Homework #5 Solution

6.2) a) $dH = C_p\,dT + \left(V - \left(\frac{\partial V}{\partial T}\right)_P\right) dP$ (equation 6.20)

$$dH = M\,dT + N\,dP$$

$$M = C_p$$

$$N = V - T\left(\frac{\partial V}{\partial T}\right)_P$$

$$\left(\frac{dM}{dP}\right)_T = \left(\frac{dC_p}{dP}\right)_T$$

$$\left(\frac{dN}{dT}\right)_P = \left[\frac{d}{dT}\left(V - T\left(\frac{\partial V}{\partial T}\right)_P\right)\right]_P = \left(\frac{\partial V}{\partial T}\right)_P - T\left(\frac{\partial^2 V}{\partial T^2}\right)_P - \left(\frac{\partial V}{\partial T}\right)_P \cdot \cancel{\frac{dT}{dT}}$$

$$= -T\left(\frac{d^2 V}{dT^2}\right)_P$$

$$\left(\frac{dM}{dP}\right)_T = \left(\frac{dN}{dT}\right)_P$$

$$\boxed{\left(\frac{dC_p}{dP}\right)_T = -T\left(\frac{d^2 V}{dT^2}\right)_P}$$

$V = \frac{RT}{P}$ for ideal Gas

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

$$\left(\frac{\partial^2 V}{\partial T^2}\right)_P = \left(\frac{\partial}{\partial T}\left(\frac{R}{P}\right)\right)_P = 0 \qquad \left(\frac{\partial C_p}{\partial P}\right)_T = 0$$

C_p is constant for ideal Gas

6.2

$$\partial U = C_v dT + \left[T \left(\frac{\partial P}{\partial T}\right)_V - P \right] \partial V$$

$$\partial H = C_p dT + \left[V - T \left(\frac{\partial V}{\partial T}\right)_P \right] dP$$

$$dH = dU + PdV + VdP$$

$$C_p dT + \left[V - T\left(\frac{\partial V}{\partial T}\right)_P \right] dP = C_v dT + \left[T \cdot \left(\frac{\partial P}{\partial T}\right)_V - P \right] dV + PdV + VdP$$

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

multiply each term w/ $\left(\frac{1}{dT}\right)_V$

$$\boxed{C_p = C_v + T \left(\frac{\partial V}{\partial T}\right)_P \left(\frac{\partial P}{\partial T}\right)_V}$$

exp. 6.2 (B)

$$C_p - C_v = \beta T V \left(\frac{\beta}{K}\right)$$

$$\left(\frac{\partial P}{\partial T}\right)_V = \frac{\beta}{K} \quad \text{(equa 6.34)}$$

$$\beta = \frac{1}{V}\left(\frac{\partial V}{\partial T}\right)_P \quad \text{(equa. 3.2)}$$

$$C_p - C_v = \frac{1}{\cancel{V}}\left(\frac{\partial V}{\partial T}\right)_P T \cancel{V} \left(\frac{\partial P}{\partial T}\right)_V$$

$$\boxed{C_p = C_v + T \left(\frac{\partial V}{\partial T}\right)_P \left(\frac{\partial P}{\partial T}\right)_V}$$

6.4 a)

$$P(v-b) = RT$$

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

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

$$= C_v\,dT + \left[\cancel{\frac{TR}{V-b} - \frac{TR}{V-b}}\right] dV$$

$$\boxed{dU = C_v\,dT}$$ C_v is constant so $U = U(t)$

b) $H = U + PV$

$$dH = dU + V\,dP + P\,dV$$

$$dU = T\,dS - P\,dV$$

$$C_p = \left(\frac{\partial H}{\partial T}\right)_p = \left(\frac{\partial U + \cancel{V\partial P} + P\partial V}{\partial T}\right)_p = \left(\frac{T\partial S}{\partial T}\right)_p$$

$$dS = C_v\frac{dT}{T} + \left(\frac{\partial P}{\partial T}\right)_V dV \quad \text{(equa 6.33)}$$

$$C_p = \left(\frac{C_v\,\partial T + \frac{RT}{V-b}\,\partial V}{\partial T}\right)_p$$

$$V = \frac{TR}{P} + b \qquad \left(\frac{\partial V}{\partial T}\right)_p = \frac{R}{P}$$

$$C_p = C_v + P\left(\frac{\partial V}{\partial T}\right)_p$$

$$\boxed{C_p = C_v + R}$$

C_p is constant since C_v & R is constant

so $\gamma = C_p/C_v$ is also constant

6.4c)

