Problem 1

Consider the following reaction which occurs at T=298 K and P = 1 bar. (1 mole of H_2CO_3)

$H_2CO_3 \rightarrow HCO_3^- + H^+$

	H_2CO_3	HCO_3^-	H^+
ΔH (kJ)	-699.65	-691.99	0
S (J/K)	187.4	91.2	0
ΔG (kJ)	-623.08	-586.77	0

a) Using the data in the table, calculate ΔG for this reaction.
b) Calculate the equilibrium constant K.
c) If the initial amount of H_2CO_3 is 1 mole, how many moles of each reactant and product will be present once the reaction reaches equilibrium?

a) $\Delta G = G_{products} - G_{reactants} = \left(-586.77 \frac{kJ}{mol}\right) - \left(-623.08 \frac{kJ}{mol}\right)$

$= 36.3 \ kJ/mol$

b) $K = \exp(-\Delta G/RT) = \exp\left(-\frac{36.3 \times 10^3 \ J/mol}{(8.31 \ J/mol \ K)(298 K)}\right) = 4.2 \times 10^{-7}$

c) Invoke law of mass action :

	H_2CO_3	HCO_3^{-}	H^+
Initial	1	0	0
final	1-x	x	x
change	-x	+x	+x

$K = \frac{[H^+][HCO_3^{-}]}{[H_2CO_3]} = \frac{(x)(x)}{(1-x)} = \frac{x^2}{1-x}$

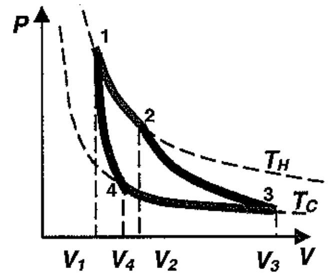
It is possible to solve this quadratic equation.

we approximate : $x^2/_{1-x} \sim x^2$ $\quad x = \sqrt{K} = 6.5 \times 10^{-4}$ moles

at equilibrium : H^+, HCO_3^{-} : 6.5×10^{-4} moles

H_2CO_3 : $1 - 6.5 \times 10^{-4}$ moles $\sim$ 1 mole

Problem 2 Consider a Carnot cycle where the working substance is a van der Waals gas (1-2 and 3-4 are isotherms, 2-3 and 4-1 – adiabats). The temperatures of the hot and cold reservoirs are T_H and T_C, respectively. Calculate the efficiency of this heat engine and compare it with that for the Carnot cycle with an ideal gas.



$$\epsilon = \frac{\delta Q_H - \delta Q_C}{\delta Q_H}$$ ⟹ need to calculate heat in/out for each step of cycle.

1-2: Isothermal expansion $(T = T_H)$ $\Delta U = \delta W + \delta Q$

$$\delta W_{12} = -\int_{V_1}^{V_2} dV\, P(V) = -\int_{V_1}^{V_2} dV \left[\frac{N k_B T_H}{V - Nb} - \frac{N^2 a}{V^2}\right] =$$

$$= -N k_B T_H \ln\left(\frac{V_2 - Nb}{V_1 - Nb}\right) + N^2 a \left(\frac{1}{V_1} - \frac{1}{V_2}\right)$$

$$U_{vdw} = U_{ideal} - \frac{N^2 a}{V}$$

$$\Delta U_{vdw}^{1-2} = \left[\frac{f}{2} N k_B T_H - \frac{N^2 a}{V_2}\right] - \left[\frac{f}{2} N k_B T_H - \frac{N^2 a}{V_1}\right] = N^2 a \left(\frac{1}{V_1} - \frac{1}{V_2}\right)$$

$$\delta Q_{12} = \Delta U_{vdw}^{1\cdot 2} - \delta W = N^2 a \left(\frac{1}{V_1} - \frac{1}{V_2}\right) + N k_B T_H \ln\left(\frac{V_2 - Nb}{V_1 - Nb}\right)$$
$$- N^2 a \left(\frac{1}{V_1} - \frac{1}{V_2}\right)$$

$$\delta Q_{12} = N k_B T_H \ln\left(\frac{V_2 - Nb}{V_1 - Nb}\right)$$

and by same argument $\delta Q_{34} = N k_B T_C \ln\left(\frac{V_4 - Nb}{V_3 - Nb}\right)$

Since steps 2-3 and 4-1 are adiabats, no heat is exchanged here.

