Chapter 4 Auxiliary Functions

1. * $dU = TdS - PdV - \delta w'$ $\qquad \therefore U = U(S,V)$

   or $dS = \frac{dU}{T} + \frac{P}{T}dV + \frac{\delta w'}{T}$ $\qquad S = S(U,V)$

   * S, V are not a convenient independent variables.

   * T, P are the most convenient independent variables for experimental operation.

   * T, V are the most convenient independent variables for theoretical investigation.

   ∵ For a closed system, fixed volume.

   $\Rightarrow$ quantization of energy levels is fixed.

   $\Rightarrow$ Boltzmann factor ($e^{\frac{-\varepsilon_i}{kT}}$) and partition function ($P = \sum e^{-\frac{\varepsilon_i}{kT}}$) are constant at constant T, V.

   * Some thermodynamic functions are not amenable to experimental measurement, however, they are related to some other measurable quantity.

   e.g. $\left(\frac{\partial U}{\partial S}\right)_V = T$, $\quad \left(\frac{\partial U}{\partial V}\right)_S = -P$,

   * Defined functions:

H ≡ U + PV	(Enthalpy)
A ≡ U – TS	(Helmholtz Free Energy)
G ≡ H – TS	(Gibbs Free Energy)

2. $\Delta U = Q - W$

   $\therefore U_2 - U_1 = Q_P - P(V_2 - V_1)$

   $(U_2 + PV_2) - (U_1 + PV_1) = Q_P$

   $(\mathrm{H}_2 - \mathrm{H}_1)_\mathrm{P} = Q_P$

   i.e. $\boxed{\Delta H_P = Q_P}$

3. Helmholtz Free Energy : A

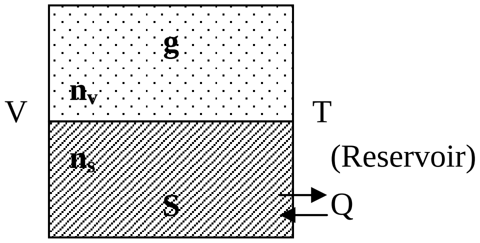
   $A \equiv U - TS$

   $(A_2 - A_1) = (U_2 - U_1) - (T_2\mathrm{S}_2 - T_1\mathrm{S}_1)$

   $(A_2 - A_1) = (Q - W) - (T_2\mathrm{S}_2 - T_1\mathrm{S}_1)$

$$\text{For isothermal process}: T_2 = T_1 = T$$
$$Q \le Q_{rev} = T(S_2 - S_1) = T\Delta S$$
$$\therefore (A_2 - A_1) \le -W$$
$$i.e.\quad (A_2 - A_1) + T\Delta S_{irr} = -W \ldots\ldots\ldots\ldots\ldots\ldots\ldots \oplus$$
$$(\text{or } W_{\max} = W + T\Delta S_{irr})$$
$$\therefore dA + TdS_{irr} = -\delta W$$
$$\text{For constant } (T,V): \quad \delta W = 0$$
$$dA + TdS_{irr} = 0$$
$$\because dS_{irr} > 0, \qquad dA_{T,V} < 0 \qquad\qquad \text{(Spontaneous)}$$
$$\text{Reversible} \qquad dS_{irr} = 0, \quad dA_{T,V} = 0$$
$$\text{Therefore} \qquad dA_{T,V} \le 0$$
$$\text{Criterion for equilibrium : At constant T, V} \qquad dA_{T,V} \le 0$$
$$i.e.\quad A_{T,V} \downarrow \ (non-equilibrium)$$
$$A_{T,V} = A_{\min} \ (at\ equilibrium)$$

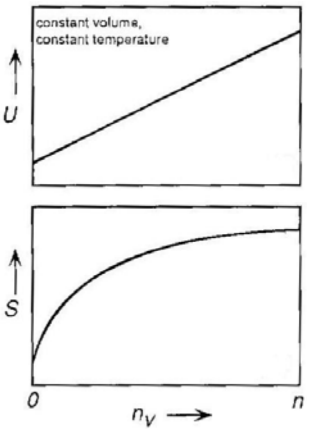
<u>EX:</u> Constant T, V sublimation of solid