$P(V-b)^{\gamma} = \text{constant}$

$P = \frac{TR}{(V-b)}$

$P(V-b)^{\gamma} = TR(V-b)^{\gamma-1}$

$\partial(TR(V-b)^{\gamma-1}) = R\,\partial(T\cdot(V-b)^{\gamma-1})$

$= R[(V-b)^{\gamma-1}\partial T + T\,\partial(V-b)^{\gamma-1}] \quad \ldots\ldots (1)$

For Mechanical Reversible $\quad \partial S = 0$

from equation (6.33)

$\partial S = \frac{C_v \partial T}{T} + \left(\frac{\partial P}{\partial T}\right)_v dV$

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

$\partial S = \frac{C_v\,dT}{T} + \frac{R}{V-b}\,dV$

$= \frac{C_v\,dT}{T} + \frac{C_p - C_v}{V-b}\,dV$

$C_v \frac{dT}{T} = \frac{C_v - C_p}{V-b}\,dV$

$\frac{dT}{T} = \frac{C_v - C_p}{C_v}\,\frac{dV}{V-b}$

$dT = (1-\gamma)\,\frac{T\,dV}{V-b} \quad \ldots\ldots (2)$

$\partial(V-b)^{\gamma-1} = (\gamma-1)(V-b)^{\gamma-2}\,\partial V \quad \ldots\ldots (3)$

6.4c cont sub ② & ③ into ①

$$\partial(TR(v-b)^{\gamma-1}) = R\left[T(1-\gamma)(v-b)^{\gamma-2}dV + T(\gamma-1)(V-b)^{\gamma-2}dV\right]$$

$$\partial(TR(v-b)^{\gamma-1}) = 0$$

$$\partial(TR(v-b)^{\gamma-1}) = \partial(P(V-b)^{\gamma}) = 0$$

so, $\boxed{P(V-b)^{\gamma} = \text{constant}}$

6.11

From Equation 6.59

$$\frac{G^R}{RT} = 2B\rho + \frac{3}{2}C\rho^2 - \ln Z$$

$$\rho = \frac{1}{V}$$

$$\boxed{G^R = RT\left[\frac{2B}{V} + \frac{3C}{2V^2} - \ln Z\right]}$$

$$\boxed{H^R = RT^2\left[\left(\frac{B}{T} - \frac{dB}{dT}\right)\frac{1}{V} + \left(\frac{C}{T} - \frac{1}{2}\frac{dC}{dT}\right)\frac{1}{V^2}\right]}$$

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

$$= -R\left[\frac{2B}{V} + \frac{3C}{2V^2} - \ln Z\right] + RT\left[\left(\frac{B}{T} - \frac{dB}{dT}\right)\frac{1}{V} + \left(\frac{C}{T} - \frac{1}{2}\frac{dC}{dT}\right)\frac{1}{V^2}\right]$$

$$= R\left[\left(\frac{B}{T} - \frac{dB}{T}\right)\frac{T}{V} + \left(\frac{C}{T} - \frac{dC}{2dT}\right)\frac{T}{V^2} - \frac{2B}{V} - \frac{3C}{2V^2} + \ln Z\right]$$

$$= R\left[\frac{B}{V} - \frac{dB}{V} + \frac{C}{V^2} - \frac{TdC}{2dT}\frac{1}{V^2} - \frac{2B}{V} - \frac{3C}{2V^2} + \ln Z\right]$$

$$\boxed{S^R = R\left[-\frac{1}{V}(B + dB) - \frac{1}{V^2}\left(2C - \frac{T}{2}\frac{dC}{dT}\right) + \ln Z\right]}$$

6.14 Redlich/Kwong equation: $\Omega := 0.08664 \qquad \Psi := 0.42748$

$$\beta := \overrightarrow{\left(\Omega \cdot \frac{Pr}{Tr}\right)} \quad \textbf{(3.50)} \qquad q := \overrightarrow{\left(\frac{\Psi}{\Omega \cdot Tr^{1.5}}\right)} \quad \textbf{(3.51)}$$

