3.1 $\rho = \frac{P}{RT}$ $\rho = \rho(P,T)$

$$d\rho = \left(\frac{\partial \rho}{\partial T}\right)_P dT + \left(\frac{\partial \rho}{\partial P}\right)_T dP$$

$$\beta = (-)\frac{1}{\rho}\left(\frac{\partial \rho}{\partial T}\right)_P \qquad k = \frac{1}{\rho}\left(\frac{\partial \rho}{\partial P}\right)_T$$

(−) because density decreases as T increases

$$d\rho = -\rho \beta dT + \rho k \, dP$$

$$\frac{d\rho}{\rho} = k\,dP - \beta\,dT$$

$$\ln \frac{\rho_2}{\rho_1} = k(P_2 - P_1) - \beta\cancelto{0}{(T_2 - T_1)} \qquad \frac{\rho_2}{\rho_1} = 1.01$$

$$\ln 1.01 = 44.18 \times 10^{-6}(P_2 - 1)$$

$$\boxed{P_2 = 226.2 \text{ bar}}$$

3.5 $k = 3.9 \times 10^{-6} - 0.1 \times 10^{-9} P$ $P_1 = 1\text{atm}$ $P_2 = 3000\text{atm}$ $T_1 = T_2 =$ isothermal must assume $V =$ const

$$\frac{dV}{V} = \beta dT - k dP$$

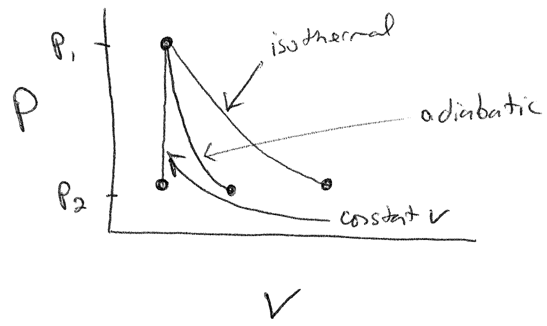
$$dV = V\beta \cancelto{0}{dT} - V k dP$$

$W = F \times L$

$$W = -\int P dV = +V\int_1^{3000} P(3.9\times10^{-6} - 0.1\times10^{-9}P)\,dP = \boxed{16.65 \text{ atm} \cdot ft^3}$$

3.8 $P_1 = 8\,bar$ $P_2 = 1\,bar$

$T_1 = 600\,K$



Constant V

$W = 0 \quad \Delta U = Q = C_v(T_2 - T_1) \quad \Delta H = C_p \Delta T$

$T_2 = T_1 \dfrac{P_2}{P_1} \qquad \Delta T = -525\,K$

so: $\boxed{\Delta U = -10.91 \frac{kJ}{mol} \quad \Delta H = -15.28 \frac{kJ}{mol} \quad W = 0 \quad Q = -10.91 \frac{kJ}{mol}}$

Constant T

$\Delta U = \Delta H = 0 \qquad Q = W$

$\boxed{W = RT \ln \dfrac{P_2}{P_1} = -10.37 \frac{kJ}{mol} = Q \qquad \Delta H = 0 \quad \Delta U = 0}$

Adiabatic

$Q = 0 \quad \Delta U = W = C_v \Delta T$

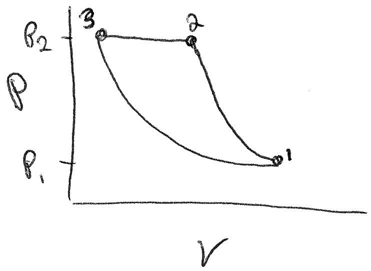
$T_2 = T_1 \left(\dfrac{P_2}{P_1}\right)^{\frac{R}{C_P}} = 331.23\,K$

$\boxed{W = \Delta U = -5.586 \frac{kJ}{mol} \qquad \Delta H = -7.821 \frac{kJ}{mol} \qquad Q = 0}$

(2)

3.18

$T_1 = 30°C \quad P_1 = 100\,kPa$



a) step $1 \to 2$: adiabatic compression to $P_2 = 500\,kPa$

$Q_{12} = 0\ \frac{kJ}{mol} \qquad \Delta U_{12} = W_{12} = C_v \Delta T_{12} \qquad T_2 = T_1 \left(\frac{P_2}{P_1}\right)^{\frac{R}{C_P}}$

