x}\right)_y = -1} \longrightarrow (15)$$

$\downarrow$

<u>cyclic Relation.</u>

E.g. Among the thermodynamic variables P, V and T, the following relation holds good.

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

## Lecture-24

Calculation of fundamental and derived properties using Equations of state and other measured quantities:

Relation of ds in terms of independent properties T and V and independent properties T and p:

$$s = s(T,V)$$

$$ds = \left(\frac{\partial s}{\partial T}\right)_V dT + \left(\frac{\partial s}{\partial V}\right)_T dV$$

from, eq$^n$. (16), $\left(\frac{\partial s}{\partial T}\right)_V = \frac{C_V}{T}$

and eq$^n$. (12), $\left(\frac{\partial s}{\partial V}\right)_T = \left(\frac{\partial P}{\partial T}\right)_V$

$$\Rightarrow \boxed{ds = \frac{C_V}{T} dT + \left(\frac{\partial P}{\partial T}\right)_V dV} \longrightarrow (18)$$

On integration,

$$\boxed{\Delta s = \int \frac{C_V}{T} dT + \int \left(\frac{\partial P}{\partial T}\right)_V dV} \longrightarrow (19)$$

Again, $s = s(T,P)$

$$ds = \left(\frac{\partial s}{\partial T}\right)_P dT + \left(\frac{\partial s}{\partial P}\right)_T dp$$

From, eq$^n$. (17), $\left(\frac{\partial s}{\partial T}\right)_P = \frac{C_P}{T}$

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

$$\Rightarrow \quad \boxed{ds = \frac{C_p}{T}dT - \left(\frac{\partial V}{\partial T}\right)_p dp} \longrightarrow (20)$$

On integration,

$$\boxed{\Delta s = \int \frac{C_p}{T}dT - \int \left(\frac{\partial V}{\partial T}\right)_p dp} \longrightarrow (21)$$

## Relation of du in terms of independent properties T and V:

$$U = U(T, V)$$

$$dU = \left(\frac{\partial U}{\partial T}\right)_V dT + \left(\frac{\partial U}{\partial V}\right)_T dV$$

since, $C_V = \left(\frac{\partial U}{\partial T}\right)_V$

and $\quad dU = TdS - PdV$

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

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

from eq$^n$. (12), $\left(\frac{\partial S}{\partial V}\right)_T = \left(\frac{\partial P}{\partial T}\right)_V$

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

Thus, $\boxed{dU = C_V dT + \left[T\left(\frac{\partial P}{\partial T}\right)_V - P\right]dV} \longrightarrow (22)$

on integration, $\boxed{\Delta U = \int C_V dT + \int \left[T\left(\frac{\partial P}{\partial T}\right)_V - P\right]dV} \longrightarrow (23)$

$$H = H(T, P)$$

$$dH = \left(\frac{\partial H}{\partial T}\right)_P dT + \left(\frac{\partial H}{\partial P}\right)_T dp$$

Since, $C_p = \left(\frac{\partial H}{\partial T}\right)_P$

and, $dH = Tds + vdp$ [Eq$^n$. 5]

$$\left(\frac{\partial H}{\partial P}\right)_T = T\left(\frac{\partial s}{\partial P}\right)_T + v\left(\frac{\partial P}{\partial P}\right)_T$$

$$= T\left(\frac{\partial s}{\partial P}\right)_T + v$$

Since, $\left(\frac{\partial s}{\partial P}\right)_T = -\left(\frac{\partial v}{\partial T}\right)_P$ [Eq$^n$. (13)]

Thus, $\boxed{dH = C_p dT + \left[v - T\left(\frac{\partial v}{\partial T}\right)_P\right] dp}$ $\rightarrow$ (24)

For ideal gas, $Pv = RT$

$$\Rightarrow v = \frac{RT}{P}$$

$$\Rightarrow \left(\frac{\partial v}{\partial T}\right)_P = \frac{R}{P}$$

Thus, from eq$^n$. (24), $dH = C_p dT + \underbrace{\left[v - \frac{RT}{P}\right]}_{0} dp$

$\boxed{dH = C_p dT}$ $\rightarrow$ (25)

only for ideal gas.

Since, volume expansivity,

$$\beta = \frac{1}{V}\left(\frac{\partial V}{\partial T}\right)_P \Rightarrow \boxed{\left(\frac{\partial V}{\partial T}\right)_P = \beta V} \quad \rightarrow (26)$$

and, isothermal compressibility,

$$K = -\frac{1}{V}\left(\frac{\partial V}{\partial P}\right)_T \Rightarrow \boxed{\left(\frac{\partial V}{\partial P}\right)_T = -KV} \quad \rightarrow (27)$$

From Eq$^n$. (13), $\left(\frac{\partial S}{\partial P}\right)_T = -\left(\frac{\partial V}{\partial T}\right)_P$

using eq$^n$. (26), we get-

$$\boxed{\left(\frac{\partial S}{\partial P}\right)_T = -\beta V} \quad \longrightarrow (28)$$

Since, $dH = TdS + VdP$ [Eq$^n$. 5]

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

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

$$= V + T(-\beta V) \quad \underline{\text{using Eq}^n\text{. (28)}}$$

$$= V - \beta T V$$

$$\boxed{\left(\frac{\partial H}{\partial P}\right)_T = (1-\beta T)V} \quad \longrightarrow (29)$$

From eq$^n$. (24),

$$dH = C_p dT + \left[V - T\left(\frac{\partial V}{\partial T}\right)_p\right] dp$$

using Eq$^n$. (26),

$$\left(\frac{\partial V}{\partial T}\right)_p = \beta V$$

$$dH = C_p dT + [V - T\beta V] dp$$

$$\boxed{dH = C_p dT + (1 - \beta T)V dp} \longrightarrow (30)$$

From Eq$^n$. (20),

$$ds = \frac{C_p}{T} dT - \left(\frac{\partial V}{\partial T}\right)_p dp$$

using Eq$^n$. (26),

$$\left(\frac{\partial V}{\partial T}\right)_p = \beta V$$

$$\boxed{ds = C_p \frac{dT}{T} - \beta V dp} \longrightarrow (31)$$

## Internal Energy as a Function of P:

$$U = H - PV$$

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

$$= \underbrace{(1-\beta T)V}_{\text{Eq}^n.\ (29)} - P\underset{\substack{\uparrow \\ \text{Eq}^n.\ (27)}}{(-KV)} - V$$

$$= V - \beta TV + KPV - V$$

$$= KPV - \beta TV$$

$$\boxed{\left(\frac{\partial U}{\partial P}\right)_T = (KP - \beta T)V} \longrightarrow (32)$$

* The equations, incorporating 'β' and 'K', although general, are usually applied only to liquids. Because 'β' and 'V' are weak functions of pressure for liquids, they are usually assumed constant.

If $V = V(T, P)$

$$dV = \left(\frac{\partial V}{\partial T}\right)_P dT + \left(\frac{\partial V}{\partial P}\right)_T dp$$

Using Eq$^n$. (26) & (27),

$$dV = \beta V dT - KV dp$$

$$\Rightarrow \frac{dV}{V} = \beta dT - K dp$$

At constant volume,

$$\boxed{\left(\frac{\partial P}{\partial T}\right)_V = \frac{\beta}{K}} \longrightarrow (33)$$

From eq$^n$. (22),

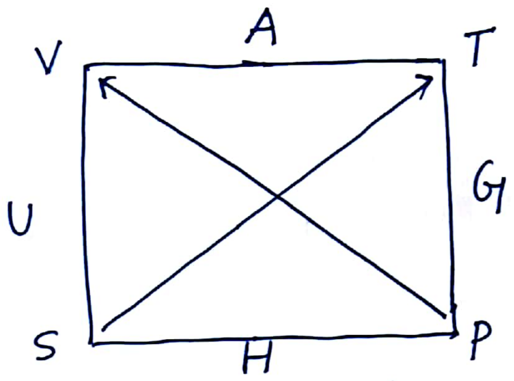
$$\boxed{dU = C_V dT + \left(\frac{\beta}{K}T - P\right) dV} \longrightarrow (34)$$

From eq$^n$. (18),

$$\boxed{dS = \frac{C_V}{T} dT + \frac{\beta}{K} dV} \longrightarrow (35)$$

# Thermodynamic Mnemonic diagram    Lecture-25

- A number of the most useful Maxwell relations can be remembered conveniently in terms of a simple mnemonic diagram. The diagram was presented by Max Born [1954 Nobel prize in physics].



Thermodynamic potential: A, G, H, U.

- Mnemonic diagram consists of a square with arrows pointing upward along the two diagonals.
- The sides are labelled with the four common thermodynamic potentials A, G, H and U, in alphabetical order clockwise around the diagram, the helmholtz potential at the top.
- The two corners at the left are labelled with 'V' and 'S' and the two corners at the right are labelled with 'T' and 'P'.

- Each of the four thermodynamic potentials appearing on the square is flanked by independent variables.
- 'U' is a function of 'V' and 's'.

  'A' is a function of 'V' and 'T'.

  'G' is a function of 'T' and 'p'.

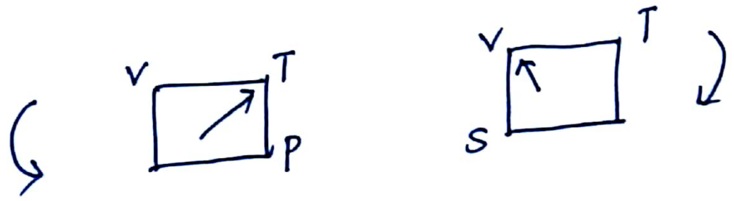
  'H' is a function of 's' and 'p'.
- In the differential expression for each of the potentials, in terms of the differentials of its variables, the associated algebraic sign is indicated by the diagonal arrow.
- An arrow pointing away from a variable implies a positive coefficient, whereas an arrow pointing toward a variable implies negative coefficient.
- Based on the above scheme, we can write the following equations:

$$\left.\begin{aligned} dU &= -PdV + Tds \\ dA &= -PdV - SdT \\ dG &= -SdT + Vdp \\ dH &= Tds + Vdp \end{aligned}\right\} \text{Fundamental property Relations.}$$

- Finally the Maxwell relations can be read from the diagram. We then deal only with the corners of the diagram.

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

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



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

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

**Question**: One mole of propane gas is to be expanded from $0.001 m^3$ to $0.04 m^3$ while in contact with a heating bath at 100 °C. The expansion is not reversible. The heat extracted from the bath is 600 J. Using the vander waals equation of state, determine the work for the expansion.

**Solution**: To find the work, we apply the first law;

$$\Delta U = Q + W \longrightarrow (1)$$

Since we know, $Q = 600 J$, we just need to find $\Delta U$.

From the problem, we find that information about temp. (T) and volume (V) is given. Thus, we start with:

$$U = U(T, V)$$

$$\Rightarrow dU = \left(\frac{\partial U}{\partial T}\right)_V dT + \left(\frac{\partial U}{\partial V}\right)_T dV \longrightarrow (2)$$

$$\left(\frac{\partial U}{\partial T}\right)_V = C_V \longrightarrow (3)$$

From property relations, we have-

$$dU = TdS - PdV$$

$$\Rightarrow \left(\frac{\partial U}{\partial V}\right)_T = T\left(\frac{\partial S}{\partial V}\right)_T - P\left(\frac{\partial V}{\partial V}\right)_T \rightarrow (4)$$

From Maxwell relation:

$$\left(\frac{\partial S}{\partial V}\right)_T = \left(\frac{\partial P}{\partial T}\right)_V \longrightarrow (5)$$

using eq$^n$. (5) in eq$^n$. (4), we get-

$$\left(\frac{\partial U}{\partial V}\right)_T = T\left(\frac{\partial P}{\partial T}\right)_V - P \longrightarrow (6)$$

using eq$^n$. (3) and eq$^n$. (6) in eq$^n$. (2),

$$dU = C_V dT + \left[T\left(\frac{\partial P}{\partial T}\right)_V - P\right] dV$$

On Integration,

$$\Delta U = \underbrace{\int C_V dT}_{0 \text{ (as temp. is constant)}} + \int\left[T\left(\frac{\partial P}{\partial T}\right)_V - P\right] dV$$

$$\Delta U = \int\left[T\left(\frac{\partial P}{\partial T}\right)_V - P\right] dV \longrightarrow (7)$$

From the van der waals equations, we have

$$P = \frac{RT}{V-b} - \frac{a}{V^2}$$

$$\Rightarrow \left(\frac{\partial P}{\partial T}\right)_V = \frac{R}{V-b} \longrightarrow (8)$$

using eq$^n$. (8) in eq$^n$. (7), we get-

$$\Delta U = \int\left[\frac{RT}{V-b} - P\right] dV$$

~~using eq$^n$.~~

$$= \int\left[\frac{RT}{V-b} - \left\{\frac{RT}{V-b} - \frac{a}{V^2}\right\}\right] dV$$

$$\Delta U = \int_{v_i}^{v_f} \frac{a}{V^2}\, dV = a\int_{v_i}^{v_f} V^{-2}\, dV = -a\left(\frac{1}{V}\right)_{v_i}^{v_f}$$

since, $a = \frac{27}{64}\,\frac{R^2 T_c^2}{P_c}$

For propane, $T_c = 369.8\ K$

$P_c = 42.48\ bar$

$$\therefore a = \frac{27}{64}\,\frac{(83.14\ cm^3\, bar\, mol^{-1}\, K^{-1})^2 (369.8\ K)^2}{(42.48\ bar)}$$

$$= 9.4 \times 10^6\ \frac{cm^6\, bar^{\cancel{2}}\, mol^{-2}\, \cancel{K^2}\, \cancel{K^2}}{\cancel{bar}}$$

$$\therefore a = 9.4 \times 10^6\ \frac{cm^6\, bar}{mol^2}$$

Thus, $\Delta U = -9.4\times 10^6\ \frac{cm^6\, bar}{mol^2}\left[\frac{1}{v_f} - \frac{1}{v_i}\right]$

$v_i = 0.001\ m^3/mol$

$v_f = 0.04\ m^3/mol$

$$= -9.4\times 10^6\ \frac{cm^6\, bar}{mo\cancel{l^2}}\left[\frac{1}{0.04} - \frac{1}{0.001}\right]\frac{\cancel{mol}}{m^3}$$

$$= 9165 \times 10^6 \times \frac{\cancel{(10^{-6}\ m^3)^2}\,(10^5\ N/m^2) \times (10^{-12}\ m^6)}{(mol)\ (m^3)}$$

$\boxed{\Delta U = 916\ J/mol.}$ ~~solution~~

Thus, from (1),

$W = \Delta U - Q = 916 - 600$

$\boxed{W = 316\ J/mol}$ solution

# Helmholtz and Gibbs Energies

We had to consider the entropy change of both the system and its surroundings to determine the sign of $\Delta S_{universe}$ and establish whether a process is spontaneous or not. Although of great fundamental and theoretical importance, the criterion that $dS \geqslant 0$ for a spontaneous process is too restrictive for practical applications.

