1. In 1897 Berthelot proposed a small modification to Van der Waal's equation for one mole of a non-ideal gas:

$$\left(P + \frac{A}{TV^2}\right)(V - b) = RT,$$

where A and b are empirical constants, and R is the universal gas constant. Following the approach in class for van der Waal's equation, find expressions for the critical volume, temperature and pressure.
[Give your answer in terms of A, b, and R.]

$$P = \frac{RT}{V-b} - \frac{A}{TV^2}$$

$$0 = \left.\frac{dP}{dV}\right|_{T_c} = -\frac{RT_c}{(V-b)^2} + 2\frac{A}{T_c V^3} \Rightarrow \frac{2A}{T_c V^3} = \frac{RT_c}{(V-b)^2} \quad (*)$$

$$0 = \left.\frac{d^2P}{dV^2}\right|_{T_c} = 2\frac{RT_c}{(V-b)^3} - 6\frac{A}{T_c V^4} \overset{(*)}{=} \frac{2RT_c}{(V-b)^3} - \frac{3}{V}\left(\frac{RT_c}{(V-b)^2}\right) \quad (**)$$

$$(**) \Rightarrow \frac{2}{V-b} - \frac{3}{V} = 0 \Rightarrow 2V = 3(V-b) \Rightarrow \boxed{V_c = 3b}$$

$$\text{So } (*) \Rightarrow \frac{2A}{T_c(3b)^3} = \frac{RT_c}{(2b)^2} \Rightarrow T_c^2 = \frac{2A}{R}\cdot\frac{4}{27}\frac{1}{b}$$

$$\Rightarrow \boxed{T_c = \left(\frac{8}{27}\frac{A}{Rb}\right)^{1/2}}$$

$$\text{So } P_c = \frac{RT_c}{V_c - b} - \frac{A}{T_c V_c^2} = \frac{1}{T_c}\left[\frac{RT_c^2}{2b} - \frac{A}{(3b)^2}\right]$$

$$= \frac{1}{T_c}\left[\frac{1}{2b}\left(\frac{8}{27}\frac{A}{b}\right) - \frac{1}{9}\frac{A}{b^2}\right] = \frac{1}{T_c}\frac{A}{b^2}\frac{1}{27}$$

$$= \frac{1}{27}\frac{A}{b^2}\left(\frac{8}{27}\frac{A}{b}\frac{1}{R}\right)^{-1/2} = \left[\frac{1}{27\cdot 8}\frac{A}{b^3}R\right]^{1/2}$$

$$\Rightarrow \boxed{P_c = \frac{1}{6b}\left(\frac{1}{6}\frac{AR}{b}\right)^{1/2}}$$

2. The linear approximation for the equation of state of fresh water near room temperature (T_0) and atmospheric pressure (p_0) is

$$\rho = \rho_0 \left[1 - \alpha_T(T - T_0) + \alpha_p(p - p_0)\right],$$

in which ρ_0 is the density at temperature T_0 and pressure p_0, α_T is the thermal expansion coefficient (assumed constant), and α_p is the isothermal compressibility (assumed constant).

A fixed mass, M, of water at pressure p_0 and temperature T_0 is compressed isothermally from a volume V_0 to a slightly smaller volume $V_1 = V_0 - \Delta V$, with $\Delta V \ll V_0$.

a) Find an expression for the external work required to compress the water, accurate to $(\Delta V)^2$.

b) Find an expression for the heat that left the system during the isothermal compression.

[Give your answers in terms of p_0, V_0, ΔV and α_p.]

a) $T = T_0$ ISOTHERMAL $\Rightarrow \rho = \rho_0[1 + \alpha_p(p - p_0)]$ (*)

WANT $\Delta W = \int_{V_0}^{V_1} p\, dV$

WHERE (*) $\Rightarrow p = p_0 + \frac{1}{\alpha_p}\left(\frac{\rho}{\rho_0} - 1\right) = p_0 + \frac{1}{\alpha_p}\left(\frac{M/V}{M/V_0} - 1\right) = p_0 + \frac{1}{\alpha_p}\left(\frac{V_0}{V} - 1\right)$

So $\Delta W = \int_{V_0}^{V_1} p_0 + \frac{1}{\alpha_p}\left(\frac{V_0}{V} - 1\right) dV = \left(p_0 - \frac{1}{\alpha_p}\right)(V_1 - V_0) + \frac{V_0}{\alpha_p} \ln(V_1/V_0)$

USE $V_1 = V_0 - \Delta V$

$\Rightarrow \Delta W = \left(p_0 - \frac{1}{\alpha_p}\right)(-\Delta V) + \frac{V_0}{\alpha_p} \ln\left(\frac{V_0 - \Delta V}{V_0}\right)$

$\Delta V \ll V_0 \Rightarrow \quad = -\left(p_0 - \frac{1}{\alpha_p}\right)\Delta V + \frac{V_0}{\alpha_p}\left(-\frac{\Delta V}{V_0} - \frac{1}{2}\frac{\Delta V^2}{V_0^2}\right)$

$= -p_0 \Delta V - \frac{1}{2}\frac{V_0 \Delta V^2}{\alpha_p V_0^2}$

EXTERNAL WORK IS $\boxed{\Delta W_{EXT} = -\Delta W = p_0 \Delta V + \frac{1}{2}\frac{1}{\alpha_p}\frac{\Delta V^2}{V_0}}$

b) GENERALLY $dU = \delta Q - \delta W$. BUT ISOTHERMAL $\Rightarrow dU = 0$

So $\delta Q = \delta W$

HEAT THAT LEAVES THE SYSTEM IS $\Delta Q_{OUT} = -\Delta Q = -\Delta W = \Delta W_{EXT}$

