Phys 344

Assignment 8. Solutions.

5.12.

$$dU = TdS - pdV \qquad (\text{1st Law}) \qquad ①$$

$$dH = TdS + Vdp \qquad (H = U + PV) \qquad ②$$

$$dF = -SdT - pdV \qquad (F = U - TS) \qquad ③$$

$$dG = -SdT + Vdp \qquad (G = H - TS) \qquad ④.$$

①: $$\left(\frac{\partial T}{\partial V}\right)_S = -\left(\frac{\partial p}{\partial S}\right)_V \qquad \left(\because \frac{\partial}{\partial V}\left(\frac{\partial U}{\partial S}\right) = \frac{\partial}{\partial S}\left(\frac{\partial U}{\partial V}\right)\right)$$

②: $$\left(\frac{\partial T}{\partial p}\right)_S = \left(\frac{\partial V}{\partial S}\right)_p \qquad \left(\because \frac{\partial}{\partial p}\left(\frac{\partial H}{\partial S}\right) = \frac{\partial}{\partial S}\left(\frac{\partial H}{\partial p}\right)\right)$$

③: $$\left(\frac{\partial S}{\partial V}\right)_T = \left(\frac{\partial p}{\partial T}\right)_V \qquad \left(\because \frac{\partial}{\partial V}\left(\frac{\partial F}{\partial T}\right) = \frac{\partial}{\partial T}\left(\frac{\partial F}{\partial V}\right)\right)$$

④: $$-\left(\frac{\partial S}{\partial p}\right)_T = \left(\frac{\partial V}{\partial T}\right)_p \qquad \left(\because \frac{\partial}{\partial p}\left(\frac{\partial G}{\partial T}\right) = \frac{\partial}{\partial T}\left(\frac{\partial G}{\partial p}\right)\right).$$

5.13. $\beta = \frac{1}{V}\left(\frac{\partial V}{\partial T}\right)_p$ $\quad dG = -SdT + VdP$

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

Since $\lim_{T\to 0} S = 0$ $\left\{ \begin{array}{l} \text{3rd Law.} \\ \text{regardless } P \\ (\text{independent of } P) \end{array} \right.$

$\therefore \left(\frac{\partial S}{\partial p}\right)_T \longrightarrow 0$ as $T \to 0$.

V = finite @ $T = 0$.

$\therefore \beta = -\frac{1}{V}\left(\frac{\partial S}{\partial p}\right)_T \longrightarrow 0$ at $T = 0$.

5.14.

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

a). $S = S(T, V)$.

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

b). $V = V(T, p)$

$$dV = \left(\frac{\partial V}{\partial T}\right)_p dT + \left(\frac{\partial V}{\partial p}\right)_T dp.$$

$$dS = \frac{C_V}{T} dT + \left(\frac{\partial S}{\partial V}\right)_T \left(\frac{\partial V}{\partial T}\right)_p dT + \left(\frac{\partial S}{\partial V}\right)_T \left(\frac{\partial V}{\partial p}\right)_T dp.$$

$$= \left[\frac{C_V}{T} + \left(\frac{\partial S}{\partial V}\right)_T \left(\frac{\partial V}{\partial T}\right)_p\right] dT + \left(\frac{\partial S}{\partial p}\right)_{\cancel{T}} dp.$$

$$\left(\frac{\partial S}{\partial T}\right)_p = \frac{C_V}{T} + \left(\frac{\partial S}{\partial V}\right)_T \left(\frac{\partial V}{\partial T}\right)_p. \quad , \quad \boxed{C_p = T\left(\frac{\partial S}{\partial T}\right)_p}$$

$$C_p = C_V + T \cdot \left(\frac{\partial S}{\partial V}\right)_T \left(\frac{\partial V}{\partial T}\right)_p.$$

c). $$\left(\frac{\partial S}{\partial V}\right)_T = \left(\frac{\partial p}{\partial T}\right)_V = -\frac{\left(\frac{\partial V}{\partial T}\right)_p}{\left(\frac{\partial V}{\partial p}\right)_T}. \qquad \boxed{\beta = \frac{1}{V}\left(\frac{\partial V}{\partial T}\right)_p}$$

$$C_p - C_V = -T \cdot \frac{\left(\frac{\partial V}{\partial T}\right)_p^2}{\left(\frac{\partial V}{\partial p}\right)_T} \qquad K_T = -\frac{1}{V}\left(\frac{\partial V}{\partial p}\right)_T.$$

$$C_p - C_V = -T\frac{(\beta V)^2}{-K_T \cdot V} = \frac{TV\beta^2}{K_T}.$$

* Another approach: To relate C_p and C_V,

we need to relate $\left(\frac{\partial S}{\partial T}\right)_P$ and $\left(\frac{\partial S}{\partial T}\right)_V$.