Let's consider a system with its volume and temperature held constant. The criterion that $dS \geqslant 0$ for a spontaneous process does not apply to a system at constant temperature and volume because the system is not isolated.; If the criterion $dS \geqslant 0$ does not apply, then what is the criterion for a spontaneous process that we can use for a system at constant temperature and volume?

Let's start with the expression of the First Law of thermodynamics,

$$dU = dQ + dW \longrightarrow (1)$$

$$dW = -PdV$$

since $V = const$; $dW = 0$

From clausius inequality,

$$dS \geq \frac{dQ}{T} \Rightarrow dQ \leq TdS$$

Thus, from (1),

$$dU \leq TdS \quad (\text{constant } 'V')$$

$$\Rightarrow ~~dU \leq T~~ \; dU - TdS \leq 0$$

$$\Rightarrow dU - d(TS) \leq 0 \quad (\text{constant } 'T')$$

$$\Rightarrow d(U - TS) \leq 0$$

$$\boxed{A = U - TS} \longrightarrow (2)$$

↳ Helmholtz energy (Thermodynamic state function)

$$\Rightarrow \boxed{dA \leq 0} \quad (\text{constant } 'T' \; \& \; 'V') \longrightarrow (3)$$

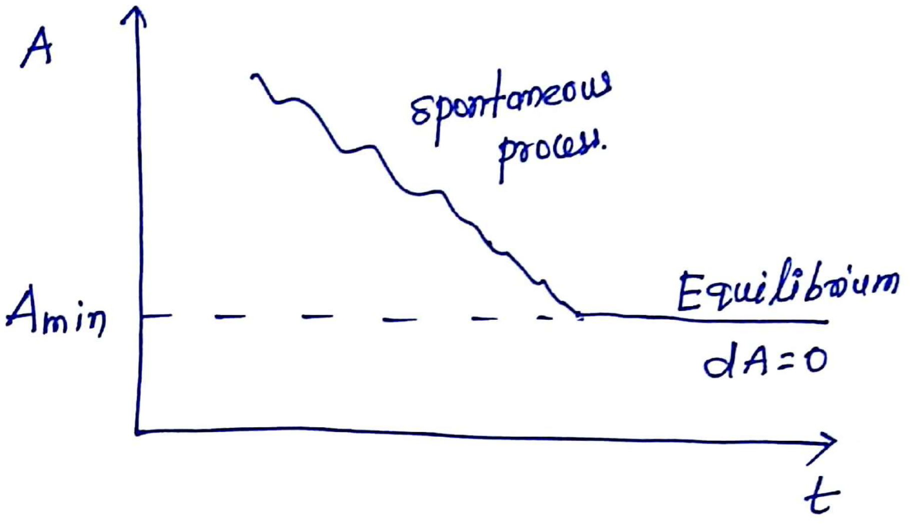
It is the analog of the criterion that $dS \geq 0$ for a spontaneous process to occur in an isolated system

In a system held at constant 'T' and 'V', the Helmholtz energy will decrease until all the possible spontaneous processes have occurred, at which time the system will be in equilibrium and 'A' will be a minimum. At equilibrium $dA = 0$.

For an isothermal change from one state to another,

$$\Delta A = \Delta U - T\Delta S \quad \longrightarrow (4)$$

& $$\Delta A = \Delta U - T\Delta S \leq 0 \quad \text{(at constant 'T' \& 'V')} \quad \longrightarrow (5)$$



For a reversible path, $\Delta S = \frac{q_{rev}}{T}$

Thus, from (4),

$$\Delta A = \Delta U - q_{rev}$$

But from first law, $q_{rev} + W_{rev} = \Delta U$

$$\Delta U - q_{rev} = W_{rev}$$

Thus, $\boxed{\Delta A = W_{rev}}$ (isothermal, reversible) $\longrightarrow (6)$

If $\Delta A < 0$, the process will occur spontaneously and $W_{rev}$ represents the work that can be done by the system if this change is carried out reversibly. This quantity is the maximum work that could be obtained.

If $\Delta A > 0$, the process will not occur spontaneously and $W_{rev}$ represents the work that must be done on the system to produce the change in a reversible manner.

## GIBBS FREE ENERGY

Most reactions occur at constant pressure rather than at constant volume because they are open to the atmosphere. Let's see what the criterion of spontaneity is for a system at constant temperature and pressure.

From 1st law,

$$dQ + dW = dU$$

$$\Rightarrow dQ - PdV = dU$$

$$\Rightarrow dQ = dU + PdV$$

since, ~~dQ~~ $dS \geq \frac{dQ}{T}$

$$\Rightarrow dQ \leq TdS$$

$$\Rightarrow dU + PdV \leq TdS$$

$$\Rightarrow dU + PdV - TdS \leq 0$$

$$\Rightarrow dU + d(PV) - d(TS) \leq 0$$

$$\Rightarrow d[U + PV - TS] \leq 0$$

Gibbs Energy ← $\boxed{G = U + PV - TS = H - TS}$ → (7)

$\boxed{dG \leq 0}$ (constant T & P)

$\longrightarrow (8)$

In a system at constant 'T' and 'P', the Gibbs energy will decrease as the result of any spontaneous processes until the system reaches equilibrium, where $dG = 0$.

Also,

$$\Delta G = \Delta H - T\Delta S \leq 0 \quad (\text{constant 'T' \& 'P'})$$

The equality holds for a reversible process, whereas the inequality holds for an irreversible process.

Lecture-31

For closed system,

$$(dG_i)_{T,P} \leq 0 \longrightarrow (1)$$

[consider a ~~sy~~ closed system composed of pure species 'i' in mechanical and thermal equilibrium and, therefore, at constant T and P.]

The subscripts "T" and "P" remind us that this expression is valid only at constant temperature and pressure, which are the criteria for thermal and mechanical equilibrium, respectively.

Eq^n. (1) says that for a spontaneous process, the Gibbs energy of a system at constant temp. and pressure always gets smaller (or stays the same); it never increases. The system wants to minimize its Gibbs energy. Equilibrium is the state at which the system no longer changes properties; therefore, equilibrium occurs at minimum Gibbs energy.

If we have two phases 'α' and 'β', we can write the total Gibbs energy of pure species 'i' as:

$$G_i = n_i^{\alpha} g_i^{\alpha} + n_i^{\beta} g_i^{\beta} \longrightarrow (2)$$

where $n_i^\alpha$ and $n_i^\beta$ refer to the number of moles of 'i' in phases 'α' and 'β', respectively.

Differentiating Eqn. (2) and applying eqn. (1), we get:

$$dG = \underbrace{n_i^\alpha dg_i^\alpha}_{0} + g_i^\alpha dn_i^\alpha + \underbrace{n_i^\beta dg_i^\beta}_{0} + g_i^\beta dn_i^\beta \leq 0 \longrightarrow (3)$$

Two independent properties constrain the state of each phase of the pure substance i; thus, at a given T and P, $g_i^\alpha$ and $g_i^\beta$ are constant. Consequently, the first and third terms of the above expression go to zero.

Since we have a closed system, a species leaving one phase must be added to the other phase, so.

$$n = n_i^\alpha + n_i^\beta$$

$$dn = dn_i^\alpha + dn_i^\beta$$

$$0 = dn_i^\alpha + dn_i^\beta$$

$$dn_i^\alpha = -dn_i^\beta \longrightarrow (4)$$

using eqn. (4) in eqn. (3),

~~$g_i^\alpha dn_i^\alpha - g_i^\beta dn_i^\alpha \leq 0$~~ $(g_i^\beta - g_i^\alpha) dn_i^\beta \leq 0$

$$\longrightarrow (5)$$

From eq$^n$. (5), we can infer how the species in a system respond to approach equilibrium. Consider a system that initially has species in both phases 'α' and 'β'. If $g_i^\beta$ is larger than $g_i^\alpha$, $dn_i^\beta$ must be less than zero to satisfy the inequality. physically, species 'i' will transfer from phase 'β' to phase 'α', lowering the Gibbs energy of the system. Conversely if $g_i^\alpha$ is greater than $g_i^\beta$, species 'i' will transfer from phase 'α' to phase 'β'. However, if the Gibbs energies of both phases are equal, Eq$^n$. (5) becomes an equality and the system has no impetus to change. This condition represents equilibrium. Thus, the criterion for chemical equilibrium is when the Gibbs energy is at the minimum:

$$g_i^\alpha = g_i^\beta \longrightarrow (6)$$

In differential form,

$$dg_i^\alpha = dg_i^\beta \longrightarrow (7)$$

[ consider a system with two phases in equilibrium at a given 'T' and 'P'. For a small change in the equilibrium temp. dT and in equilibrium pressure dP, the differential changes in Gibbs energy of each phase must be equal:]

Applying the fundamental property relation for 'g' to each phase, we get:

$$v_i^{\alpha} dp - s_i^{\alpha} dT = v_i^{\beta} dp - s_i^{\beta} dT \longrightarrow (8)$$

Rearrangement yields:

$$\Rightarrow \quad v_i^{\alpha} dp - v_i^{\beta} dp = s_i^{\alpha} dT - s_i^{\beta} dT$$

$$\Rightarrow \quad (v_i^{\alpha} - v_i^{\beta}) dp = (s_i^{\alpha} - s_i^{\beta}) dT$$

$$\Rightarrow \quad \frac{dP}{dT} = \frac{s_i^{\alpha} - s_i^{\beta}}{v_i^{\alpha} - v_i^{\beta}} \longrightarrow (9)$$

Now we can also apply eqn. (6):

$$g_i^{\alpha} = g_i^{\beta}$$

By the definition of Gibbs energy,

$$h_i^{\alpha} - Ts_i^{\alpha} = h_i^{\beta} - Ts_i^{\beta}$$

$$\Rightarrow \quad h_i^{\alpha} - h_i^{\beta} = Ts_i^{\alpha} - Ts_i^{\beta}$$

$$\Rightarrow \quad s_i^{\alpha} - s_i^{\beta} = \frac{h_i^{\alpha} - h_i^{\beta}}{T} \longrightarrow (10)$$

Substitution of eqn. (10) in eqn. (9) yields the <u>clapeyron equation</u>:

$$\boxed{\frac{dP}{dT} = \frac{h_i^{\alpha} - h_i^{\beta}}{(v_i^{\alpha} - v_i^{\beta})T}} \longrightarrow (11)$$

## Pure Component vapor-liquid Equilibrium: The clausius-clapeyron Equation

Next we consider the specific case of vapor-liquid Equilibrium.

In this case, the molar volume of the liquid is often negligible compared to the volume of the vapor:

$$v_i^l << v_i^v \quad \text{or} \quad v^l \approx 0 \qquad \text{(Assumption I)}$$

If additionally we consider the vapor to obey the ideal gas model,

$$v_i^v = \frac{RT}{P} \qquad \text{(Assumption II)}$$

Thus, Eq$^n$. (11) becomes-

$$\frac{dP_i^{sat}}{dT} = \frac{\Delta h_{vap,i} \, P_i^{sat}}{RT^2} \longrightarrow (12)$$

where $\Delta h_{vap,i} = h_i^v - h_i^l$ and $P_i^{sat}$ represent the enthalpy of vaporization and the saturation pressure, respectively, of species 'i' at temp. T.

Separating variables,

$$\boxed{\frac{dP_i^{sat}}{P_i^{sat}} = \frac{\Delta h_{vap,i}\, dT}{RT^2}} \longrightarrow (13)$$

Eqn. (13) is called the clausius-clapeyron equation.

It can be rewritten in the form

$$d\ln P_i^{sat} = -\frac{\Delta h_{vap,i}}{R}\, d\left(\frac{1}{T}\right) \longrightarrow (14)$$

If we assume the enthalpy of vaporization is independent of temperature, that is

$$\Delta h_{vap,i} \neq \Delta h_{vap,i}(T) \qquad \text{(Assumption III)}$$

we can either definitely integrate eqn. (14) between state 1 and state 2 to get:

$$\ln \frac{P_2^{sat}}{P_1^{sat}} = -\frac{\Delta h_{vap,i}}{R}\left[\frac{1}{T_2} - \frac{1}{T_1}\right] \longrightarrow (15)$$

or write the indefinite integral of eqn. (14):

$$\ln P_i^{sat} = \text{const.} - \frac{\Delta h_{vap,i}}{RT} \longrightarrow (16)$$

In fact, Assumption III is not valid over large temperature ranges. The enthalpy of vaporization decreases as temperature increases. So, eqn. (15) & (16) can be used only over a limited temp. range. However, in surprisingly many cases, the error introduced by Assumption III is approximately offset by the errors of Assumption I and II, leading to linear behavior of $\ln P^{sat}$ vs. $1/T$ over a larger range.