$W_{12} = \Delta U_{12} = 3.679\ \frac{kJ}{mol} \qquad \Delta H_{12} = C_P(T_2 - T_1) = 5.15\ \frac{kJ}{mol}$

Step $2 \to 3$: isobaric cooling to 30°C

$T_3 = 30°C$
$P_3 = 500\,kPa$

$\Delta H_{23} = C_P(T_3 - T_2) = Q_{23} \qquad \Delta U_{23} = C_v(T_3 - T_2) \qquad W_{23} = \Delta U_{23} - Q_{23}$

$\Delta H_{23} = -5.15\ \frac{kJ}{mol} = Q_{23} \qquad \Delta U_{23} = -3.679\ \frac{kJ}{mol} \qquad W_{23} = 1.471\ \frac{kJ}{mol}$

Step $3 \to 1$: isothermal expansion

$P_3 = 500\,kPa \quad \Delta U_{31} = 0 \quad \Delta H_{31} = 0 \qquad W_{31} = RT_3 \ln\left(\frac{P_1}{P_3}\right) = -Q$

$W_{31} = -4.056\ \frac{kJ}{mol} \qquad Q_{31} = 4.056\ \frac{kJ}{mol}$

For the cycle: $Q_{cycle} = Q_{12} + Q_{23} + Q_{31} = -1.094\,kJ/mol$

$W_{cycle} = W_{12} + W_{23} + W_{31} = 1.094\,kJ/mol$

(3.18 cont)

b) Irreversible process:

Note: This only affects Q and W

$W_{12}^{IRR} = \frac{W_{12}}{0.8} = 4.598 \frac{kJ}{mol}$ $\quad Q_{12}^{IRR} = \Delta U_{12} - W_{12}^{IRR} = -0.92 \, kJ/mol$

$W_{23}^{IRR} = \frac{W_{23}}{0.8} = 1.839 \frac{kJ}{mol}$ $\quad Q_{23}^{IRR} = \Delta U_{23} - W_{23}^{IRR} = -5.518 \, kJ/mol$

$W_{31}^{IRR} = W_{31} \times 0.8 = -3.245 \frac{kJ}{mol}$ $\quad Q_{31}^{IRR} = -W_{31}^{IRR} = 3.245 \, kJ/mol$

For the cycle: $W_{cycle}^{IRR} = 3.192 \, kJ/mol$

$Q_{cycle}^{IRR} = -3.192 \, kJ/mol$

3.23

$T_1 = 303 \, K$ $\quad T_2 = 303 \, K$ $\quad T_3 = 393 \, K$

$P_1 = 1 \, bar$ $\quad P_2 = ?$ $\quad P_3 = 12 \, bar$

For ~~cycle~~ process: $\Delta U = C_V(T_3 - T_1)$ $\quad \Delta H = C_P(T_3 - T_1)$

$\Delta U = 1.871 \frac{kJ}{mol}$ $\quad \Delta H = 2.619 \frac{kJ}{mol}$

Step 1 -> 2

$P_2 = P_3 \frac{T_1}{T_3}$ $\quad W_{12} = RT_1 \ln\left(\frac{P_2}{P_1}\right)$

$W_{12} = 5.608 \frac{kJ}{mol} = -Q$

Step 2 -> 3

$W_{23} = 0$ $\quad Q_{23} = \Delta U$

For the process

$W_{process} = W_{12} + W_{23} = 5.608 \frac{kJ}{mol}$ $\quad Q_{process} = Q_{12} + Q_{23} = -3.737 \frac{kJ}{mol}$