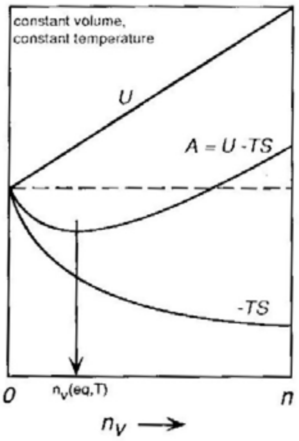


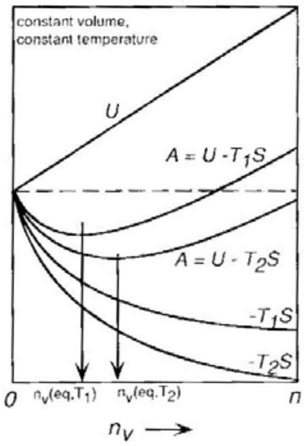
Total: n atoms

Two extreme states: 1. Solid phase only.
2. Vapor phase only.

When Solid → Vapor, U ↑ , S ↑ .







$$\text{Assume : ideal gas}$$
$$\therefore P = \frac{n_v(T)\cdot kT}{(V - V_s)}$$
$$P(T_1) = \frac{n_v(T_1)\cdot kT_1}{(V - V_{s1})}; \quad P(T_2) = \frac{n_v(T_2)\cdot kT_2}{(V - V_{s2})}$$

Usually, $\ln P(atm) = \frac{-a}{T} + b$

* If the reservoir is adiabatic, the combined system is one of constant U, V
$\triangle S_{U,V} > 0$

When P<Peq., spontaneous evaporation occurs.

$$\begin{cases} \Delta S(reservoir) = -\frac{Q}{T} \\ \Delta S(cylinder) = +\frac{Q}{T} + \Delta S_{irr} \end{cases}$$

$\therefore \Delta S_{tot} = \Delta S_{irr} > 0;$ from $\oplus: \Delta A + T\Delta S_{irr} = -W$

Cylinder (constant T, V) $\Rightarrow \Delta A_{T,V} + T\Delta S_{irr} = 0$ or $\Delta A_{T,V} = -T\Delta S_{irr}$

$$\Delta S_{irr} > 0, \quad \Delta A_{T,V} < 0$$

i.e. minimization of A, at constant T, V, is the criterion for equilibrium.

4. Gibbs Free Energy

$\because G \equiv H - TS$

$\therefore (G_2 - G_1) = (H_2 - H_1) - (T_2S_2 - T_1S_1)$

$= (U_2 - U_1) + (P_2V_2 - P_1V_1) - (T_2S_2 - T_1S_1)$

At constant T, P, i.e. $T_2 = T_1 = T$, $P_2 = P_1 = P$

$\therefore (G_2 - G_1) = (U_2 - U_1) + P(V_2 - V_1) - T(S_2 - S_1)$

1st law: $(U_2 - U_1) = Q - W$

$\therefore (G_2 - G_1) = Q - W + P(V_2 - V_1) - T(S_2 - S_1)$

Total work (K) = mechanical + chemical
electrical (W')

$\therefore W = P(V_2 - V_1) + W'$

$(G_2 - G_1) = Q - W' - T(S_2 - S_1)$

Because $Q \leqq T(S_2 - S_1)$ 【$Q - T(S_2 - S_1)$】 $\leqq 0$

$\therefore (G_2 - G_1) \leqq -W'$

i.e. $(G_2 - G_1) + T\triangle S_{irr} = -W'$

$\therefore$ at constant T, P, and no chemical work done, $W' = 0$

(fix composition => non-reacting) <=> $(G_2 - G_1) + T\triangle S_{irr} = 0$

$$\Delta G_{T,P} \le 0 \begin{cases} \text{Spontaneous process}: \Delta S_{irr} > 0, & \Delta G = (G_2 - G_1) < 0 \\ \text{At equil.(Reversible)}: \Delta S_{irr} = 0, & \Delta G = 0 \end{cases}$$

For infinitesimal change, $dG+TdS_{irr}=0$

$$\therefore dG_{T,P} \leqq 0$$

Criterion for equilibrium:

At const. T, P, $dG_{T,P} \leqq 0$

$$G_{T,P} = G_{min}$$

5. $dU = TdS-PdV$

$H \equiv U+PV$ $\quad \therefore dH = dU+PdV+VdP$

$$= (TdS-PdV)+PdV+VdP$$
$$= TdS+VdP$$

$A \equiv U-TS$ $\quad \therefore dA = dU-TdS-SdT$

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

$G \equiv H-TS$ $\quad \therefore dG = dH-TdS-SdT$

$$= (TdS+VdP)-TdS-SdT$$
$$= VdP-SdT$$

$$\therefore \quad \boxed{\begin{aligned} dU &= TdS-PdV \\ dH &= TdS+VdP \\ dA &= -PdV-SdT \\ dG &= VdP-SdT \end{aligned}} \quad \ldots\ldots\ldots\ldots\ldots\ldots\circledcirc$$

6. Variation of composition and size of system.

* For a closed system of fixed composition and size, only two independent variables are required.

* For multi-component closed system, compositions are variable.

e.g. $CO+H_2O = CO_2+H_2$

When $G = G_{min}$ at constant T, P, an unique composition exists $(n_{CO}, n_{H_2O}, n_{CO_2}, n_{H_2})$.

$G = G(T, P, n_i, n_j, n_k, \ldots\ldots\ldots\ldots)$

$$\therefore dG = \left(\frac{\partial G}{\partial T}\right)_{P,n_i,\ldots} dT + \left(\frac{\partial G}{\partial P}\right)_{T,n_N,\ldots} dP + \left(\frac{\partial G}{\partial n_i}\right)_{T,P,n_j,\ldots} dn_N + \ldots\ldots.$$

$$dG = -SdT + VdP + \sum_{n_i} \left(\frac{\partial G}{\partial n_i}\right)_{T,P,n_J,\ldots} dn_j$$

$$\text{Define}: \quad \mu_i \equiv \left(\frac{\partial G}{\partial n_i}\right)_{T,P,n_j,n_k,\ldots\ldots} \quad \text{-------------Chemical potential}$$

Similarly,

$$dU = TdS - PdV + \sum \left(\frac{\partial U}{\partial n_i}\right)_{S,V,n_j,\ldots\ldots} dn_i$$

$$dH = TdS + VdP + \sum \left(\frac{\partial H}{\partial n_i}\right)_{S,P,n_j,\ldots\ldots} dn_i$$

$$dA = -SdT - PdV + \sum \left(\frac{\partial A}{\partial n_i}\right)_{T,V,n_j,\ldots\ldots} dn_i$$

$$\text{and} \quad \boxed{\mu_i \equiv \left(\frac{\partial G}{\partial n_i}\right)_{T,P,n_j,\ldots\ldots} = \left(\frac{\partial U}{\partial n_i}\right)_{S,V,n_j,\ldots\ldots} = \left(\frac{\partial H}{\partial n_i}\right)_{S,P,n_j,\ldots\ldots} = \left(\frac{\partial A}{\partial n_i}\right)_{T,V,n_j,\ldots\ldots}}$$

$$dU = TdS - PdV + \sum \mu_i dn_i$$

$$cp. \quad dU = \delta Q - \delta W \qquad\qquad \therefore \delta W = PdV - \sum \mu_i dn_i$$

$\therefore -\sum \mu_i dn_i$ is chemical work done by system.

* Summary of criteria for equilibrium

2nd law: $S_{U,V} = S_{max}$ $\quad \therefore dS_{U,V} \geqq 0$

$dU_{S,V} \leqq 0$ $\quad U_{S,V} = U_{min}$

$dH_{S,P} \leqq 0$ $\quad H_{S,P} = H_{min}$

$dA_{T,V} \leqq 0$ $\quad A_{T,V} = A_{min}$

$dG_{T,P} \leqq 0$ $\quad G_{T,P} = G_{min}$

* When multiple phases coexist:

$$\text{At equil.}: \quad \begin{cases} T^{\alpha} = T^{\beta} = \ldots.. \\ P^{\alpha} = P^{\beta} = \ldots.. \\ \mu^{\alpha} = \mu^{\beta} = \ldots.. \end{cases} \qquad \text{Equil. conditions.}$$

7. Coefficient Relations

$$T=\left(\frac{\partial U}{\partial S}\right)_V=\left(\frac{\partial H}{\partial S}\right)_P$$