Guess: $z := 1$

Given $\quad z = 1 + \beta - q \cdot \beta \cdot \dfrac{z - \beta}{z \cdot (z + \beta)} \quad$ **(3.49)**

$$Z(\beta, q) := \text{Find}(z)$$

$$i := 1 .. 14 \qquad I_i := \ln\left(\frac{Z(\beta_i, q_i) + \beta_i}{Z(\beta_i, q_i)}\right) \quad \textbf{(6.62b)}$$

$HR_i := R \cdot T_i \cdot \left[\left(Z(\beta_i, q_i) - 1\right) - 1.5 \cdot q_i \cdot I_i\right] \quad$ **(6.64)** **The derivative in these**

$SR_i := R \cdot \left(\ln\left(Z(\beta_i, q_i)\right) - \beta_i - 0.5 \cdot q_i \cdot I_i\right) \quad$ **(6.65)** **equations equals -0.5**

$Z(\beta_i, q_i) =$	$HR_i =$ $\frac{J}{mol}$	$SR_i =$ $\frac{J}{mol \cdot K}$
0.695	$-2.302 \cdot 10^3$	-5.219
0.605	$-2.068 \cdot 10^3$	-7.975
0.772	$-3.319 \cdot 10^3$	-3.879
0.685	$-4.503 \cdot 10^3$	-6.079
0.729	$-2.3 \cdot 10^3$	-4.784
0.75	$-1.362 \cdot 10^3$	-5.231
0.709	$-4.316 \cdot 10^3$	-5.09
0.706	$-5.381 \cdot 10^3$	-5.59
0.771	$-1.764 \cdot 10^3$	-3.957
0.744	$-2.659 \cdot 10^3$	-4.486
0.663	$-1.488 \cdot 10^3$	-6.682
0.766	$-3.39 \cdot 10^3$	-3.964
0.775	$-2.122 \cdot 10^3$	-3.8
0.75	$-3.623 \cdot 10^3$	-5.132

Ans.

6.17 $T := 323.15 \cdot K$ $\quad t := \frac{T}{K} - 273.15 \quad t = 50$

The pressure is the vapor pressure given by the Antoine equation:

$$P(t) := \exp\left(13.8858 - \frac{2788.51}{t + 220.79}\right) \qquad P(50) = 36.166$$

$$\frac{d}{dt}P(t) = 1.375 \qquad P := 36.166 \cdot kPa \qquad dPdt := 1.375 \cdot \frac{kPa}{K}$$

(a) The entropy change of vaporization is equal to the latent heat divided by the temperature. For the Clapeyron equation, Eq. (6.69), we need the volume change of vaporization. For this we estimate the liquid volume by Eq. (3.63) and the vapor volume by the generalized virial correlation. For benzene:

$$\omega := 0.210 \qquad T_c := 562.2 \cdot K \qquad P_c := 48.98 \cdot bar \qquad Z_c := 0.271$$

$$V_c := 259 \cdot \frac{cm^3}{mol} \qquad T_r := \frac{T}{T_c} \qquad T_r = 0.575 \qquad P_r := \frac{P}{P_c} \qquad P_r = 0.007$$

By Eqs. (3.61), (3.62), (3.58), & (3.59)

$$B_0 := 0.083 - \frac{0.422}{T_r^{1.6}} \qquad B_0 = -0.941 \qquad B_1 := 0.139 - \frac{0.172}{T_r^{4.2}} \qquad B_1 = -1.621$$

$$V_{vap} := \frac{R \cdot T}{P} \cdot \left[1 + \left(B_0 + \omega \cdot B_1\right) \cdot \frac{P_r}{T_r}\right] \qquad V_{vap} = 7.306 \times 10^4 \frac{cm^3}{mol}$$

By Eq. (3.63), $\quad V_{liq} := V_c \cdot Z_c^{\left[(1-T_r)^{0.2857}\right]} \qquad V_{liq} = 93.15 \frac{cm^3}{mol}$

Solve Eq. (6.69) for the latent heat and divide by T to get the entropy change of vaporization:

$$\Delta S := dPdt \cdot \left(V_{vap} - V_{liq}\right) \qquad \Delta S = 100.34 \frac{J}{mol \cdot K}$$ **Ans.**

(b) Here for the entropy change of vaporization:

$$\Delta S := \frac{R \cdot T}{P} \cdot dPdt \qquad \Delta S = 102.14 \frac{J}{mol \cdot K}$$ **Ans.**