$$\epsilon = \frac{\delta Q_{12} - \delta Q_{34}}{\delta Q_{12}} = \frac{T_H \ln\left(\frac{V_2 - Nb}{V_1 - Nb}\right) - T_C \ln\left(\frac{V_4 - Nb}{V_3 - Nb}\right)}{T_H \ln\left(\frac{V_2 - Nb}{V_1 - Nb}\right)}$$

(T_H, T_C) and (V_1, V_2, V_3, V_4) are not all independent

2-3 and 4-1 : isentropic steps $\Delta S_{23} = \Delta S_{41} = 0$

$$S_{vdw} = \frac{f}{2} N k_B \ln T + N k_B \ln (V - Nb) + f(N)$$

$$\Delta S_{23} = \left(\frac{f}{2} N k_B \ln T_C - \frac{f}{2} N k_B \ln T_H\right) + \left(N k_B \ln (V_3 - Nb) - N k_B \ln (V_2 - Nb)\right)$$

$$= \frac{f}{2} N k_B \ln \frac{T_C}{T_H} + N k_B \ln \left(\frac{V_3 - Nb}{V_2 - Nb}\right) = 0$$

so : $$\frac{f}{2} N k_B \ln \frac{T_C}{T_H} = - N k_B \ln \left(\frac{V_3 - Nb}{V_2 - Nb}\right)$$

$$\frac{f}{2} \ln \frac{T_H}{T_C} = + \ln \left(\frac{V_3 - Nb}{V_2 - Nb}\right) \Rightarrow \left(\frac{T_H}{T_C}\right)^{f/2} = \frac{V_3 - Nb}{V_2 - Nb}$$

and similarly for ΔS_{41} : $\left(\frac{T_H}{T_C}\right)^{f/2} = \frac{V_4 - Nb}{V_1 - Nb}$

$$\Rightarrow \frac{V_4 - Nb}{V_1 - Nb} = \left(\frac{T_H}{T_C}\right)^{f/2} = \frac{V_3 - Nb}{V_2 - Nb}$$

Simplify expression for efficiency :

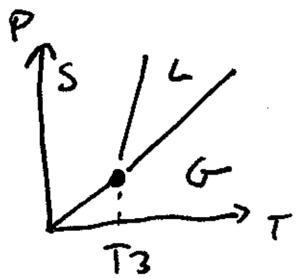
$$\epsilon = \frac{T_H \ln \frac{V_2 - Nb}{V_1 - Nb} - T_C \left(\frac{V_2 - Nb}{V_1 - Nb}\right)}{T_H \ln \frac{V_2 - Nb}{V_1 - Nb}} = \frac{T_H - T_C}{T_H}$$

efficiency ϵ is same as for Carnot cycle with ideal gas.

Problem 3 For the diatomic gas H_2 near its triple point (T_3=14 K), the latent heat of vaporization L_{vap}=1.01 kJ/mol. The liquid density is 71 kg/m^3, and the solid density is 81 kg/m^3. The melting line T_M =13.99 K + P/(3.3x10^6 Pa/K). Compute the latent heat of sublimation L_{sub} at the triple point.

The vapor pressure equation for H_2 is given as $P=P_o \exp(-L_{vap}/RT)$, where P_o is 90 MPa. Assume that the H_2 vapor can be treated as an ideal gas. Compute the slope of the sublimation line $T_{sub}(P)$ near the triple point.

a) near triple point $T_3 = 14K$:



$$\left.\begin{aligned} L_{sub} &= T_3 (S_G - S_S) \\ L_{melt} &= T_3 (S_L - S_S) \\ L_{vap} &= T_3 (S_G - S_L) \end{aligned}\right\} \quad L_{sub} = L_{melt} + \underset{\text{given}}{L_{vap}}$$

$\Rightarrow$ must calculate L_{melt}

$$L_{melt} = \frac{T_3 (V_L - V_S)}{d T_{melt} / dP} \qquad H_2: \text{ molar wt} = 2g/\text{mole}$$

$$V_L = \frac{2g/\text{mole}}{71 kg/m^3} \qquad V_S = \frac{2g/\text{mole}}{81 kg/m^3} \qquad \frac{dT_m}{dP} = \frac{1}{3.3\times10^6 \ Pa/K}$$

$$L_{melt} = (14K)\left[\frac{.002 kg/\text{mole}}{71 kg/m^3} - \frac{.002 kg/\text{mole}}{81 kg/m^3}\right]\frac{1}{3.3\times10^6 \ Pa/K}$$