3.29

$$Pv = RT + \left(b - \frac{\theta}{RT}\right)P$$

solve for v

$$v = \frac{RT}{P} + \left(b - \frac{\theta}{RT}\right) \quad (1)$$

$$\left(\frac{\partial v}{\partial P}\right)_T = -\frac{RT}{P^2} \quad (2)$$

Defn

$$K = -\frac{1}{v}\left(\frac{\partial v}{\partial P}\right)_T$$

subst (1) and (2) into definition

$$\boxed{K = \frac{RT}{P^2\left(\frac{RT}{P} + b - \frac{\theta}{RT}\right)}}$$

Next solve for P

$$P = \frac{RT}{v - b + \frac{\theta}{RT}} \quad (3)$$

3.29

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

[see note]
$$\frac{\left(\frac{\theta}{T} - \frac{d\theta}{dT}\right)}{\left(V - b + \frac{\theta}{RT}\right)^2}$$

from ③ $\left(V - b + \frac{\theta}{RT}\right) = \frac{RT}{P}$

hence

$$\boxed{\left(\frac{\partial P}{\partial T}\right)_V = \frac{P}{T} + \left(\frac{P}{RT}\right)^2\left(\frac{\theta}{T} - \frac{d\theta}{dT}\right)}$$

Note: Uses quotient rule.
$$\frac{d}{dT}\left(\frac{f}{g}\right) = \frac{g\frac{df}{dT} - f\frac{dg}{dT}}{g^2} = \frac{\frac{df}{dT}}{g} - \frac{f\frac{dg}{dT}}{g^2}$$

where $f = RT$ $\quad g = \left(V - b + \frac{\theta}{RT}\right)$

also remember θ is fctn of T

3.30

$B = -242.5 \frac{cm^3}{mol}$ $\quad C = 25200 \frac{cm^6}{mol^2}$ $\quad T = 373k$

$B' = \frac{B}{RT} = -7.817\times10^{-3} \frac{1}{bar}$ $\quad C' = -3.492\times10^{-5} \frac{1}{bar^2}$

$P_1 = 1 bar$ $\quad P_2 = 55 bar$

Must use virial equation to find V_1 and V_2. This will generate 3 values for V (since it's a cubic equation) so pick the one that makes the most sense.

a) For V_1

$$\frac{P_1 V_1}{RT} = 1 + \frac{B}{V_1} + \frac{C}{V_1^3}$$

Can either iterate to find V_1 starting with a guess of $V_1 = \frac{RT}{P_1}$ or use something like matlab to find the roots.

$$\frac{P_1}{RT} V_1^3 - V_1^2 - BV_1 - C = 0$$

using matlab: $\text{roots}([\frac{P_1}{RT} \ -1 \ -B \ -C]) =$ 30768

~~122 + 103i~~

~~122 + 103i~~

$\therefore V_1 = 30768 \frac{cm^3}{mol}$

For V_2

$$\frac{P_2}{RT} V_2^3 - V_2^2 - BV_2 - C = 0$$

using matlab: $\text{roots}([\frac{P_2}{RT} \ -1 \ -B \ -C]) =$ 241.2

~~161 + 181i~~

~~161 + 181i~~

$\therefore V_2 = 241.2 \frac{cm^3}{mol}$

$$W = -\int P\,dV \qquad \frac{PV}{RT} = 1 + \frac{B}{V} + \frac{C}{V^2}$$

$$P = \frac{RT}{V}\left(1 + \frac{B}{V} + \frac{C}{V^2}\right)$$

$$W = -RT\int_{V_1}^{V_2}\left(\frac{1}{V} + \frac{B}{V^2} + \frac{C}{V^3}\right)dV$$

$$\boxed{W = 12.62\ \text{kJ/mol}}$$

b) $W = -\int P\,dV \qquad \frac{PV}{RT} = 1 + B'P + C'P^2$

$$\cancel{P = \frac{RT}{V}(1 + B'P + C'P^2)}$$

$$V = \frac{RT}{P}\left(1 + B'P + C'P^2\right) = \frac{RT}{P} + RTB' + RTC'P$$

$$\frac{dV}{dP} = -\frac{RT}{P^2} + RTC'$$

$$dV = \left(-\frac{RT}{P^2} + RTC'\right)dP$$

$$W = -\int P\left(-\frac{RT}{P^2} + RTC'\right)dP$$

$$W = -\int_{P_1}^{P_2}\left(-\frac{RT}{P} + RTC'P\right)dP$$

$$\boxed{W = 12.596\ \frac{\text{kJ}}{\text{mol}}}$$

Work is different because we truncated virial expansion to the third virial coefficient.