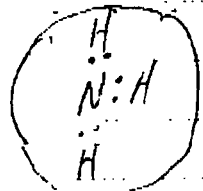
Solution for Exam #1 (P-Chem '02)

1. a(10) NH_3 : nonlinear molecule with $N = 4$ 

$C_{V,m} = 3R + (3N-6)R = 9R$

b(10) At low p., NH_3 becomes I.G. (compressibility factor $\to 1.0$)

$H = U + PV$

$$C_{p,m} = \left(\frac{\partial H_m}{\partial T}\right)_p = \left(\frac{\partial U_m}{\partial T}\right)_p + p\left(\frac{\partial V_m}{\partial T}\right)_p$$

Cycle Rule (A II .11) $\left(\frac{\partial U_m}{\partial T}\right)_p = \left(\frac{\partial U_m}{\partial T}\right)_{V_m} + \left(\frac{\partial U_m}{\partial V_m}\right)_T \left(\frac{\partial V_m}{\partial T}\right)_p$

where $\left(\frac{\partial U_m}{\partial V_m}\right)_T = T\left(\frac{\partial p}{\partial T}\right)_{V_m} - p$ Eq (2.13) $\therefore C_{p,m} = C_{V,m} + T\left(\frac{\partial p}{\partial T}\right)_{V_m}\left(\frac{\partial V}{\partial T}\right)_p$

For I.G. $pV_m = RT$, Then finally, $C_{p,m} = C_{V,m} + R$

2. See next page

3. a(5) Broad: Functional relationship among state variables.
Narrow: p-V-T relationship for a material.

b(5) Reversible process = a change that occurs through a succession of equilibrium states ~~[illegible]~~
($\Delta p = 0$ for expansion, $\Delta T = 0$ for heat flow)

c(5)
- In a closed system, entropy increases in a spontaneous change
- No process can be more efficient than a reversible process (real engine efficiency < 100%)
- $T\,dS \geq \delta q$

2. For vdW gas $\quad P_c = RT_c/(V_{mc} - b) - a/V_{mc}$

a) At critical point, $\left.\frac{\partial P}{\partial V}\right|_{T_c} = \left.\frac{\partial^2 P}{\partial V^2}\right|_{T_c} = 0$

$$\begin{cases} \frac{\partial P_c}{\partial V_c} = -\frac{RT_c}{(V_c-b)^2} + \frac{2a}{V_c^3} = 0 \\ \frac{\partial^2 P_c}{\partial V_c^2} = \frac{2RT_c}{(V_c-b)^3} - \frac{6a}{V_c^4} = 0 \end{cases}$$

$$\therefore\ a = \frac{27R^2T_c^2}{64P_c}, \quad b = \frac{RT_c}{8P_c}, \quad V_c = 3b$$

Finally, $Z_c = \frac{P_cV_c}{RT_c} = \frac{3}{8} = 0.375$

b) $H_i = \int_0^P \left[V - T\left(\frac{\partial V}{\partial T}\right)_P\right] dp \qquad$ Eq (2.33)

$= U_i + PV_m - RT$

For vdW $\begin{cases} PV_m = \frac{V_m RT}{V_m - b} - \frac{a}{V_m} \\ PV_m - RT = \frac{bRT}{V_m - b} - \frac{a}{V_m} \end{cases}$

$$U_i = \int_\infty^V \left[T\left(\frac{\partial P}{\partial T}\right)_V - P\right] dV = \int_\infty^V \left[\frac{RT}{(V_m-b)} - P\right] dV$$

$$= \int_\infty^V \frac{a}{V_m^2}\, dV = -\left.\frac{a}{V_m}\right|_\infty^{V_m} = -\frac{a}{V_m}$$

$$\therefore\ H_i = \frac{bRT}{(V_m-b)} - \frac{2a}{V_m}$$

4. a(5) $S(V_2, T_1) - S(V_1, T_1) = R\ln\left(\frac{V_2}{V_1}\right) > 0$

b(5) Entropy = degree of randomness = difficulty of predicting the condition of particles

As the volume increases, the difficulty of predicting the particle location is difficult → $\Delta S > 0$

c(5) $S_m(p,T) = S_m^\theta(T) + \int_{p^\theta}^{p} \left(\frac{\partial S_m}{\partial p}\right)_T dp = S_m^\theta(T) - R\ln\left(\frac{p}{p^\theta}\right)$

At constant p^θ; $S_m^\theta(T) = S_m^\theta(T_r) + \int_{T_r}^{T} \frac{C_{pm}}{T} dT = S_m^\circ + C_{pm}\ln\left(\frac{T}{T_r}\right)$

I.G.; $S_m(p,T) = S_m^\circ + C_{pm}\ln\left(\frac{T}{T_r}\right) - R\ln\left(\frac{p}{p^\theta}\right)$ where $S_m^\circ = S_m^\theta(T_r)$

5. a(5) $A = U - TS = q + W - TS$

$dA = \delta q + \delta W - TdS - SdT = \cancel{TdS} - pdV - \cancel{TdS} - SdT$

$\left(\frac{\partial A}{\partial T}\right)_V = -S$ as $dV = 0$ (also $\left(\frac{\partial A}{\partial V}\right)_T = -p$)

b(5) $\left[\frac{\partial}{\partial V}\left(\frac{\partial A}{\partial T}\right)_V\right]_T = -\left(\frac{\partial S}{\partial V}\right)_T$

$\left[\frac{\partial}{\partial T}\left(\frac{\partial A}{\partial V}\right)_T\right]_V = -\left(\frac{\partial p}{\partial T}\right)_V$

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

c(5) $dU = TdS - pdV$

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

6. a(5) Third Law: $U^\theta(T) = U_0^\theta + \int_0^T C_V^\theta dT$; $S(T) = S_0 + \int_0^T \frac{C_p}{T} dT$

b(5) In a cycle, we can remove only a fraction of heat remaining between T and absolute 0 K.

c(5) U_0 = Unknown (to be determined by quantum mechanics)

$S_0 = 0$

EWHA