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

$$V=\left(\frac{\partial H}{\partial P}\right)_S=\left(\frac{\partial G}{\partial P}\right)_T$$

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

8. Maxwell Relations

If Z = Z(x,y)

$$dZ=\left(\frac{\partial Z}{\partial x}\right)_y\cdot dx+\left(\frac{\partial Z}{\partial y}\right)_x\cdot dy=L\cdot dx+M\cdot dy$$

$$\because\left(\frac{\partial L}{\partial y}\right)_x=\left[\frac{\partial}{\partial y}\left(\frac{\partial Z}{\partial x}\right)_y\right]_x=\frac{\partial^2 Z}{\partial x\cdot\partial y}$$

$$\left(\frac{\partial M}{\partial x}\right)_y=\left[\frac{\partial}{\partial x}\left(\frac{\partial Z}{\partial y}\right)_x\right]_y=\frac{\partial^2 Z}{\partial x\cdot\partial y}$$

$$\therefore\left(\frac{\partial L}{\partial y}\right)_x=\left(\frac{\partial M}{\partial x}\right)_y$$

From ◎

$$\boxed{\begin{aligned}\left(\frac{\partial T}{\partial V}\right)_S&=-\left(\frac{\partial P}{\partial S}\right)_V\\ \left(\frac{\partial T}{\partial P}\right)_S&=\left(\frac{\partial V}{\partial S}\right)_P\\ \left(\frac{\partial S}{\partial V}\right)_T&=\left(\frac{\partial P}{\partial T}\right)_V\\ -\left(\frac{\partial S}{\partial P}\right)_T&=\left(\frac{\partial V}{\partial T}\right)_P\end{aligned}}$$

Maxwell

9. Reciprocal and ratio relation

* Reciprocal: $\left(\frac{\partial z}{\partial x}\right)_y=\dfrac{1}{\left(\frac{\partial x}{\partial z}\right)_y}$

* Ratio: $x=x(y,z)$ $\quad dx=\left(\frac{\partial x}{\partial y}\right)_z\cdot dy+\left(\frac{\partial x}{\partial z}\right)_y\cdot dz$ ....(1)

$$z = z(x, y) \qquad dz = \left(\frac{\partial z}{\partial x}\right)_y \cdot dx + \left(\frac{\partial z}{\partial y}\right)_x \cdot dy \text{ ....(2)}$$

* From (2) $$dz \cdot \frac{1}{\left(\frac{\partial z}{\partial x}\right)_y} = dx + \frac{\left(\frac{\partial z}{\partial y}\right)_x}{\left(\frac{\partial z}{\partial x}\right)_y} \cdot dy$$

$$\therefore dx = -\left(\frac{\partial z}{\partial y}\right)_x \cdot \left(\frac{\partial x}{\partial z}\right)_y \cdot dy + \left(\frac{\partial x}{\partial z}\right)_y \cdot dz \text{ ....(3)}$$

Compare (1), (3) $\Rightarrow \therefore \left(\frac{\partial \mathrm{x}}{\partial y}\right)_z = -\left(\frac{\partial z}{\partial y}\right)_x \cdot \left(\frac{\partial x}{\partial z}\right)_y$

i.e. $$\boxed{\left(\frac{\partial x}{\partial y}\right)_z \cdot \left(\frac{\partial y}{\partial z}\right)_x \cdot \left(\frac{\partial z}{\partial x}\right)_y = -1}$$

10. Derived equations

① S = S(T,V)

$$\therefore dS = \left(\frac{\partial S}{\partial T}\right)_V \cdot dT + \left(\frac{\partial S}{\partial V}\right)_T \cdot dV \text{...............(1)}$$

$$\because TdS_V = \delta Q_V = dU_V = nC_V dT_v$$

$$\therefore \left(\frac{\partial S}{\partial T}\right)_V = \frac{nC_V}{T} \text{...............(2)}$$

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

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

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

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

$$\alpha \equiv \frac{1}{V}\left(\frac{\partial V}{\partial T}\right)_P \qquad \beta \equiv -\frac{1}{V}\left(\frac{\partial V}{\partial P}\right)_T$$

$$\therefore \left(\frac{\partial P}{\partial T}\right)_V = \frac{V\alpha}{V\beta} = \frac{\alpha}{\beta}$$

$$\therefore dS = \frac{nC_V}{T} dT + \frac{\alpha}{\beta} dV$$

or $\boxed{TdS = nC_V dT + \frac{\alpha T}{\beta} dV}$ 1st TdS Eq.