(Lecture-47)

**Q.1** For two species, A and B, with a positive enthalpy change of mixing:

(a) Are the like interactions or the unlike interactions stronger?

**Solution:** like interaction is more stable and more strong than unlike interaction.

**Q.2** One mole of pure species exists in liquid-vapor equilibrium in a rigid container of volume $V = 1L$, a temp. of 300 K, and a pressure of 1 bar. The enthalpy of vaporization and the second virial co-efficient are:

$$\Delta h_{vap} = 16628 \text{ J/mol} ; \quad B' = -1 \times 10^{-7} \text{ m}^3/\text{J}$$

Assume the enthalpy of vaporization does not change with temp. You may neglect the molar volume of the liquid relative to that of the gas.

(a) ~~How many moles of vapor are there?~~ This container is heated until the pressure reaches 2 bar and is allowed to reach equilibrium. Both vapor and liquid phases are still present. Find the final temp. of this system.

Solution: We have,

$$\frac{dP}{dT} = \frac{\Delta h^{vap}}{(v^v - v^l)T} \longrightarrow (1)$$

Since, molar volume of liquid is negligible compared to that of the gas,

$$v^v - v^l \simeq v^v$$

Thus,

$$\frac{dP}{dT} = \frac{\Delta h^{vap}}{v^v T} \longrightarrow (2)$$

Also,

$$z = \frac{Pv^v}{RT} = 1 + B'P$$

$$\Rightarrow v^v = \frac{RT}{P}(1+B'P) = RT\left(\frac{1}{P} + B'\right)$$

substituting $v^v$ in eqn. (2),

$$\frac{dP}{dT} = \frac{\Delta h^{vap}}{RT\left(\frac{1}{P}+B'\right)T} = \frac{\Delta h^{vap}}{RT^2\left(\frac{1}{P}+B'\right)}$$

$$\Rightarrow \left(\frac{1}{P} + B'\right) dp = \frac{\Delta h^{vap}}{RT^2} dT$$

integrating,

$$\int_{1\,bar}^{21\,bar} \left(\frac{1}{P} + B'\right) dp = \frac{\Delta h^{vap}}{R} \int_{300K}^{T_2} \frac{dT}{T^2}$$

(page-2)

$$\Rightarrow \int_1^{21} \frac{dP}{P} + B' \int_1^{21} dP = \frac{\Delta h^{vap}}{R} \left( -\frac{1}{T} \right)_{300}^{T_2}$$

$$\Rightarrow \ln\left(\frac{21}{1}\right) + B'(21-1)\,\text{bar} = \frac{\Delta h^{vap}}{R}\left[-\frac{1}{T_2} + \frac{1}{300}\right]$$

$$\Rightarrow 3.045 + \left(-10^{-7}\frac{m^3}{J}\right)\left(20\times10^{5}\frac{N}{m^2}\right) = \frac{16628\ J/mol}{8.314\ J/mol\,K}\left[\frac{1}{300} - \frac{1}{T_2}\right]$$

$$\Rightarrow \boxed{T_2 = 523.3\,K} \quad \underline{\underline{\text{solution}}}.$$

[Q.3] The vapor pressure of silver (between 1234 K and 2485 K) is given by the following expression:

$$\ln P^{sat} = -\frac{14260}{T} - 0.458 \ln T + 12.23$$

where 'p' in torr and 'T' in K. Estimate the enthalpy of vaporization at 1500K.

<u>Solution</u>: we have,

$$\frac{dP^{sat}}{dT} = \frac{\Delta h^{vap} P^{sat}}{RT^2} \longrightarrow (1)$$

Given-

$$\ln P^{sat} = \frac{-14260}{T} - 0.458 \ln T + 12.23$$

$$P^{sat} = \exp\left[\frac{-14260}{T} - 0.458 \ln T + 12.23\right] \rightarrow (2)$$

Differentiate eqn. (2) w.r.t. temp,

$$\frac{dp^{sat}}{dT} = \exp\left(-\frac{14260}{T} - 0.458\ln T + 12.23\right)\left(\frac{14260}{T^2} - \frac{0.458}{T}\right)$$

$$\Rightarrow \frac{dp^{sat}}{dT} = p^{sat}\left[\frac{14260}{T^2} - \frac{0.458}{T}\right] \longrightarrow (3)$$

using eqn. (3) in eqn. (1), we get-

$$p^{sat}\left[\frac{14260}{T^2} - \frac{0.458}{T}\right] = \frac{p^{sat}\,\Delta h^{vap}}{RT^2}$$

$$\Rightarrow \Delta h^{vap} = RT^2\left[\frac{14260}{T^2} - \frac{0.458}{T}\right]$$

$$= 14260R - 0.458RT$$

$$= 14260(8.314\ \text{J/mol K}) - 0.458(8.314\ \text{J/mol K})(1500\ \text{K})$$

$$= 112845\ \text{J/mol}$$

$$\boxed{\Delta h^{vap} = 112.845\ \text{KJ/mol}}$$ Ans.

[Q.4] At a temp. of 60.6°c, benzene exerts a saturation pressure of 400 torr. At 80.1°c, its saturation pressure is 760 torr. using these data, estimate the enthalpy of vaporization of benzene. Compare it to the reported value of $\Delta h_{vap} = 35$ KJ/mol.

Soln we have,

$$\ln\left(\frac{P_2^{sat}}{P_1^{sat}}\right) = \frac{-\Delta h^{vap}}{R}\left[\frac{1}{T_2} - \frac{1}{T_1}\right]$$

given, $T_1 = 60.6 + 273 = 333.6$, $P_1^{sat} = 400$ torr.

$T_2 = 353.1\,K$, $P_2^{sat} = 760$ torr.

$R = 8.314$ J/mol-K

using these values,

$$\ln\left(\frac{760}{400}\right) = \frac{-\Delta h^{vap}}{(8.314\ J/mol\,K)}\left[\frac{1}{353.1} - \frac{1}{333.6}\right]$$

$$\Delta h^{vap} = \cancel{33}\,32235\ J/mol$$

$$\boxed{\Delta h^{vap} = 32.24\ kJ/mol.}$$ An.

[~~Q.5~~] % deviation from exp. data $= \left(\frac{35 - 32.24}{35}\right) \times 100$

$= \underline{7.9\%}$ A

i.e. Experimental value is 7.9% higher than that of calculated value.

[Q.5] Pure ethanol boils at a temperature of 63.5°c at a Pressure of 400 torr. It also boils at 78.4°c and 760 to using these data, estimate the saturation pressure for ethanol at 100°c.

<u>solution</u>: we have,

$$\ln\left(\frac{P_2^{sat}}{P_1^{sat}}\right) = -\frac{\Delta h^{vap}}{R}\left[\frac{1}{T_2} - \frac{1}{T_1}\right]$$

Given, $T_1 = 273+63.5 = 336.5\,K$, $P_1^{sat} = 400$ torr.

$T_2 = 273+78.4 = 351.4\,K$, $P_2^{sat} = 760$ torr.

using these data,

$$\ln\left(\frac{760}{400}\right) = -\frac{\Delta h^{vap}}{(8.314\ J/mol K)}\left[\frac{1}{351.4} - \frac{1}{336.5}\right]$$

$$\therefore\ \Delta h^{vap} = 42349\ J/mol$$

$$= \underline{\underline{42.35\ kJ/mol.}}$$

Now, we have to find, $P_3^{sat}$ at $T_3 = 373\,K$.

$$\ln\left(\frac{P_3^{sat}}{P_1^{sat}}\right) = -\frac{42349}{8.314}\left[\frac{1}{T_3} - \frac{1}{T_1}\right]$$

$$\underline{\underline{P_3^{sat} = 1759\ torr.}}$$

# Antoine Equation

- A mathematical expression derived from the Clausius-Clapeyron relation
- Relation between the vapor pressure and the temperature of pure substances
- First proposed by Ch. Antoine, a French researcher, in 1888

$$T = \frac{B}{A - \log P} - C$$

where: $P$ is the absolute vapor pressure of a substance,

$T$ is the temperature of the substance

$A$, $B$ and $C$ are substance-specific coefficients (i.e., constants or parameters)

$\log$ is typically either $\log_{10}$ or $\log_e$

A simpler form of the equation with only two coefficients :

$$\log P = A - \frac{B}{T}$$

Source: https://www.tau.ac.il/~tsirel/dump/Static/knowino.org/wiki/Antoine_equation.html

## Validity ranges

- The Antoine equation cannot be used for the entire vapor pressure range from the triple point to the critical point because it is not flexible enough.

- Therefore two sets of coefficients are commonly used: one set for vapor pressures at temperatures below the normal boiling point (NBP) and one set for vapor pressures at temperatures above the normal boiling point.

## Example sets of coefficients

| | *A* | *B* | *C* | *T* minimum | *T* maximum |
|---|---|---|---|---|---|
| Water below the NBP | 8.07131 | 1730.63 | 233.426 | 1 | 100 |
| Water above the NBP | 8.14019 | 1810.94 | 244.485 | 99 | 374 |
| Ethanol below the NBP | 8.20417 | 1642.89 | 230.300 | -57 | 80 |
| Ethanol below the NBP | 7.68117 | 1332.04 | 199.200 | 77 | 243 |

The coefficients in Table 1 are for temperatures in °C and absolute pressures in mmHg when using $\log_{10}$ as the logarithmic function.

Source: https://www.tau.ac.il/~tsirel/dump/Static/knowino.org/wiki/Antoine_equation.html

# JOULE-THOMSON EXPANSION

Lecture No. 32/33

# JOULE-THOMSON EXPANSION

# Throttling valves

- Throttling valves are any kind of ***flow-restricting devices*** that cause a ***significant pressure drop*** in the fluid.
- Some familiar examples are :

(*a*) An adjustable valve

(*b*) A porous plug

(*c*) A capillary tube

# Joule Thomson effect

- ☐ Unlike turbines, they produce a ***pressure drop without involving any work***.
- ☐ The ***pressure drop*** in the fluid is often **accompanied** by a large ***drop in temperature***, and for that reason throttling devices are commonly used in refrigeration and air-conditioning applications.
- ☐ The magnitude of the temperature drop (or, sometimes, the temperature rise) during a throttling process is governed by a property called the ***Joule Thomson coefficient.***

# Joule Thomson effect

- ☐ Throttling valves are usually small devices, and the flow through them may be assumed to be adiabatic ($q \approx 0$) since there is neither sufficient time nor large enough area for any effective heat transfer to take place.
- ☐ Also, there is no work done ($w = 0$), and the change in potential energy, if any, is very small.
- ☐ Even though the exit velocity is often considerably higher than the inlet velocity, in many cases, the increase in kinetic energy is insignificant.
- ☐ Then the conservation of energy equation for this single-stream steady-flow device reduces to (See Equation 12 of Lecture 9):

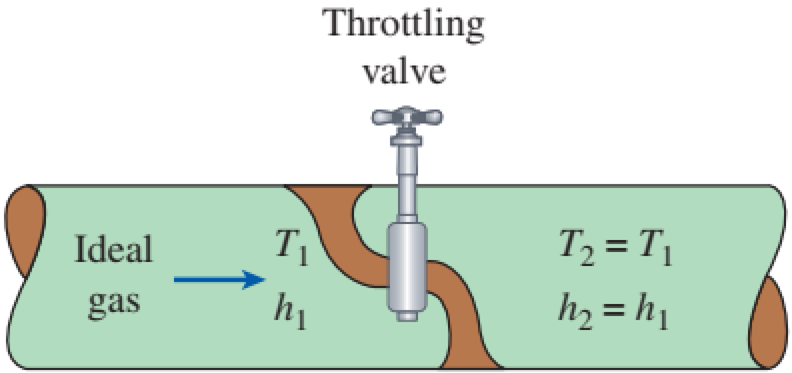
$$h_i = h_{out}$$

# Isenthalpic Process

$$h_{in} = h_{out}$$

That is, enthalpy values at the inlet and exit of a throttling valve are the same.

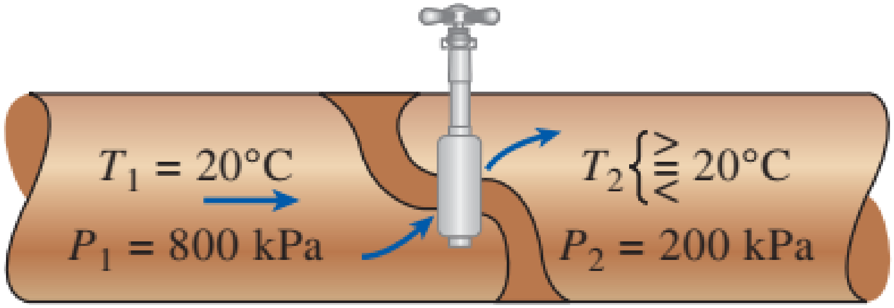
For this reason, a throttling valve is sometimes called an ***isenthalpic device***.



The temperature of an ideal gas does not change during a throttling ($h$ = constant) process since $h = h(T)$

# Joule-Thomson coefficient

- ☐ Temperature of the fluid may remain unchanged, or it may even increase or decrease during a throttling process.