$$S = S(T, V) = S[T, V(T, P)].$$

$$\left(\frac{\partial S}{\partial T}\right)_P = \left(\frac{\partial S}{\partial T}\right)_V + \left(\frac{\partial S}{\partial V}\right)_T \left(\frac{\partial V}{\partial T}\right)_P . \qquad \text{— ①}$$

$$\therefore \quad C_p = C_V + T\left(\frac{\partial S}{\partial V}\right)_T \left(\frac{\partial V}{\partial T}\right)_P .$$

** Note: To ~~prov~~ show eq. ①:

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

$$dP = \left(\frac{\partial P}{\partial T}\right)_V dT + \left(\frac{\partial P}{\partial V}\right)_T dV .$$

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

$$= \left[\left(\frac{\partial S}{\partial T}\right)_P + \left(\frac{\partial S}{\partial P}\right)_T \left(\frac{\partial P}{\partial T}\right)_V\right] dT + \left(\frac{\partial S}{\partial P}\right)_T \left(\frac{\partial P}{\partial V}\right)_T dV$$

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

$$\therefore \quad \left(\frac{\partial S}{\partial T}\right)_P = \left(\frac{\partial S}{\partial T}\right)_V + \left(\frac{\partial S}{\partial V}\right)_T \left(\frac{\partial V}{\partial T}\right)_P ; \qquad \left(\frac{\partial S}{\partial V}\right)_T = \left(\frac{\partial S}{\partial P}\right)_T \left(\frac{\partial P}{\partial V}\right)_T .$$

d). Ideal Gas. $pV = NkT$. $\quad V = \frac{NkT}{p}$.

$$\beta = \frac{1}{V}\left(\frac{\partial V}{\partial T}\right)_p = \frac{1}{V}\cdot\frac{Nk}{p} = \frac{1}{T}$$

$$K_T = -\frac{1}{V}\left(\frac{\partial V}{\partial p}\right)_T = \left(\frac{-1}{V}\right)\cdot\left(-\frac{NkT}{p^2}\right) = \frac{1}{p}$$

$$\therefore \frac{TV\beta^2}{K_T} = \frac{T\cdot V\cdot\left(\frac{1}{T}\right)^2}{\frac{1}{p}} = \frac{pV}{T} = Nk.$$

$$\therefore \quad C_p - C_v = \frac{TV\beta^2}{K_T} = Nk.$$

e). ~~Since $K_T > 0$, $T > 0$, $V > 0$~~.

Since $K_T > 0$. $\quad$ ($K_T = -\frac{1}{V}\left(\frac{\partial V}{\partial p}\right)_T$.

when pressure increases, volume decreases

$T > 0$

$V > 0$ $\quad$ $\left(\frac{\partial V}{\partial p}\right)_T < 0 \Rightarrow K_T > 0$)

$$\therefore \quad C_p - C_v = \frac{TV\beta^2}{K_T} > 0. \Rightarrow C_p > C_v.$$

f). Water : $T = 298\ K$. $V = 18.068\ cm^3 = 1.81 \times 10^{-5}\ m^3$ (1 mol)

$\beta = 2.57 \times 10^{-4}\ K^{-1}$, $\kappa_T = 4.52 \times 10^{-10}\ Pa^{-1}$, $C_p = 75.3\ J/K$.

$$C_p - C_v = \frac{TV\beta^2}{\kappa_T} = \frac{298 \times 1.81 \times 10^{-5} \times (2.57 \times 10^{-4})^2}{4.52 \times 10^{-10}} = 7.88 \times 10^{-1}\ J/K$$

$$= 0.788\ J/K.$$

about 1% of C_p.

Mercury : $T = 298\ K$, $\beta = 1.81 \times 10^{-4}\ K^{-1}$, $\kappa_T = 4.04 \times 10^{-11}\ Pa$.

(1 mol). $V = 14.81\ cm^3 = 1.48 \times 10^{-5}\ m^3$. $C_p = 27.98\ J/K$.

$$C_p - C_v = \frac{TV\beta^2}{\kappa_T} = \frac{298 \times 1.48 \times 10^{-5} \times (1.81 \times 10^{-4})^2}{4.04 \times 10^{-11}} = 3.58\ J/K.$$

about 10% of C_p.

~~g) At low temperatures, the volume of a solid is not strongly dependent on pressure, and K~~

g). For a solid, V and κ_T do not strongly depend on temperature. Therefore,

$$C_p - C_v \propto T\beta^2.$$

i.e. C_p and C_v deviate at higher temperatures.