② One mole ideal gas: $\left(\frac{\partial U}{\partial V}\right)_T = 0$ U = U(T)!!

$$dU = TdS - PdV$$

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

$$= T\left(\frac{\partial P}{\partial T}\right)_V - P \qquad \text{(Maxwell)}$$

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

$$= P - P = 0$$

Exercise: $\boxed{\left(\frac{\partial U}{\partial P}\right)_T = 0}$

③ One mole ideal gas: $\left(\frac{\partial H}{\partial P}\right)_T = 0$ H = H(T)!!

$$\because dH = TdS + VdP$$

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

$$= T\left[-\left(\frac{\partial V}{\partial T}\right)_P\right] + V \qquad \text{(Maxwell)}$$

$$= -T \times \left(\frac{R}{P}\right) + V$$

$$= -V + V = 0$$

Exercise: $\boxed{\left(\frac{\partial H}{\partial V}\right)_T = 0}$

④ S = S(T, P)

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

$$\delta Q_{rev} = TdS = T \cdot \left[\left(\frac{\partial S}{\partial T}\right)_P \cdot dT + \left(\frac{\partial S}{\partial P}\right)_T \cdot dP\right]$$

$$\therefore \delta Q_{rev,P} = T \cdot \left(\frac{\partial S}{\partial T}\right)_P \cdot dT_P$$

$$\therefore \left(\frac{\delta Q_{rev}}{dT}\right)_P = C_P = T\left(\frac{\partial S}{\partial T}\right)_P$$

$$\boxed{C_P = T \cdot \left(\frac{\partial S}{\partial T}\right)_P = \left(\frac{\partial H}{\partial T}\right)_P}$$

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

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

$$\therefore dS = \frac{C_P}{T} dT - V\alpha dP$$

Or $\boxed{TdS = C_P dT - TV\alpha dP}$ 2nd TdS

$\boxed{TdS = \frac{\beta C_V}{\alpha} dP + \frac{C_P}{\alpha V} dV}$ 3rd TdS

$\boxed{TdS = C_V dT + \frac{\alpha T}{\beta} dV}$ 1st TdS

⑤ G = H-TS

$$\frac{G}{T} = \frac{H}{T} - S$$

$$\therefore \left[\frac{\partial \left(G/T\right)}{\partial T}\right]_P = \left[\frac{\partial \left(H/T\right)}{\partial T}\right]_P - \left[\frac{\partial S}{\partial T}\right]_P$$

$$= \frac{T \cdot \left(\frac{\partial H}{\partial T}\right)_P - H}{T^2} - \frac{C_P}{T}$$

$$= -\frac{H}{T^2} + \frac{1}{T}\left(\frac{\partial H}{\partial T}\right)_P - \frac{C_P}{T}$$

$$= -\frac{H}{T^2} + \frac{C_P}{T} - \frac{C_P}{T}$$

$$\therefore \boxed{\left[\frac{\partial \left(G/T\right)}{\partial T}\right]_P = -\frac{H}{T^2}}$$ Gibbs-Helmholtz equation

And $$\boxed{\left[\frac{\partial\left(\Delta G/T\right)}{\partial T}\right]_P = -\frac{\Delta H}{T^2}}$$

$$\Rightarrow \left[\frac{\partial\left(\mathrm{G}_2/\mathrm{T}\right)}{\partial \mathrm{T}}\right]_P - \left[\frac{\partial\left(G_1/T\right)}{\partial T}\right]_P = \left[-\frac{H_2}{T^2}\right] - \left[-\frac{H_1}{T^2}\right] = -\frac{H_2 - H_1}{T^2} = -\frac{\Delta H}{T^2}$$

$$\Downarrow$$

$$\left[\frac{\partial\left(\frac{\mathrm{G}_2 - G_1}{T}\right)}{\partial T}\right]_P = \left[\frac{\partial\left(\frac{\Delta G}{T}\right)}{\partial T}\right]_P = -\frac{\Delta H}{T^2}$$