- ☐ The temperature behavior of a fluid during a throttling (h = constant) process is described by the ***Joule-Thomson coefficient***, defined as:

$$\mu = \left(\frac{\partial T}{\partial P}\right)_h$$

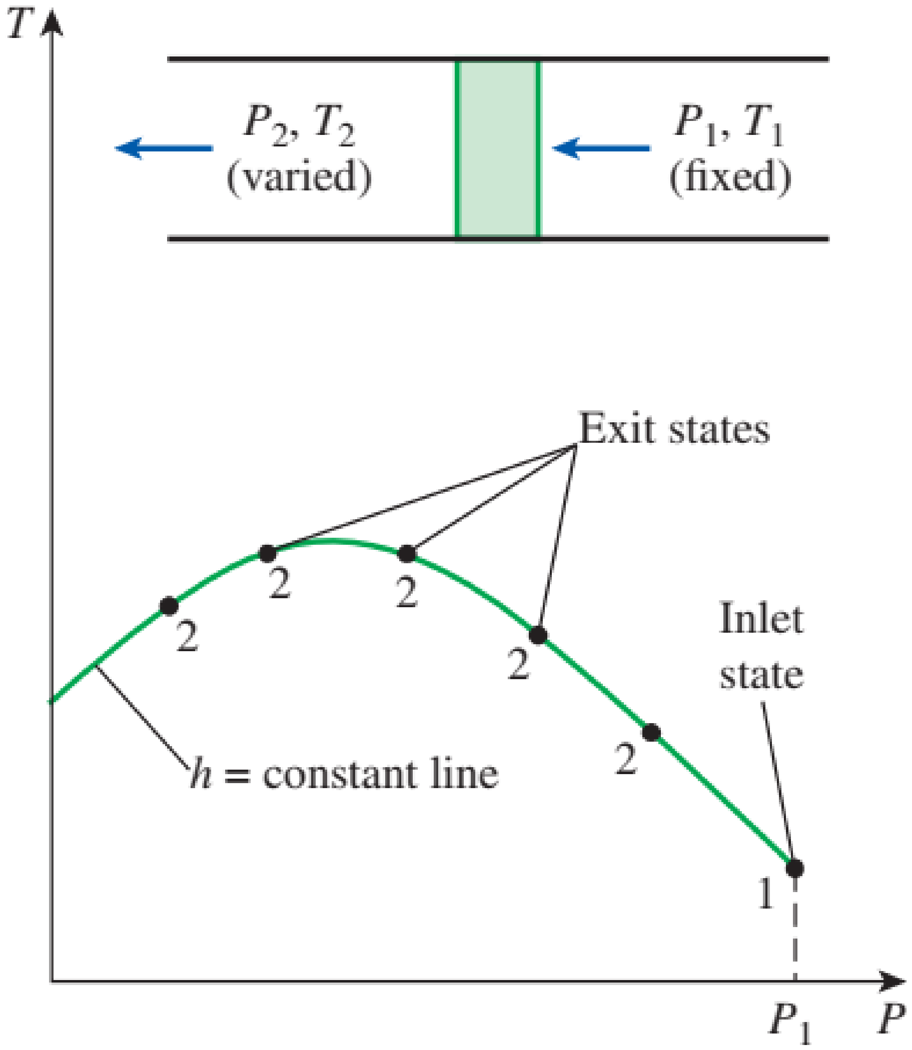
# Joule-Thomson coefficient

- ☐ Thus the Joule-Thomson coefficient is a measure of the change in temperature with pressure during a constant-enthalpy process.

- ☐ If

$$\mu_{JT} \begin{cases} < 0 & \text{Temperature increases} \\ = 0 & \text{Temperature remains constant} \\ > 0 & \text{Temperature decreases} \end{cases}$$

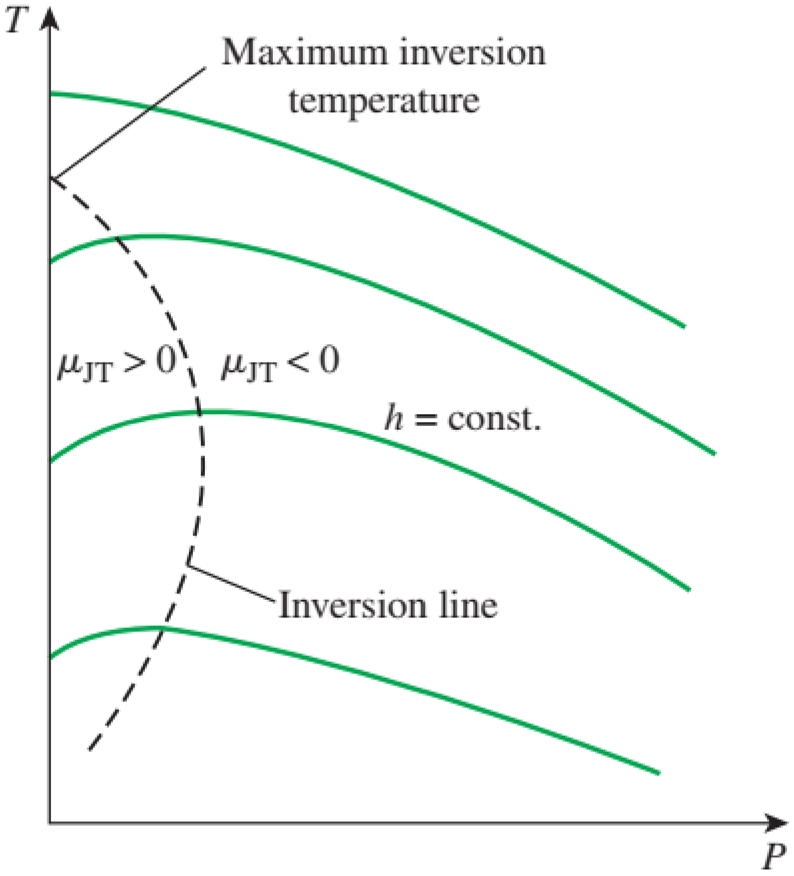
# Development of an *h* = constant line on a *P-T* diagram.



# Development of an $h$ = constant line on a $P$-$T$ diagram.

- ☐ A careful look at its defining equation reveals that the Joule-Thomson coefficient represents the slope of $h$ = constant lines on a $T$-$P$ diagram.
- ☐ Such diagrams can be easily constructed from temperature and pressure measurements alone during throttling processes.
- ☐ A fluid at a fixed temperature and pressure $T_1$ and $P_1$ (thus fixed enthalpy) is forced to flow through a porous plug, and its temperature and pressure downstream ($T_2$ and $P_2$) are measured.
- ☐ The experiment is repeated for different sizes of porous plugs, each giving a different set of $T_2$ and $P_2$. Plotting the temperatures against the pressures gives us an $h$ = constant line on a $T$-$P$ diagram.

- ❑ Repeating the experiment for different sets of inlet pressure and temperature and plotting the results, we can construct a *T-P* diagram for a substance with several *h* = constant lines.



Constant-enthalpy lines of a substance on a *T-P* diagram

- Some constant-enthalpy lines on the *T-P* diagram pass through a point of zero slope.
- The line that passes through these points is called the inversion line, and the temperature at a point where a constant-enthalpy line intersects the inversion line is called the inversion temperature.
- The temperature at the intersection of the *P = 0* line (ordinate) and the upper part of the inversion line is called the maximum inversion temperature.
- The slopes of the $h$ = constant lines are negative ($\mu_{JT} < 0$) at states to the right of the inversion line and positive ($\mu_{JT} > 0$) to the left of the inversion line.

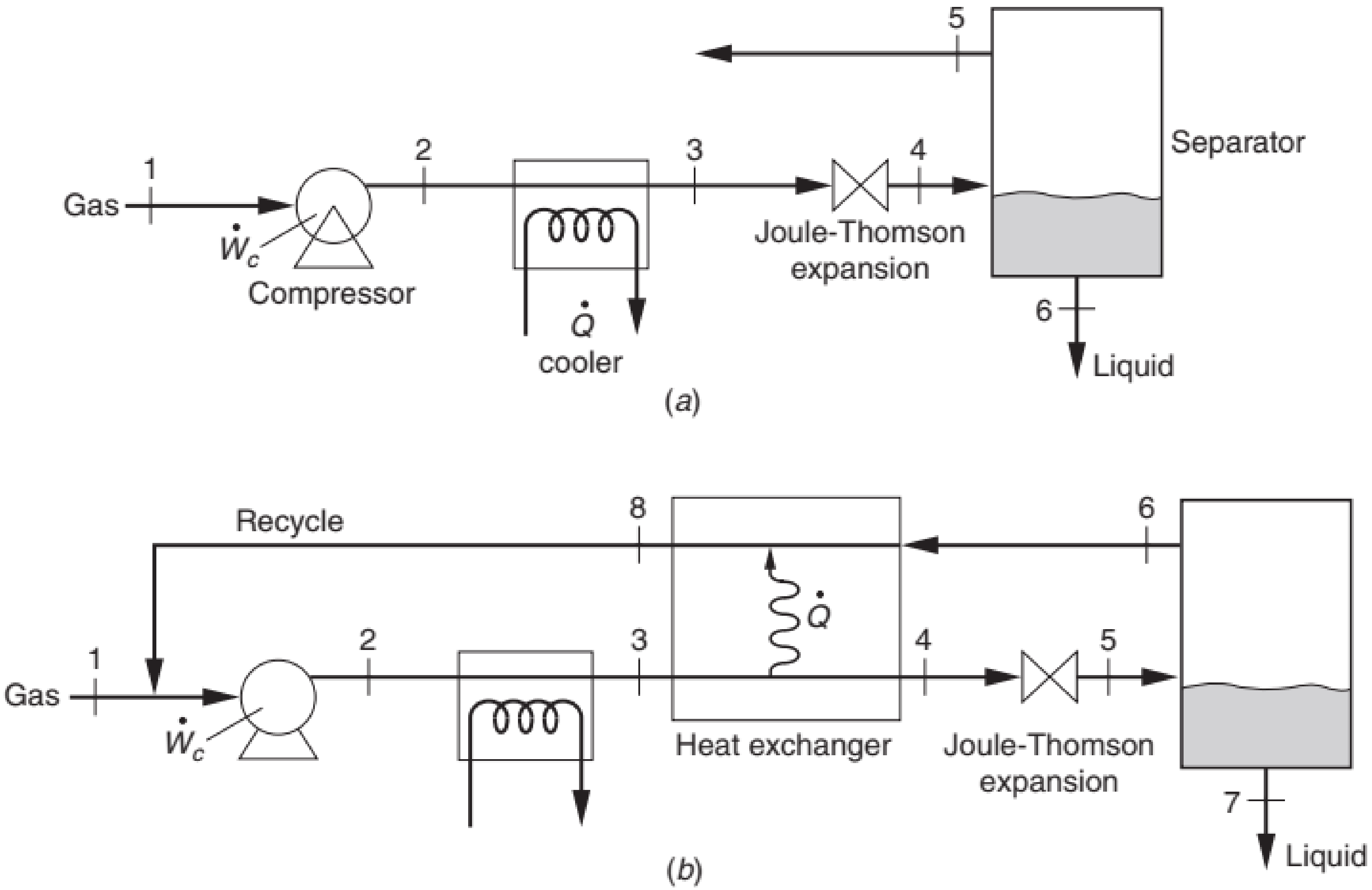
- ☐ A throttling process proceeds along a constant-enthalpy line in the direction of decreasing pressure, that is, from right to left.
- ☐ Therefore, the temperature of a fluid increases during a throttling process that takes place on the right-hand side of the inversion line.
- ☐ However, the fluid temperature decreases during a throttling process that takes place on the left-hand side of the inversion line.
- ☐ It is clear from this diagram that a cooling effect cannot be achieved by throttling unless the fluid is below its maximum inversion temperature.
- ☐ This presents a problem for substances whose maximum inversion temperature is well below room temperature.

- The decrease in temperature as the pressure drops corresponds to a decrease in molecular kinetic energy, the molecular potential energy must be increasing or else energy conservation would be violated. We can say the molecules are more stable when they are closer together at the higher pressure and, consequently, that attractive forces are dominant in this region. The temperature will increase as pressure decreases, indicating that repulsive forces dominate the behavior in this region.
- These two regions are separated by the inversion line, where the slope of T vs. P is zero and where attractive and repulsive interactions exactly balance.
- For a given pressure, the temperature at which these interactions balance is known as the **Boyle temperature**.

# Liquefaction

- Joule-Thomson expansion can be used to liquefy gases if it is performed in the region where $\mu_{JT} > 0$ to the left of the inversion line.
- Liquefaction is an important process industrially (e.g. liquid nitrogen and helium).