$\Rightarrow \boxed{\Delta Q_{OUT} = p_0 \Delta V + \frac{1}{2}\frac{1}{\alpha_p}\frac{(\Delta V)^2}{V_0}}$

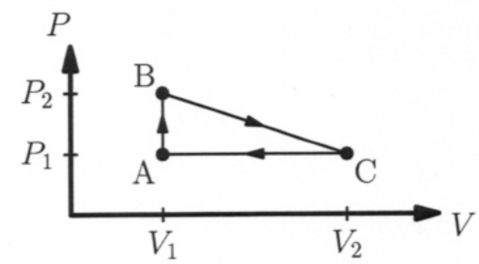
3. Suppose an ideal gas operates in a heat engine whose triangular cycle on a PV diagram is shown to the right. The pressure and volume at B and C are related by $P_2V_1 = P_1V_2$.

    a) What is the total work performed by this engine?

    b) What is the total heat input to the engine?

    c) Evaluate the efficiency of this engine.

    [Give your answers in terms of any or all of P_1, V_1, V_2 and the adiabatic constant γ.]



a) $\Delta W_{TOTAL} = \oint P\,dV$ IS AREA OF PV DIAGRAM $= \frac{1}{2}(P_2-P_1)(V_2-V_1)$ (*)

[EXPLICITLY $\oint P\,dV = \int_A^B P\,dV + \int_B^C P\,dV + \int_C^A P\,dV = 0 + \frac{1}{2}(P_1+P_2)(V_2-V_1) + P_1(V_1-V_2)$]

IN TERMS OF JUST P_1, USE $P_2 = P_1\frac{V_2}{V_1}$ $\Rightarrow$ $\boxed{\Delta W_{TOTAL} = \frac{1}{2}P_1\left(\frac{V_2}{V_1}-1\right)(V_2-V_1) = \frac{1}{2}\frac{P_1}{V_1}(V_2-V_1)^2}$

b) $\Delta Q_{AB} \overset{\text{(ISOCHORIC)}}{=} \Delta U_{AB} = C_V\,\Delta T_{AB} = C_V\left(\frac{P_2V_1}{nR} - \frac{P_1V_1}{nR}\right) = \frac{C_V}{nR}(P_2-P_1)V_1 = \frac{1}{\gamma-1}(P_2-P_1)V_1$

(NOTE $P_2 > P_1$, SO $\Delta Q_{AB} > 0 \Rightarrow$ HEAT IN)

$\Delta Q_{BC} = \Delta U_{BC} + \Delta W_{BC}$

BUT $P_2V_1 = P_1V_2 = nRT \Rightarrow \Delta T_{BC} = 0 \Rightarrow \Delta U_{BC} = 0$

SO $\Delta Q_{BC} = \Delta W_{BC} = \frac{1}{2}(P_1+P_2)(V_2-V_1)$

(NOTE $\Delta Q_{BC} > 0$, SO HEAT IN)

$\Delta Q_{CA} < 0$ (HEAT OUT) SINCE VOLUME DECREASES AT CONSTANT PRESSURE

SO $Q_{IN,TOTAL} = \frac{1}{\gamma-1}(P_2-P_1)V_1 + \frac{1}{2}(P_1+P_2)(V_2-V_1)$

$= \frac{1}{\gamma-1}P_1\left(\frac{V_2}{V_1}-1\right)V_1 + \frac{1}{2}P_1\left(1+\frac{V_2}{V_1}\right)(V_2-V_1)$

$\Rightarrow \boxed{Q_{IN,TOTAL} = P_1\left[\frac{1}{\gamma-1}(V_2-V_1) + \frac{1}{2}\frac{1}{V_1}(V_2^2-V_1^2)\right]}$

c) EFFICIENCY IS $\eta = \frac{\Delta W_{TOTAL}}{Q_{IN,TOTAL}} = \frac{\frac{1}{2}\frac{P_1}{V_1}(V_2-V_1)^2}{P_1\left[\frac{1}{\gamma-1}(V_2-V_1) + \frac{1}{2}\frac{1}{V_1}(V_2^2-V_1^2)\right]}$

$\Rightarrow \boxed{\eta = \frac{1}{2}\frac{(V_2-V_1)/V_1}{\frac{1}{\gamma-1} + \frac{1}{V_1}(V_2+V_1)} = \frac{V_2-V_1}{\frac{2}{\gamma-1}V_1 + (V_1+V_2)}}$

4. For a mole of graphite, the heat capacity at constant pressure is well represented over a wide range of temperatures by

$$C_p = a + bT - c\frac{1}{T^2},$$

in which a, b and c are constants.

Suppose a mole of graphite is heated at constant pressure from temperature T_1 to temperature T_2. Find an expression for its increase in entropy during this process. [Give your answer in terms of a, b, c, T_1, and T_2.]

USE 1^{ST} LAW IN TERMS OF ENTHALPY:

$$dH = \underbrace{\delta Q}_{=TdS} + \underbrace{VdP}_{=0 \text{ ISOBARIC}} = TdS$$

ALSO $dH = C_p\, dT$

SO $dS = C_P \frac{1}{T} dT$

$$= \left(a + bT - c\frac{1}{T^2}\right)\frac{1}{T}dT$$

$$= \left(\frac{a}{T} + b - c\frac{1}{T^3}\right)dT$$

$$\Rightarrow \Delta S = \int_{T_1}^{T_2} \frac{a}{T} + b - c\frac{1}{T^3}\, dT = \left(a \ln T + bT + \frac{1}{2}c\frac{1}{T^2}\right)\Big|_{T_1}^{T_2}$$

$$\Rightarrow \boxed{\Delta S = a \ln(T_2/T_1) + b(T_2 - T_1) + \frac{1}{2}c\left(\frac{1}{T_2^2} - \frac{1}{T_1^2}\right)}$$