Or $\dfrac{G_2 - G_1}{T} = \dfrac{H_2 - H_1}{T} - \left(S_2 - S_1\right);$ $\qquad \dfrac{\Delta G}{T} = \dfrac{\Delta H}{T} - \Delta S$

$$\left[\frac{\partial\left(\Delta G/T\right)}{\partial T}\right]_P = \left[\frac{\partial\left(\Delta H/T\right)}{\partial T}\right]_P - \left[\frac{\partial\left(\Delta S\right)}{\partial T}\right]_P$$

$$= \frac{T\left[\frac{\partial\left(\Delta H\right)}{\partial T}\right]_P - \Delta H}{T^2} - \frac{\Delta C_P}{T}$$

$$= \frac{T \cdot \Delta C_P - \Delta H}{T^2} - \frac{\Delta C_P}{T} = -\frac{\Delta H}{T^2}$$

$$\because \left[\frac{\partial\left(1/T\right)}{\partial \mathrm{T}}\right]_P = \frac{-1}{T^2} \qquad \therefore \boxed{\left[\frac{\partial\left(G/T\right)}{\partial\left(1/T\right)}\right]_P = H}$$

and $$\left[\frac{\partial\left(\Delta G/T\right)}{\partial\left(1/T\right)}\right]_P = \Delta H$$

$$\begin{cases} \text{Measure } G(T), & \text{Plot } \left(G/T\right) \text{ vs } \left(1/T\right), & \text{slope is } H(T) \\ \text{Measure } \Delta G(T), & \text{Plot } \left(\Delta G/T\right) \text{vs } \left(1/T\right), & \text{slope is } \Delta H(T) \end{cases}$$

⑥ A＝U－TS

A/T＝U/T－S

$$\therefore \left[\frac{\partial\left(A/T\right)}{\partial T}\right]_V = -\frac{U}{T^2}; \qquad \left[\frac{\partial\left(\Delta A/T\right)}{\partial T}\right]_V = -\frac{\Delta U}{T^2}$$

⑦ $$C_P - C_V = \left(\frac{\partial V}{\partial T}\right)_P \cdot \left[P + \left(\frac{\partial U}{\partial V}\right)_T\right] \text{..............(Eq. 2.8)}$$

$$\because dA = -SdT - PdV \qquad \therefore \left(\frac{\partial A}{\partial V}\right)_T = -P$$

and $\because A = U - TS$

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

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

$$\therefore C_P - C_V = \left(\frac{\partial V}{\partial T}\right)_P \cdot \left[-\left(\frac{\partial U}{\partial V}\right)_T + T\left(\frac{\partial P}{\partial T}\right)_V + \left(\frac{\partial U}{\partial V}\right)_T\right]$$

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

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

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

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

$$= -\frac{T\left[\left(\frac{\partial V}{\partial T}\right)_P\right]^2}{\left(\frac{\partial V}{\partial P}\right)_T}$$

because $\alpha \equiv \frac{1}{V}\left(\frac{\partial V}{\partial T}\right)_P \qquad \therefore \left(\frac{\partial V}{\partial T}\right)_P = V\alpha$

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

$$\therefore C_P - C_V = -\frac{TV^2\alpha^2}{-\beta V}$$

$$\boxed{C_P - C_V = \frac{TV\alpha^2}{\beta}} \qquad C_P \to C_V \begin{cases} 1.\, \alpha \to 0 \\ 2.\, T \to 0 \begin{cases} C_V \to 0 \\ C_P \to 0 \end{cases} \end{cases}$$

*** EX:** Al＝26.98 g/mole, T＝20℃＝298K

C_p＝24.36 J/mole.K ρ＝2.70 g/cm^3

α＝7.05×10^{-5} K^{-1}; β＝1.20×10^{-6} atm^{-1}

Cv＝?

Sol: V＝M/ρ＝26.98/2.70＝10 cm^3/mole＝0.01 l/mole

$$C_V = C_P - \frac{TV\alpha^2}{\beta} = 24.36 - \frac{298\times 0.01\times\left(7.05\times 10^{-5}\right)^2}{1.2\times 10^{-6}}\times\frac{8.314}{0.082}$$

$$= 23.13 \ {}^{\mathrm{J}}\!\!\diagup_{\mathrm{mole}\cdot\mathrm{K}}$$