5.15.
$$C_V = \left(\frac{\partial U}{\partial T}\right)_V . \qquad C_p = \left(\frac{\partial H}{\partial T}\right)_p .$$

$$H = U + pV .$$

$$H(T,p) = U(T, V(T,p)) + pV(p,T) .$$

$$C_p = \left(\frac{\partial H}{\partial T}\right)_p = \left(\frac{\partial U}{\partial T}\right)_V + \left(\frac{\partial U}{\partial V}\right)_T \left(\frac{\partial V}{\partial T}\right)_p + p\left(\frac{\partial V}{\partial T}\right)_p .$$

$$= C_V + \left(\frac{\partial V}{\partial T}\right)_p \left[\left(\frac{\partial U}{\partial V}\right)_T + p\right] \qquad \left[p = -\left(\frac{\partial F}{\partial V}\right)_T\right]$$

$$= C_V + \left(\frac{\partial V}{\partial T}\right)_p \left[\left(\frac{\partial U}{\partial V}\right)_T - \left(\frac{\partial F}{\partial V}\right)_T\right] . \qquad F = U - TS .$$

$$= C_V + \left(\frac{\partial V}{\partial T}\right)_p \left[\frac{\partial (U-F)}{\partial V}\right]_T . \qquad U - F = TS .$$

$$= C_V + \left(\frac{\partial V}{\partial T}\right)_p \cdot T \cdot \left(\frac{\partial S}{\partial V}\right)_T .$$

$$C_p - C_V = T \cdot \left(\frac{\partial V}{\partial T}\right) \left(\frac{\partial S}{\partial V}\right)_T .$$

Then,
same as (5.14).

isentropic : $S = \text{const.}$

5.16. $K_S = -\frac{1}{V}\cdot\left(\frac{\partial V}{\partial P}\right)_S \qquad K_T = -\frac{1}{V}\left(\frac{\partial V}{\partial P}\right)_T.$

$$V = V(P, T) = V(P, T(S, P))$$

$$\left(\frac{\partial V}{\partial P}\right)_S = \left(\frac{\partial V}{\partial P}\right)_T + \left(\frac{\partial V}{\partial T}\right)_P \left(\frac{\partial T}{\partial P}\right)_S. \qquad \beta = \frac{1}{V}\left(\frac{\partial V}{\partial T}\right)_P$$

$$-V\cdot K_S = -VK_T + V\beta\left(\frac{\partial T}{\partial P}\right)_S.$$

$$K_T - K_S = \beta\left(\frac{\partial T}{\partial P}\right)_S.$$

$V = V(P, S)$
$= V[P, T(P, S)]$

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

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

$$= V\beta\cdot\frac{T}{C_P}.$$

$$\therefore K_T = K_S + \frac{VT\beta^2}{C_P}.$$

5.20. Ground state: $U=0,\ S=0$.

Excited state: $U = 10.2\,eV$, $S = k\ln 4$
$= 1.63\times10^{-18}\,J$. $= 1.38\times10^{-23}\cdot\ln 4 = 1.91\times10^{-23}\,J/K$.

$F = U - TS$.

when $F=0$. $T = \dfrac{U}{S} = \dfrac{1.63\times10^{-18}}{1.91\times10^{-23}} = 8.54\times10^{4}\,K$.

when $T > 8.54\times10^{4}\,K$, $F < 0$ (spontaneously excited)

when $T < 8.54\times10^{4}\,K$, $F > 0$.

5.21 Heat capacity C is extensive, since $C \propto m$.
specific heat c is intensive, $c = \dfrac{C}{m}$. — property of the material.

5.22. ideal gas.
$\mu(T,P) = \mu^{o}(T) + kT\ln(P/P^{o})$ (5.40).

$\mu = -kT\ln\left[\dfrac{V}{N}\left(\dfrac{2\pi m kT}{h^2}\right)^{3/2}\right]$ (3.63).

$PV = NkT$
$\dfrac{V}{N} = \dfrac{kT}{P}$

(3.63): $\mu = -kT\ln\left[\dfrac{A}{P}(kT)^{5/2}\right]$ wher $A = \left(\dfrac{2\pi m}{h^2}\right)^{3/2}$

$= -kT\left[\ln A(kT)^{5/2}\right] + kT\ln P$.

$= -\frac{5}{2}kT\ln kT - kT\ln A + kT\ln P$

$= \underbrace{-\frac{5}{2}kT\ln kT}_{=\ \mu^{o}(T)} + kT\ln P/P_o$ $(P_o = A)$