$$= 162 \ J/\text{mole}.$$

$$L_{sub} = L_{melt} + L_{vap} = 162\frac{J}{\text{mole}} + 1010\frac{J}{\text{mole}} = \underline{\underline{1172 \ J/\text{mole}}}$$

b) Solid - Gas phase line : sublimation

$$\frac{dP}{dT} = \frac{L_{sub}}{T_3}\frac{1}{V_G - V_S} \qquad \text{since } V_G >> V_S$$

$$\frac{dP}{dT_{sub}} = \frac{L_{sub}}{V_G T_3}$$

treating H_2 as ideal gas : $P_3 V_G = RT_3 \Rightarrow V_G = \frac{RT_3}{P_3}$

$$V_G = \frac{(8.3\,J/mol\,K)(14K)}{P_o \exp(-L_{vap}/RT_3)} = \frac{116.2\,J/mol}{9\times10^7 Pa \exp\left(\frac{-100J/mol}{(8.3J/molK)(14K)}\right)}$$

$$= \frac{116.2J/mol}{15,114.5\ Pa} = .0077\ m^3/mole$$

so finally $\frac{dP}{dT} = \frac{L_{sub}}{T_3 V_G} = \frac{1172\ J/mole}{(14K)(.0077m^3/mole)}$

$$= 1.09\times10^4\ Pa/K.$$

Problem 5 A cylinder closed with a piston is filled with the saturated water vapor at T = 100 °C. The vapor is heated up by 1°C, and, at the same time, the piston is moved to prevent condensation and to keep the vapor saturated (the system is "moving" along the coexistence curve). Find the relative change in the vapor volume, $\Delta V/V$. Assume that the vapor is an ideal gas, the latent heat of vaporization L_{vap}=40.7 kJ/mol, and the vapor density is negligible in comparison with the water density.

Clausius - Clapeyron eq'n for liquid-gas coexistence curve:

$$\frac{\Delta P}{\Delta T} = \frac{L_{vap}}{T(V_G - V_L)} \sim \frac{L_{vap}}{T V_G} \Rightarrow \Delta P = \frac{L_{vap}}{T V_G} \Delta T$$

since we have an ideal gas

$$\frac{P_i V_i}{T_i} = \frac{P_f V_f}{T_f}$$ and for small temperature changes $$\frac{\Delta P}{P} \sim -\frac{\Delta V}{V}$$

So we see $$\frac{\Delta V}{V} = -\frac{\Delta P}{P} = -\frac{L_{vap}}{T V_G P} \Delta T$$

$$\frac{\Delta V}{V} = \frac{-L_{vap} \Delta T}{(P V_G) T} = \frac{-L_{vap} \Delta T}{(RT) T} = -\frac{L_{vap}}{R} \frac{\Delta T}{T^2}$$

$$= \frac{(-40.7 \text{ kJ/mol})(1\text{K})}{(8.3 \text{ J/mol K})(373\text{K})^2} = -0.035$$

[3.5%]

Problem 5 The vdW gas undergoes an isothermal expansion from volume V_1 to volume V_2. Calculate the change in the Helmholtz free energy.

$$F = F(T, V, N) \qquad dF = \frac{\partial F}{\partial T} dT + \frac{\partial F}{\partial V} dV + \frac{\partial F}{\partial N} dN$$

$$= -S dT - P dV + \mu dN = -P dV$$

$$\Delta F = \int_{V_1}^{V_2} dF = -\int_{V_1}^{V_2} P dV \qquad P = \frac{RT}{V-Nb} - \frac{N^2 a}{V^2}$$

$$\Delta F = -\int_{V_1}^{V_2} dV \left[\frac{RT}{V-Nb} - \frac{N^2 a}{V^2} \right] = RT \ln V-Nb \Big|_{V=V_1}^{V=V_2} + N^2 a \left(\frac{-1}{V} \right) \Big|_{V=V_1}^{V=V_2}$$

$$= RT \ln \frac{V_2 - Nb}{V_1 - Nb} - \left(\frac{1}{V_2} - \frac{1}{V_1} \right) = \mathrm{I} - \mathrm{II}$$

since $S_{vdw} = \frac{f}{2} R \ln T + R \ln (V-Nb) + f(N)$

here $\Delta S_{vdw} = R \ln \frac{V_2 - Nb}{V_1 - Nb}$

$\mathrm{I} = -T \Delta S_{vdw}$

$\Delta F = \Delta u - T \Delta S \quad \Rightarrow \quad \mathrm{II} = \Delta u.$