# (a) Basic liquefaction process using Joule–Thomson expansion
# (b) Linde process



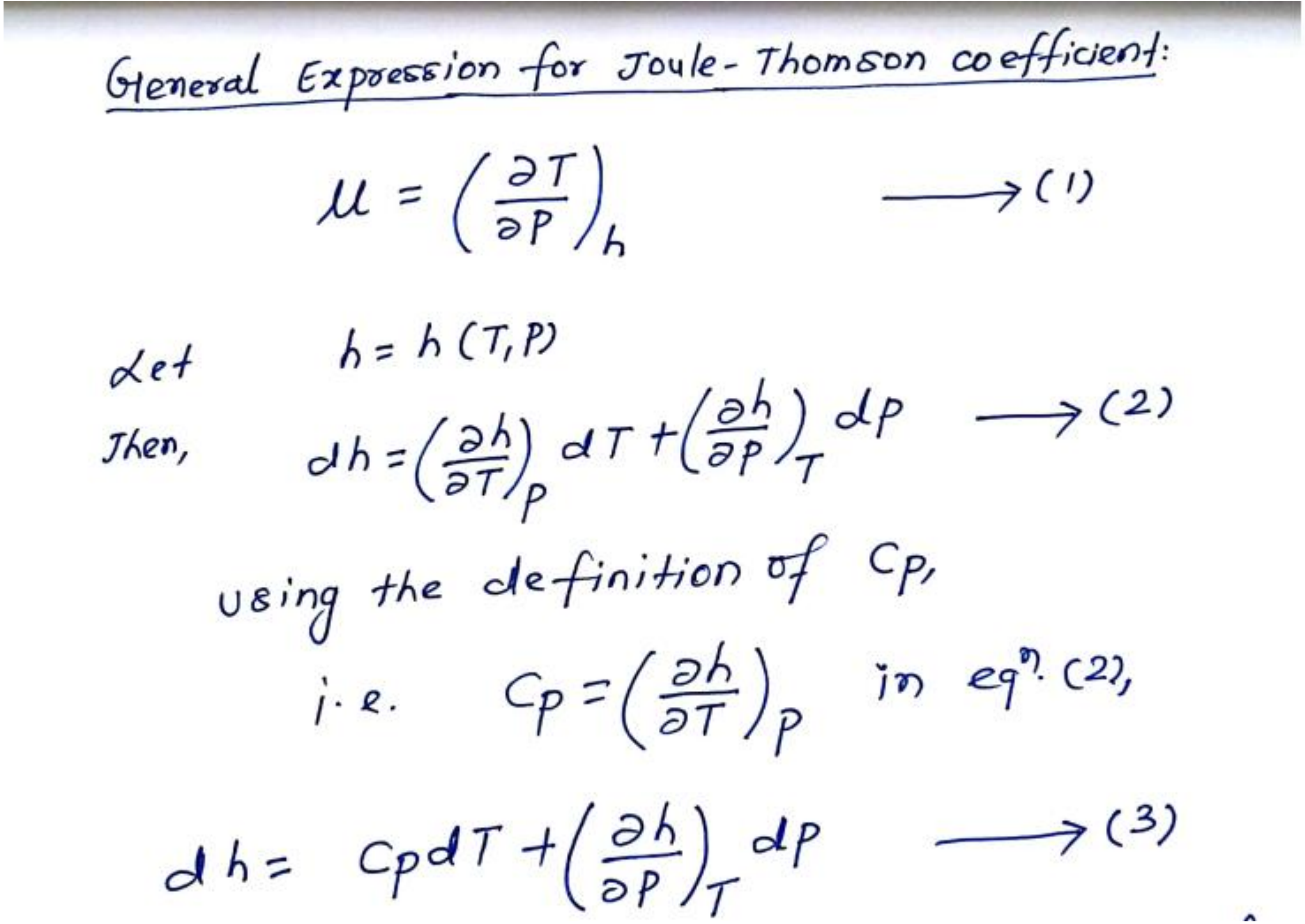
# Liquefaction

- The gas is first compressed from state 1 to 2 to increase its pressure. However, during compression, the temperature of the gas also rises. It is then cooled from state 2 to state 3 to lower its temperature.
- These two processes are intended to bring it to the left region of inversion curve and to put it in a state where a throttling process will bring it into the two phase region.
- It now goes through an isenthalpic Joule-Thomson expansion, from state 3 to state 4, where the temperature drops low enough to lead to condensation.
- The vapor and liquid streams at states 5 and 6, respectively, are then separated.

# Liquefaction

- ☐ An improvement to the liquefaction process is shown in Figure b. In this process, an additional heat exchanger is employed to recover the energy from the non-condensed gas. This gas is then recycled. The process depicted in Figure b is known as the ***Linde process***.

# General Expression for Joule-Thomson Coefficient



<u>General Expression for Joule-Thomson coefficient:</u>

$$\mu = \left(\frac{\partial T}{\partial P}\right)_h \qquad \longrightarrow (1)$$

Let $h = h(T, P)$

Then, $$dh = \left(\frac{\partial h}{\partial T}\right)_P dT + \left(\frac{\partial h}{\partial P}\right)_T dP \qquad \longrightarrow (2)$$

using the definition of $C_p$,

i.e. $C_p = \left(\frac{\partial h}{\partial T}\right)_P$ in eq$^n$. (2),

$$dh = C_p dT + \left(\frac{\partial h}{\partial P}\right)_T dP \qquad \longrightarrow (3)$$

# General Expression for Joule-Thomson Coefficient

Now, we choose the entropy to be a function of T and P, i.e. $S = S(T, P)$

$$dS = \left(\frac{\partial S}{\partial T}\right)_P dT + \left(\frac{\partial S}{\partial P}\right)_T dP \longrightarrow (4)$$

Substituting this into

$$dh = Tds + vdp \longrightarrow (5)$$

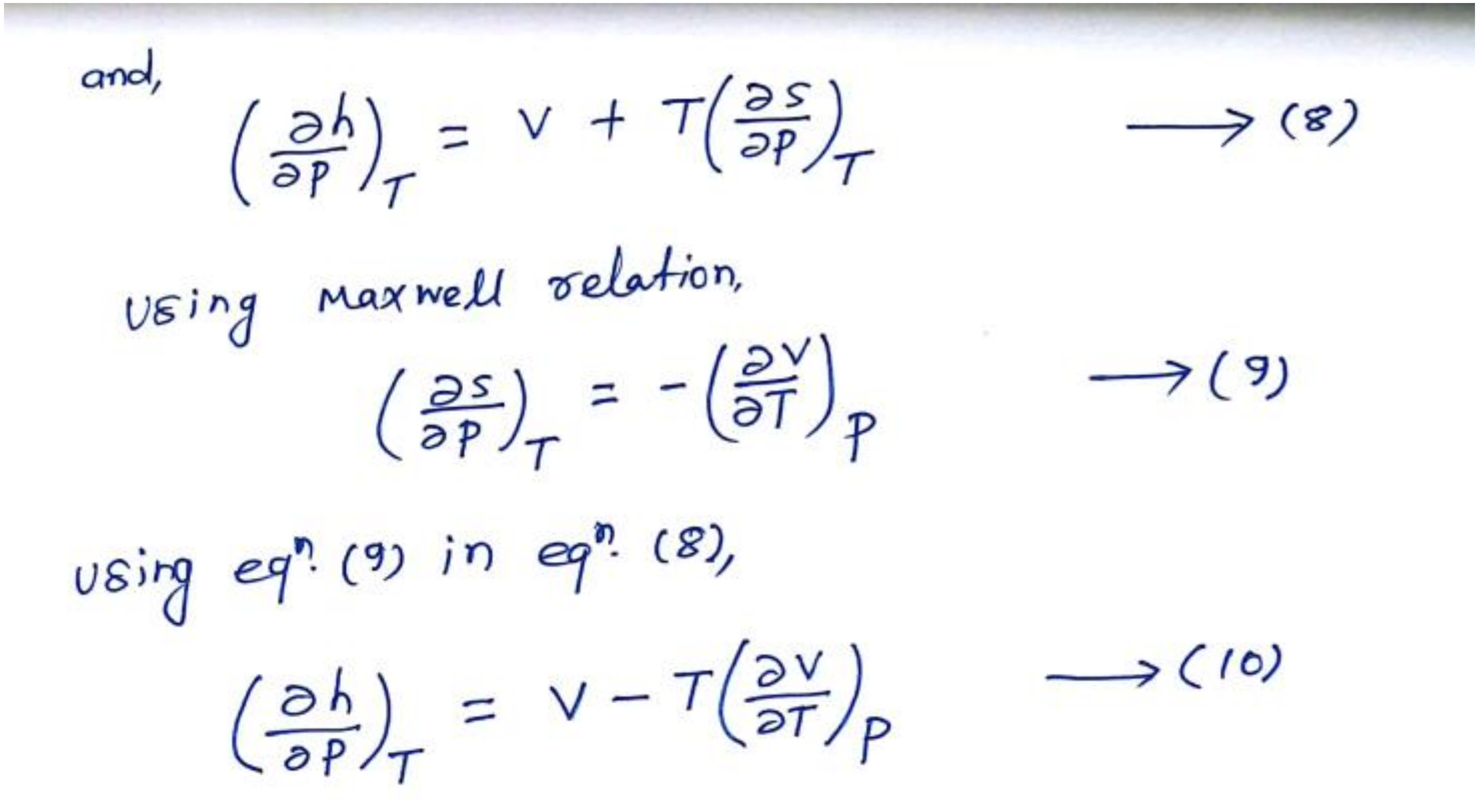
$$\Rightarrow \quad dh = T\left(\frac{\partial S}{\partial T}\right)_P dT + T\left(\frac{\partial S}{\partial P}\right)_T dp + vdp$$

$$dh = T\left(\frac{\partial S}{\partial T}\right)_P dT + \left[v + T\left(\frac{\partial S}{\partial P}\right)_T\right] dp \longrightarrow (6)$$

Comparing eq$^n$. (3) and eq$^n$. (6),

$$\left(\frac{\partial S}{\partial T}\right)_P = \frac{C_P}{T} \longrightarrow (7)$$

# General Expression for Joule-Thomson Coefficient



and,

$$\left(\frac{\partial h}{\partial p}\right)_T = v + T\left(\frac{\partial s}{\partial p}\right)_T \longrightarrow (8)$$

using maxwell relation,

$$\left(\frac{\partial s}{\partial p}\right)_T = -\left(\frac{\partial v}{\partial T}\right)_p \longrightarrow (9)$$

using eq$^n$. (9) in eq$^n$. (8),

$$\left(\frac{\partial h}{\partial p}\right)_T = v - T\left(\frac{\partial v}{\partial T}\right)_p \longrightarrow (10)$$

# General Expression for Joule-Thomson Coefficient

using eqn. (10) in eqn. (3),

$$\boxed{dh = C_p dT + \left[v - T\left(\frac{\partial v}{\partial T}\right)_p\right] dp} \longrightarrow (11)$$

For constant enthalpy process, $h = \text{const.}$ ; $dh = 0$

Thus,

$$C_p dT + \left[v - T\left(\frac{\partial v}{\partial T}\right)_p\right] dp = 0$$

$$\Rightarrow C_p dT = -\left[v - T\left(\frac{\partial v}{\partial T}\right)_p\right] dp$$

$$\Rightarrow \boxed{\mu = \left(\frac{\partial T}{\partial p}\right)_h = -\frac{1}{C_p}\left[v - T\left(\frac{\partial v}{\partial T}\right)_p\right]} \longrightarrow (12)$$

# General Expression for Joule-Thomson Coefficient

→

For an ideal gas, $V = \frac{RT}{P}$

$$\left(\frac{\partial V}{\partial T}\right)_P = \frac{R}{P}$$

using eqⁿ. (12), $\mu = -\frac{1}{C_p}\left[\frac{RT}{P} - \frac{RT}{P}\right] = 0.$

$$\therefore \underline{\mu = 0}$$

//

# Residual properties

Lecture-29/30

The definition for the generic residual property is:

$$M^R = M - M^{ig} \longrightarrow (1)$$

where 'M' is the molar value of any extensive thermodynamic property e.g., V, U, H, S, or G.

Note that 'M' and 'M ig', the actual and ideal-gas properties, are at the same T and P.

The residual volume, for example, is:

$$V^R = V - V^{ig} = V - \frac{RT}{P}$$

$$\text{Because } V = \frac{ZRT}{P},$$

the residual volume and the compressibility factor are related:

$$V^R = \frac{ZRT}{P} - \frac{RT}{P}$$

$$V^R = \frac{RT}{P}(Z-1) \longrightarrow (2)$$

From fundamental property relations for homogeneous fluids of constant composition,

$$dG = VdP - SdT \longrightarrow (3)$$

Now,

$$d\left(\frac{G}{RT}\right) = \frac{1}{RT}dG - \frac{G}{RT^2}dT \longrightarrow (4)$$

using eq$^n$. (3) in eq$^n$. (4),

$$d\left(\frac{G}{RT}\right) = \frac{1}{RT}(Vdp - SdT) - \frac{G}{RT^2}dT$$

$$= \frac{V}{RT}dp - \frac{S}{RT}dT - \frac{G}{RT^2}dT$$

$$= \frac{V}{RT}dp - \frac{S}{RT}dT - \frac{(H-TS)}{RT^2}dT$$

$$= \frac{V}{RT}dp - \cancel{\frac{S}{RT}dT} - \frac{H}{RT^2}dT + \cancel{\frac{SdT}{RT}}$$

$$\boxed{d\left(\frac{G}{RT}\right) = \frac{V}{RT}dp - \frac{H}{RT^2}dT} \longrightarrow (5)$$

* The advantage of this equation is that all terms are dimensionless; moreover, in contrast to eq$^n$. (3), the enthalpy rather than entropy appears on the right side.

From eq$^n$, (5),

$$\frac{V}{RT} = \left[\frac{\partial(G/RT)}{\partial P}\right]_T \longrightarrow (6)$$

$$\frac{H}{RT} = -T\left[\frac{\partial(G/RT)}{\partial T}\right]_P \longrightarrow (7)$$

The remaining properties are given by-

$$\frac{S}{R} = \frac{H}{RT} - \frac{G}{RT} \longrightarrow (8)$$

$$\frac{U}{RT} = \frac{H}{RT} - \frac{PV}{RT} \longrightarrow (9)$$

* When we are given $G/RT = g(T,P)$, we can evaluate all other thermodynamic properties by simple mathematical operations.

* The Gibbs energy when given as a function of T & P, serves as a generating function for the other thermodynamic properties, and implicitly represents complete property information.

Equation (5), written for the special case of an ideal gas, becomes -

$$d\left(\frac{G^{ig}}{RT}\right) = \frac{V^{ig}}{RT}dp - \frac{H^{ig}}{RT^2}dT \longrightarrow (10)$$

Subtracting Eqn. (10) from Eqn. (5) gives -

$$d\left(\frac{G^{R}}{RT}\right) = \frac{V^{R}}{RT}dp - \frac{H^{R}}{RT^2}dT \longrightarrow (11)$$

Eqn. (11) : This fundamental residual-property relation applies to fluids of constant composition.

other useful forms are :

$$\frac{V^R}{RT} = \left[\frac{\partial(G^R/RT)}{\partial P}\right]_T \longrightarrow (12)$$

$$\frac{H^R}{RT} = -T\left[\frac{\partial(G^R/RT)}{\partial T}\right]_P \longrightarrow (13)$$

From Eqⁿ. (5),

$$d\left(\frac{G^R}{RT}\right) = \frac{V^R}{RT}\,dP \quad (\text{constant temp})$$

Integration from zero pressure to arbitrary pressure P,

$$\frac{G^R}{RT} = \left(\frac{G^R}{RT}\right)_{P=0} + \int_0^P \frac{V^R}{RT}\,dP \quad (\text{const. } T)$$

For convenience, define

$$\left(\frac{G^R}{RT}\right)_{P=0} \cong J \equiv \text{constant, independent of } T =$$

May be arbitrarily set equal to zero.

Thus,

$$\frac{G^R}{RT} = J + \int_0^P \frac{Z-1}{P}\,dP \quad (\text{using eq}^n\text{ 2}) \longrightarrow (14)$$

The derivative of this equation in combination with Eq. (13) gives,

$$\frac{H^R}{RT} = -T\int_0^P \left(\frac{\partial Z}{\partial T}\right)_P \frac{dP}{P} \longrightarrow (15)$$

The defining equation for the Gibbs energy,

$$G = H - TS,$$

may also be written for the special case of an ideal gas, $G^{ig} = H^{ig} - TS^{ig}$; by difference,

$$G^R = H^R - TS^R \text{ , and}$$

$$\frac{S^R}{R} = \frac{H^R}{RT} - \frac{G^R}{RT} \longrightarrow (16)$$

combining this equation with Eqs. (14) and (15) gives

$$\frac{S^R}{R} = -T\int_0^P \left(\frac{\partial Z}{\partial T}\right)_P \frac{dP}{P} - \int_0^P (Z-1)\frac{dP}{P} \longrightarrow (17)$$

The compressibility factor is defined as $Z = PV/RT$;

* The compressibility factor is defined as $Z = PV/RT$; values of 'Z' and of $(\partial Z/\partial T)_P$ may be calculated from experimental PVT data, and integrals can be evaluated by numerical or graphical methods.

Alternatively, the integrals may be evaluated analytically when 'Z' is expressed as a function of 'T' and 'P' by a volume-explicit equation of state..

# Residual properties from the virial Equations of state

The two-term virial equation gives,

$$Z-1=\frac{BP}{RT}$$

substituting in Eq^n. (14) reduces it to

$$\frac{G^R}{RT}=\frac{BP}{RT} \longrightarrow (18)$$

From Eq^n. (4 13),

$$\frac{H^R}{RT}=-T\left[\frac{\partial(G^R/RT)}{\partial T}\right]_P$$

$$=-T\frac{\partial}{\partial T}\left[\frac{BP}{RT}\right]_P$$

$$=-T\left(\frac{P}{R}\right)\left[\frac{1}{T}\frac{dB}{dT}-\frac{B}{T^2}\right]$$

$$\frac{H^R}{RT}=\frac{P}{R}\left[\frac{B}{T}-\frac{dB}{dT}\right] \longrightarrow (19)$$

From eq^n. (16),

$$\frac{S^R}{R}=\frac{H^R}{RT}-\frac{G^R}{RT}=\frac{P}{R}\left[\frac{B}{T}-\frac{dB}{dT}\right]-\frac{BP}{RT}=-\frac{P}{R}\frac{dB}{dT}$$

$$\frac{S^R}{R}=-\frac{P}{R}\frac{dB}{dT} \longrightarrow (20)$$

* Evaluation of residual enthalpies and residual entropies is straightforward for given values of T, P, provided one has sufficient data to evaluate B and dB/dT.

We have, $PV = ZRT$

$\rho = \frac{1}{V} \rightarrow$ molar volume

$\downarrow$ Molar density

In the alternative form,

$$P = Z\rho RT \longrightarrow (21)$$

Differentiation gives:

$$dP = RT(Z\,d\rho + \rho\,dZ) \qquad (\text{Const. } T)$$

Dividing by eqn. (21),

$$\frac{dP}{P} = \frac{RT(Z\,d\rho + \rho\,dZ)}{RTZ\rho} = \frac{d\rho}{\rho} + \frac{dZ}{Z}$$

using eqn. (14),

$$Z = \frac{PV}{RT}$$

$P \to 0;$ $Z \to 1$

$P \to P:$ $Z \to Z$

$\rho \to 0$

$P \to 0$

$$\frac{G^R}{RT} = \int (Z-1)\left\{\frac{d\rho}{\rho} + \frac{dZ}{Z}\right\}$$

$$= \int (Z-1)\frac{dZ}{Z} + \int (Z-1)\frac{d\rho}{\rho}$$

$$= \cancel{\int\left(1 - \frac{dZ}{Z}\right)}$$

$$= \int_1^Z \left(1 - \frac{1}{Z}\right) dZ + \int_0^\rho (Z-1)\frac{d\rho}{\rho}$$

$$= (Z - \ln Z)_1^Z + \int_0^\rho (Z-1)\frac{d\rho}{\rho}$$

$$\boxed{\frac{G^R}{RT} = (Z - \ln Z - 1) + \int_0^\rho (Z-1)\frac{d\rho}{\rho}} \longrightarrow (22)$$

From eq$^n$. (11),

$$\frac{H^R}{RT^2}\, dT = \frac{V^R}{RT}\, dp - d\left(\frac{G^R}{RT}\right)$$

$$= (Z-1)\frac{dp}{p} - d\left(\frac{G^R}{RT}\right) \quad [\text{using eq}^n.\ 2]$$

Division by dT & restriction to constant '$\rho$' gives-

$$\Rightarrow \frac{H^R}{RT^2} = \frac{(Z-1)}{P}\left(\frac{\partial P}{\partial T}\right)_\rho - \left[\frac{\partial\left(G^R/RT\right)}{\partial T}\right]_\rho \longrightarrow (23)$$

Differentiation of eq$^n$. (21) provides the first derivative on the right, and differentiation of eq$^n$. (22) provides

Thus, from eq$^n$. (21),

$$\left(\frac{\partial P}{\partial T}\right)_\rho = \frac{\partial}{\partial T}(Z\rho RT)_\rho$$

$$= \rho R\left[Z + T\frac{\partial Z}{\partial T}\right]$$

from eq$^n$. (22),

$$\left[\frac{\partial\left(G^R/RT\right)}{\partial T}\right]_\rho = \int_0^\rho \left(\frac{\partial Z}{\partial T}\right)_\rho \frac{d\rho}{\rho} + \frac{\partial Z}{\partial T} - \frac{1}{Z}\frac{\partial Z}{\partial T}$$

on substitution in eq$^n$. (23),

$$\frac{H^R}{RT^2} = \left(\frac{Z-1}{P}\right)\left(\rho RZ + \rho RT\frac{\partial Z}{\partial T}\right) - \int_0^\rho \left(\frac{\partial Z}{\partial T}\right)_\rho \frac{d\rho}{\rho} - \frac{\partial Z}{\partial T} + \frac{1}{Z}\frac{\partial Z}{\partial T}$$

$$\Rightarrow \frac{H^R}{RT} = T(Z-1)\left(\frac{\rho RZ}{P} + \frac{\rho RT}{P}\frac{\partial Z}{\partial T}\right) - T\int_0^\rho \left(\frac{\partial Z}{\partial T}\right)_\rho \frac{d\rho}{\rho} - T\frac{\partial Z}{\partial T} + \frac{T}{Z}\frac{\partial Z}{\partial T}$$

$$= T(Z-1)\left(\frac{\rho R Z}{Z\rho R T} + \frac{\rho R T}{Z\rho R T}\frac{\partial Z}{\partial T}\right) - T\int_0^{\rho}\left(\frac{\partial Z}{\partial T}\right)_{\rho}\frac{d\rho}{\rho} - T\frac{\partial Z}{\partial T} + \frac{T}{Z}\frac{\partial Z}{\partial T}$$

$$= T(Z-1)\left(\frac{1}{T} + \frac{1}{Z}\frac{\partial Z}{\partial T}\right) - T\int_0^{\rho}\left(\frac{\partial Z}{\partial T}\right)_{\rho}\frac{d\rho}{\rho} - T\frac{\partial Z}{\partial T} + \frac{T}{Z}\frac{\partial Z}{\partial T}$$

$$= (TZ-T)\left(\frac{1}{T} + \frac{1}{Z}\frac{\partial Z}{\partial T}\right) - T\int_0^{\rho}\left(\frac{\partial Z}{\partial T}\right)_{\rho}\frac{d\rho}{\rho} - T\frac{\partial Z}{\partial T} + \frac{T}{Z}\frac{\partial Z}{\partial T}$$

$$= Z + \cancel{T\frac{\partial Z}{\partial T}} - 1 - \cancel{\frac{T}{Z}\frac{\partial Z}{\partial T}} - T\int_0^{\rho}\left(\frac{\partial Z}{\partial T}\right)_{\rho}\frac{d\rho}{\rho} - \cancel{T\frac{\partial Z}{\partial T}} + \cancel{\frac{T}{Z}\frac{\partial Z}{\partial T}}$$

$$= -T\int_0^{\rho}\left(\frac{\partial Z}{\partial T}\right)_{\rho}\frac{d\rho}{\rho} + Z - 1$$

Thus,

$$\boxed{\frac{H^R}{RT} = -T\int_0^{\rho}\left(\frac{\partial Z}{\partial T}\right)_{\rho}\frac{d\rho}{\rho} + Z - 1} \longrightarrow (24)$$

The residual entropy is found from eqn. (16),

$$\frac{S^R}{R} = -T\int_0^{\rho}\left(\frac{\partial Z}{\partial T}\right)_{\rho}\frac{d\rho}{\rho} + \cancel{Z} - \cancel{1} - \cancel{Z} + \ln Z + \cancel{1} - \int_0^{\rho}(Z-1)\frac{d\rho}{\rho}$$

$$\boxed{\frac{S^R}{R} = \ln Z - T\int_0^{\rho}\left(\frac{\partial Z}{\partial T}\right)_{\rho}\frac{d\rho}{\rho} - \int_0^{\rho}(Z-1)\frac{d\rho}{\rho}} \longrightarrow (25)$$

# Residual properties by cubic Equation of state

The generic cubic equation of state:

$$P = \frac{RT}{V-b} - \frac{a(T)}{(V+\epsilon b)(V+\sigma b)} \quad ; \ \sigma, \epsilon = \text{constants.}$$

Divide by $\rho RT$ & substitute $V = 1/\rho$

$$\frac{P}{\rho RT} = \frac{\cancel{RT}}{\rho \cancel{RT}(V-b)} - \frac{a(T)}{\rho RT(V+\epsilon b)(V+\sigma b)}$$

$$\Rightarrow \quad Z = \frac{1}{\rho\left(\frac{1}{\rho}-b\right)} - \frac{a(T)}{\rho RT\left(\frac{1}{\rho}+\epsilon b\right)\left(\frac{1}{\rho}+\sigma b\right)}$$

$$= \frac{1}{(1-b\rho)} - \frac{a(T)}{\cancel{\rho} RT\,\frac{(1+\epsilon\rho b)}{\cancel{\rho}}\,\frac{(1+\sigma\rho b)}{\rho}}$$

$$= \frac{1}{(1-b\rho)} - \frac{\rho\, a(T)}{RT(1+\epsilon\rho b)(1+\sigma\rho b)}$$

$$q = \frac{a(T)}{bRT}$$

$$\frac{a(T)}{RT} = qb$$

$$Z = \frac{1}{(1-b\rho)} - q\,\frac{\rho b}{(1+\epsilon\rho b)(1+\sigma\rho b)} \quad \longrightarrow (26)$$

The two quantities needed for evaluation of $G^R$, $H^R$ & $S^R$ are $Z-1$ ~~&~~ and $\left(\frac{\partial Z}{\partial T}\right)_\rho$. Thus, from eqn (26),

$$Z-1 = \frac{1}{(1-\rho b)} - 1 - q\frac{\rho b}{(1+\epsilon\rho b)(1+\sigma\rho b)}$$

$$= \frac{1-1+\rho b}{(1-\rho b)} - q\frac{\rho b}{(1+\epsilon\rho b)(1+\sigma\rho b)}$$

$$Z-1 = \frac{\rho b}{(1-\rho b)} - q\frac{\rho b}{(1+\epsilon\rho b)(1+\sigma\rho b)} \longrightarrow (27)$$

$$\left(\frac{\partial Z}{\partial T}\right)_\rho = -\left(\frac{dq}{dT}\right)\frac{\rho b}{(1+\epsilon\rho b)(1+\sigma\rho b)} \longrightarrow (28)$$

The integrals are evaluated as follows:

$$\int_0^\rho (Z-1)\frac{d\rho}{\rho} = \int_0^\rho \frac{\rho b}{(1-\rho b)}\frac{d(\rho b)}{\rho b} - q\int_0^\rho \frac{d(\rho b)}{(1+\epsilon\rho b)(1+\sigma\rho b)}$$

$$\int_0^\rho \left(\frac{\partial Z}{\partial T}\right)_\rho \frac{d\rho}{\rho} = -\frac{dq}{dT}\int_0^\rho \frac{d(\rho b)}{(1+\epsilon\rho b)(1+\sigma\rho b)}$$

These two equations simplify to

$$\int_0^\rho (Z-1)\frac{d\rho}{\rho} = -\ln(1-\rho b) - qI \;; \int_0^\rho \left(\frac{\partial Z}{\partial T}\right)_\rho \frac{d\rho}{\rho} = -\frac{dq}{dT}I$$

where, $$I = \int_0^{\rho} \frac{d(\rho b)}{(1+\epsilon \rho b)(1+\sigma \rho b)}$$

<u>case I</u>: $\epsilon \neq \sigma$

$$I = \frac{1}{\sigma - \epsilon} \ln\left(\frac{1+\sigma \rho b}{1+\epsilon \rho b}\right)$$

we have, $\beta = \frac{bP}{RT}$ ; $Z = \frac{P}{\rho RT}$

$$\frac{\beta}{Z} = \frac{b\cancel{P}}{\cancel{RT}} \times \frac{\rho \cancel{RT}}{\cancel{P}} = \rho b$$

$$I = \frac{1}{\sigma - \epsilon} \ln\left(\frac{Z+\sigma\beta}{Z+\epsilon\beta}\right) \longrightarrow (29)$$

<u>case II</u>: $\epsilon = \sigma$

$$I = \frac{\rho b}{1+\epsilon \rho b} = \frac{\beta}{Z+\epsilon\beta}$$

using this, we get-

$$\boxed{\frac{G^R}{RT} = Z-1-\ln(Z-\beta)-qI} \rightarrow (30)$$

$$\boxed{\frac{H^R}{RT} = Z-1+\left[\frac{d\ln\alpha(T_r)}{d\ln T_r}-1\right]qI} \rightarrow (31)$$

$$\boxed{\frac{S^R}{R} = \ln(Z-\beta)+\frac{d\ln\alpha(T_r)}{d\ln T_r}qI} \rightarrow (32)$$

# APPENDIX G

# THERMODYNAMIC PROPERTY DERIVATIVES AND THE BRIDGMAN TABLE

In Section 2.10 and Table 2.2 we showed the five useful equations for calculating the changes in common thermodynamic properties with changes in $T$ and $P$. Those five satisfy the needs of most undergraduates and most working engineers. However some uncommon problems require other mathematical relations among thermodynamic properties; those can be found using the methods in this appendix.

These relations can all be derived starting with the property equation (Eq. 2.32), and the definitions of $h$, $g$, $a$, $C_P$ and $C_V$. The derivations are shown in many thermodynamics books and form a favorite exercise in differential calculus for graduate students. All 168 of the possible relations between the variables $u$, $h$, $s$, $g$, $a$, v, $P$, and $T$ can be worked out quickly and easily using a Bridgman table, Table G.1 (thus missing out on all that fun calculus and algebra).

For any of the properties $u$, $h$, $s$, $g$, and $a$ we can write a two-term Taylor series expansion of the derivative. For example, for $s$ as a function of $T$ and $P$,

$$ds = \left(\frac{\partial s}{\partial T}\right)_P dT + \left(\frac{\partial s}{\partial P}\right)_T dP \tag{G.1}$$

Comparing this to Eq. 2.35

$$ds = \frac{C_P}{T} dT - \left(\frac{dv}{dT}\right)_P dP \tag{2.35}$$

We see that these are the same if

$$\left(\frac{\partial s}{\partial T}\right)_P = \frac{C_P}{T} \text{ and } \left(\frac{\partial s}{\partial P}\right)_T = -\left(\frac{dv}{dT}\right)_P \tag{G.2}$$

The first of these comes from the definition of the entropy; the second comes from one of the Maxwell relations. Many thermodynamics texts spend considerable effort showing how these come about and how to derive any of the other derivatives of this type we might need. These derivatives are all of the form $(\partial a/\partial b)_c$ where $a$, $b$, and $c$ are any of the following variables, $T$, $P$, $v$, $u$, $h$, $s$, $g$, and $a$. Taking 3 variables at a time from a list of 8 allows for 336 combinations, and thus 336 such derivatives, but half of those are the reciprocals of others so there are only 168 such derivatives among this list of variables. Of these 168 the most useful 10 are shown in Table 2.2. But some of the others are sometimes useful; they are easily found from Table G.1

**Example G.1** Show the construction of the first six derivatives in Table 2.2 from the Bridgman table.

$$\left(\frac{\partial u}{\partial T}\right)_P = \frac{(\partial u)_P}{(\partial T)_P} = \frac{[\text{Eq.BT.4}]}{[\text{Eq.BT.2}]} = \frac{C_P - P(\partial v/\partial T)_P}{1} = C_P - P(\partial v/\partial T)_P \tag{G.3}$$

$$\left(\frac{\partial u}{\partial P}\right)_T = \frac{(\partial u)_T}{(\partial P)_T} = \frac{[\text{Eq.BT.101}]}{-[\text{Eq.BT.2}]} = \frac{T(\partial v/\partial T)_P + P(\partial v/\partial P)_T}{-1} = -[T(\partial v/\partial T)_P + P(\partial v/\partial P)_T] \tag{G.4}$$

$$\left(\frac{\partial h}{\partial T}\right)_P = \frac{(\partial h)_P}{(\partial T)_P} = \frac{[\text{Eq.BT.5}]}{[\text{Eq.BT.2}]} = \frac{C_P}{1} = C_P \tag{G.5}$$

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*Physical and Chemical Equilibrium for Chemical Engineers*, Second Edition. Noel de Nevers.

$$\left(\frac{\partial h}{\partial P}\right)_T = \frac{(\partial h)_T}{(\partial P)_T} = \frac{[\text{Eq.BT.11}]}{-[\text{Eq.BT.2}]}$$

$$= \frac{-v + T(\partial v/\partial T)_P}{-1} = v - T(\partial v/\partial T)_P \tag{G.6}$$

$$\left(\frac{\partial s}{\partial T}\right)_P = \frac{(\partial s)_P}{(\partial T)_P} = \frac{[\text{Eq.BT.3}]}{[\text{Eq.BT.2}]} = \frac{C_P/T}{1} = C_P/T \tag{G.7}$$

$$\left(\frac{\partial s}{\partial P}\right)_T = \frac{(\partial s)_T}{(\partial P)_T} = \frac{[\text{Eq.BT.9}]}{-[\text{Eq.BT.2}]} = \frac{(\partial v/\partial T)_P}{-1} = -(\partial v/\partial T)_P \tag{G.8}$$

These were easy, because the denominators were all = ± 1. The following example shows a more complex derivative taken from a practical problem.

**Example G.2** A rigid container is filled completely with saturated liquid propane at 100 psia. We now transfer heat to it, allowing time for perfect thermal mixing, and ask how fast does the pressure rise as we introduce heat. From the first law we know that for a closed system at constant volume $dU = m du = dQ$, so we are asking for $(\partial P/\partial u)_V$. This is one of the 168 derivatives derivable from Table G.1 but not one of the 10 most often used. This example is a very simplified version of the problem addressed in [1].

From Table G.1

$$\left(\frac{\partial P}{\partial u}\right)_V = \frac{(\partial P)_V}{(\partial u)_V} = \frac{-[\text{Eq.BT.1}]}{[\text{Eq.BT.15}]} = \frac{-(\partial v/\partial T)_P}{C_P(\partial v/\partial P)_T + T(\partial v/\partial T)_P^2}$$

$$= \frac{-1}{C_P\dfrac{(\partial v/\partial P)_T}{(\partial v/\partial T)_P} + T(\partial v/\partial T)_P} \tag{G.9}$$

Taking values from [2],

$$T \approx 55°\text{F} = 515°\text{R}; \quad C_P \approx 0.6\,\frac{\text{Btu}}{\text{lbm}°\text{F}};$$
$$\left(\frac{\partial v}{\partial P}\right)_T \approx -10^{-6}\,\frac{\text{ft}^3/\text{lbm}}{\text{psi}}$$

and

$$\left(\frac{\partial v}{\partial T}\right)_P \approx 3.9\cdot 10^{-5}\,\frac{\text{ft}^3/\text{lbm}}{°\text{F}}.$$

Thus

$$\left(\frac{\partial P}{\partial u}\right)_V = \\ = \frac{-1}{0.6\,\dfrac{\text{Btu}}{\text{lbm}°\text{F}}\dfrac{-10^{-6}\,\dfrac{\text{ft}^3/\text{lbm}}{\text{psi}}}{3.9\cdot 10^{-5}\,\dfrac{\text{ft}^3/\text{lbm}}{°\text{F}}} + 515°\text{R}\left(3.9\cdot 10^{-5}\,\dfrac{\text{ft}^3/\text{lbm}}{°\text{F}}\right)} \tag{G.A}$$

The first term in the denominator, after simple cancellation of units becomes

$$0.6\,\frac{\text{Btu}}{\text{lbm psi}}\frac{-10^{-6}}{3.9\cdot 10^{-5}} = -0.01538\,\frac{\text{Btu}}{\text{lbm psi}},$$

while the second becomes

$$515°\text{R}\left(3.9\cdot 10^{-5}\,\frac{\text{ft}^3/\text{lbm}}{°\text{F}}\right)\cdot\left(\frac{\text{Btu}}{778\text{ ft lbf}}\right)\cdot\left(\frac{144\text{ lbf/ft}^2}{\text{psi}}\right)$$
$$= 0.00372\,\frac{\text{Btu}}{\text{lbm psi}}$$

and

$$\left(\frac{\partial P}{\partial u}\right)_V = \frac{-1}{(-0.01538 + 0.00371)\dfrac{\text{Btu/lbm}}{\text{psi}}}$$
$$= 85.7\,\frac{\text{psi}}{\text{Btu/lbm}} = 253\,\frac{\text{kPa}}{\text{kJ/kg}} \tag{G.B}$$

which shows that heating liquids in closed containers leads to rapid pressure rises. ■

## PROBLEMS

See the Common Units and Values for Problems and Examples.

**G.1** Show the derivation of the $P$ and $T$ derivatives of $g$ and $a$ using Table G.1 and compare them to the values in Table 2.2.

**G.2** Estimate the change in enthalpy, $h$, of liquid propane at 55°F, as it is isothermally compressed from 100 psia to 1000 psia, using values from Example G.2. Over this pressure range for liquid propane, $v$ is practically constant $\approx 0.0304$ ft$^3$/lbm. Compare the result with the interpolated value of 1.75 Btu/lbm from [2].

**G.3** Show the forms that the five equations in Table 2.2 take for an ideal gas.

**G.4** To convince yourself of the utility of Table G.1, derive the formula for $(\partial P/\partial u)_V$ without using Table G.1.

## TABLE G.1 BRIDGMAN TABLE

This version, presented by Hougen et al. [3], is much more compact than the original by Bridgman [4]. Its use is illustrated in Examples G.1 and G.2.

### 1. Pressure Constant and Pressure Variable

$$(\partial v)_P = -(\partial P)_V = (\partial v/\partial T)_P \qquad \text{(BT.1)}$$

$$(\partial T)_P = -(\partial P)_T = 1 \qquad \text{(BT.2)}$$

$$(\partial s)_P = -(\partial P)_S = C_P/T \qquad \text{(BT.3)}$$

$$(\partial u)_P = -(\partial P)_U = C_P - P(\partial v/\partial T)_P \qquad \text{(BT.4)}$$

$$(\partial h)_P = -(\partial P)_H = C_P \qquad \text{(BT.5)}$$

$$(\partial a)_P = -(\partial P)_A = -[s + P(\partial v/\partial T)_P] \qquad \text{(BT.6)}$$

$$(\partial g)_P = -(\partial P)_G = -s \qquad \text{(BT.7)}$$

### 2. Temperature Constant and Temperature Variable

$$(\partial v)_T = -(\partial T)_V = -(\partial v/\partial P)_T \qquad \text{(BT.8)}$$

$$(\partial s)_T = -(\partial T)_S = (\partial v/\partial T)_P \qquad \text{(BT.9)}$$

$$(\partial u)_T = -(\partial T)_U = T(\partial v/\partial T)_P + P(\partial v/\partial P)_T \qquad \text{(BT.10)}$$

$$(\partial h)_T = -(\partial T)_H = -v + T(\partial v/\partial T)_P \qquad \text{(BT.11)}$$

$$(\partial a)_T = -(\partial T)_A = P(\partial v/\partial P)_T \qquad \text{(BT.12)}$$

$$(\partial g)_T = -(\partial T)_G = -v \qquad \text{(BT.13)}$$

### 3. Volume Constant and Volume Variable

$$(\partial s)_V = -(\partial v)_S = (1/T)[C_P(\partial v/\partial P)_T + T(\partial v/\partial T)_P^2] \qquad \text{(BT.14)}$$

$$(\partial u)_V = -(\partial v)_U = C_P(\partial v/\partial P)_T + T(\partial v/\partial T)_P^2 \qquad \text{(BT.15)}$$

$$(\partial h)_V = -(\partial v)_H = C_P(\partial v/\partial P)_T + T(\partial v/\partial T)_P^2 - v(\partial v/\partial T)_P \qquad \text{(BT.16)}$$

$$(\partial a)_V = -(\partial v)_A = -s(\partial v/\partial P)_T \qquad \text{(BT.17)}$$

$$(\partial g)_V = -(\partial v)_G = -[v(\partial v/\partial T)_P + s(\partial v/\partial P)_T] \qquad \text{(BT.18)}$$

### 4. Entropy Constant and Entropy Variable

$$(\partial u)_S = -(\partial s)_U = (P/T)[C_P(\partial v/\partial P)_T + T(\partial v/\partial T)_P^2] \qquad \text{(BT.19)}$$

$$(\partial h)_S = -(\partial s)_H = -(vC_P/T) \qquad \text{(BT.20)}$$

$$(\partial a)_S = -(\partial s)_A = (1/T)[P(\partial v/\partial P)_T + T(\partial v/\partial T)_P^2] + sT(\partial v/\partial T)_P\} \qquad \text{(BT.21)}$$

$$(\partial g)_S = -(\partial s)_G = -(1/T)[vC_P - sT(\partial v/\partial T)_P] \qquad \text{(BT.22)}$$

### 5. Internal Energy Constant and Internal Energy Variable

$$(\partial h)_U = -(\partial u)_H = v[C_P - P(\partial v/\partial T)_P] - P[C_P(\partial v/\partial P)_T + T(\partial v/\partial T)_P^2] \qquad \text{(BT.23)}$$

$$(\partial a)_U = -(\partial u)_A = P[C_P(\partial v/\partial P)_T + T(\partial v/\partial T)_P^2] + s[T(\partial v/\partial T)_P + P(\partial v/\partial P)_T] \qquad \text{(BT.24)}$$

$$(\partial g)_U = -(\partial u)_G = v[C_P - P(\partial v/\partial P)_T] + s[T(\partial v/\partial T)_P + P(\partial v/\partial P)_T] \qquad \text{(BT.25)}$$

### 6. Enthalpy Constant and Enthalpy Variable

$$(\partial a)_H = -(\partial h)_A = -[s + P(\partial v/\partial T)_P]\cdot[v - T(\partial v/\partial T)_P] + PC_P(\partial v/\partial T)_P \qquad \text{(BT.26)}$$

$$(\partial g)_H = -(\partial h)_G = -v(C_P + s) + Ts(\partial v/\partial T)_P \qquad \text{(BT.27)}$$

**7. Helmholz Energy Constant and Helmholz Energy Variable**

$$(\partial a)_G = -(\partial g)_A = -s[v + P(\partial v/\partial P)_T] - Pv(\partial v/\partial T)_P \tag{BT.28}$$

### Comments on the Bridgman Table

1. Making up your own Bridgman table is harder than it looks (and it looks pretty hard!). According to Hougen et al. [3] Nobel Prize physicist Percy Bridgman, who invented it, had 2 errors in the first one he published in [5].
2. The properties $v$, $u$, $h$, $s$, $g$, and $a$ are all shown lower case, indicating that they apply to one lbm or one kg or one mol or lbmol. One can convert them to properties for some specified mass or number of mots by multiplying them by $m$ or $n$.
3. These use only the constant-pressure heat capacity, the most commonly-used heat capacity, (see Table A.9).
4. The derivative $(\partial v/\partial P)_T$ can be derived in algebraic form with either a $v$-explicit EOS or (as its reciprocal) from a $P$- explicit EOS. But $(\partial v/\partial T)_P$ cannot be easily derived algebraically with a $P$-explicit EOS. All the commonly used EOSs (see section 2.11 and Appendix F) are $P$-explicit, and cannot be solved to give simple algebraic expressions for $(\partial v/\partial T)_P$. For liquids and solids these two derivatives are equal to the coefficient of thermal expansion and the isothermal compressibility, (see Appendix D). Various numerical techniques approximate $(\partial v/\partial T)_P$; if all else fails, one can evaluate it by

$$\left(\frac{\partial v}{\partial T}\right)_P = -\frac{(\partial P/\partial T)_V}{(\partial P/\partial v)_T} \tag{BT.30}$$

which can be computed algebraically from a $P$- explicit EOS.
5. The derivatives that incorporate $v$ cannot be easily programmed using $P$-explicit equations of state.
6. If you must derive thermodynamic relations without the Bridgman table, you will use the historically important *Maxwell Relations*; $(\frac{\partial T}{\partial v})_s = (\frac{\partial P}{\partial s})_v$ : $(\frac{\partial T}{\partial P})_s = -(\frac{\partial v}{\partial S})_P$ :$(\frac{\partial S}{\partial v})_T = (\frac{\partial P}{\partial T})_v$ and $(\frac{\partial S}{\partial P})_T =-(\frac{\partial v}{\partial T})_P$. If you have a Bridgman table you need never use these, but as a student of thermodynamic history you should know about them.

## REFERENCES

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3. Hougen, O. A., K. M. Watson, and R. A. Ragatz, *Chemical Process Principles,* Part II *Thermodynamics*, ed. 2. New York: Wiley, p. 545 (1947).
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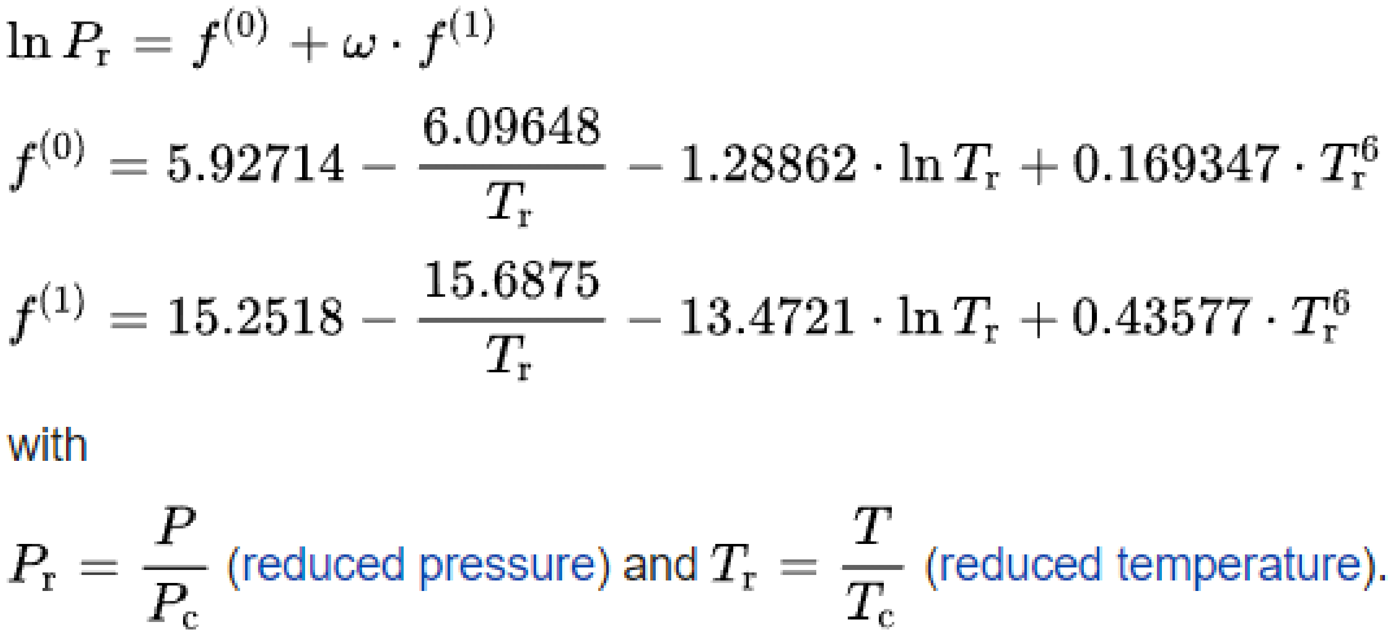
# Lee–Kesler Method

The Lee–Kesler method allows the estimation of the saturated vapor pressure at a given temperature for all components for which the critical pressure Pc, the critical temperature Tc, and the acentric factor ω are known.



$$\ln P_r = f^{(0)} + \omega \cdot f^{(1)}$$

$$f^{(0)} = 5.92714 - \frac{6.09648}{T_r} - 1.28862 \cdot \ln T_r + 0.169347 \cdot T_r^6$$

$$f^{(1)} = 15.2518 - \frac{15.6875}{T_r} - 13.4721 \cdot \ln T_r + 0.43577 \cdot T_r^6$$

with

$P_r = \frac{P}{P_c}$ (reduced pressure) and $T_r = \frac{T}{T_c}$ (reduced temperature).

# Edmister Equation & Edmister Charts

# Edmister Equation

- Edmister Equation, is a correlation used to calculate acentric factor of pure liquids, if critical pressure, temp., and boiling point are known.
- $\boldsymbol{\omega} = \underline{3\ [\log(P_c\ /\ 14.7)]}\ -\ 1$
- $7\ [T_c / T_b\ -1]$
- This equation can be rearranged for calculating critical pressure of liquids.
- But it was observed, that Edmister equation was more suitable for hydrocabons, as it predicted closely for hydrocarbon vapor-liquid mixtures.

# THE EFFECT OF PRESSURE ON HEAT CAPACITY

- For many substances changes in $C_p$ is considered to be negligible with pressure changes. For. Eg. water, air etc.
- Usually, the data on heat capacities given in the handbooks, are, usually for the ideal gas state, using empirical formula:
- $\mathbf{C'_p = a + bT + cT^2 + dT^3}$ where the superscript ( ‘ ) refers to the ideal gas state.
- The ideal gas values can be used for the real gases at low pressures only
- At high pressures the effect of pressure on the specific heat may be appreciable.

# Edmister charts

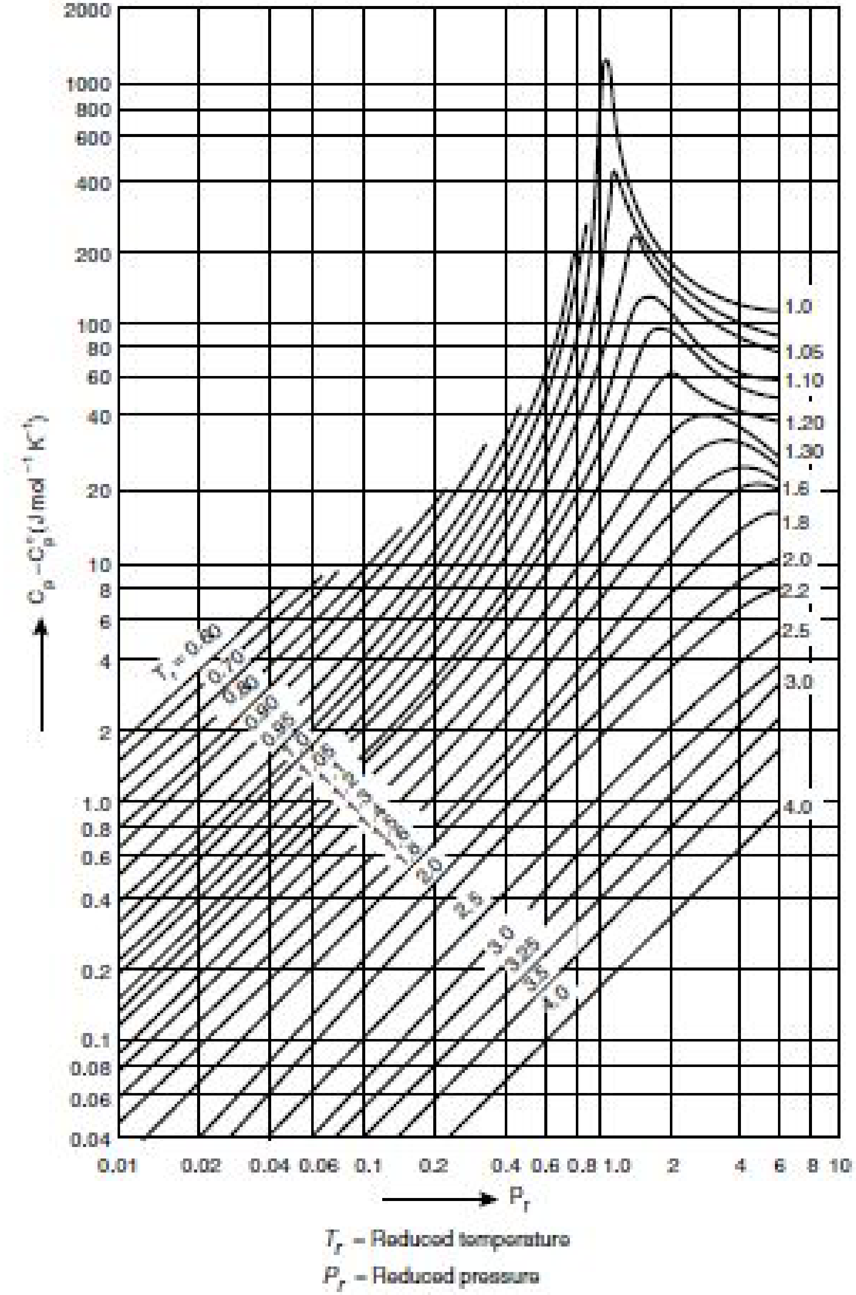


Figure 3.2. Excess heat capacity chart (reproduced from Sterbacek *et al.* (1979), with permission)

### 6.4.13 Gibbs–Helmholtz Equation

The Gibbs–Helmholtz equation provides the effect of temperature on Gibbs free energy. Consider Eq (6.18).

$$dG = -S\,dT + V\,dP \qquad (6.18)$$

At constant pressure, the above equation reduces to

$$\left(\frac{\partial G}{\partial T}\right)_P = -S \tag{6.72}$$

Even though this equation gives the effect of temperature on $G$ it will be convenient for practical calculations to replace $S$ in terms of measurable quantities. This can be done as follows.

Noting that $d(u/v) = (v\,du - u\,dv)/v^2$, the derivative of $G/T$ can be written as

$$\left(\frac{\partial(G/T)}{\partial T}\right)_P = \frac{T(\partial G/\partial T)_P - G}{T^2}$$

Use Eq. (6.72) to eliminate $(\partial G/\partial T)_P$ from the above equation.

$$\left(\frac{\partial(G/T)}{\partial T}\right)_P = \frac{-TS - G}{T^2}$$

Since by definition, $G = H - TS$, the above equation can be simplified as

$$\boxed{\left(\frac{\partial(G/T)}{\partial T}\right)_P = -\frac{H}{T^2}} \tag{6.73}$$

Equation (6.73) is known as *Gibbs–Helmholtz equation* and it finds wide application in the analysis of chemical reaction equilibria. Integration of Eq. (6.73) yields

$$\frac{G}{T} = -\int \frac{H}{T^2}\,dT + G' \tag{6.74}$$

where $G'$ is a constant of integration. The enthalpy of a substance can be written as

$$H = \int C_P\,dT + H'$$

where $H$□ is a constant of integration whose value is known by the choice of reference state at which enthalpy is arbitrarily set equal to zero. Expressing $C_P$ as a power function of $T$ as

$C_P = a + bT + cT^2$, $H = H$□ $+ aT + (1/2)\,bT^2 + (1/3)\,cT^3$. Substituting these in Eq. (6.74), we get