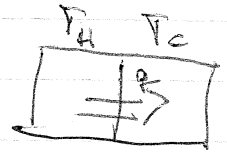
Problem Set 3, sample solutions Mar. 9, R

(1) (p1)

(a) final Temp. T_f: insulated container – adiabatic process, no work

$\Rightarrow \Delta U = 0$ (1st law)



$m_H = 165g$ $T_H = 373.15K$

$m_c = 145g$ $T_c = 273.15K$

Thus

$+q_H = -q_c$

given off by hot water — absorbed by cold water

(unknown)

$$n_H C_m^{water}(T_H - T_f) = -n_c(T_c - T_f) C_m^{water}$$

solve for T_f $\quad n_H T_H - n_f T_f = -n_c T_c + n_c T_f$

$$T_f = \frac{1}{n_H + n_c}(n_c T_c + n_H T_H)$$

but n_c and n_H are $\propto m_c, m_H$, respectively

$$\Rightarrow T_f = \frac{1}{m_H + m_c}(m_c T_c + m_H T_H)$$

$= 326K$
$= 53.2°C$ } (agrees to "common sense"!)

Entropy This process is irreversible.

Reversible model process:

(i) reversibly heat cold water to T_f

(ii) " cool hot " " "

(p2)

$$\Delta S = \Delta S_1 + \Delta S_2$$

$$= n_C C_m \ln \frac{T_f}{T_C} + n_H C_m \ln \frac{T_f}{T_H}$$

$$n_i = \frac{m_i}{M} \; ; \; M = 18.015 \frac{g}{mol}$$

$$n_H = 9.16 \text{ mol}$$

$$n_C = 8.05 \text{ mol}$$

$$\Delta S_1 = 107.1 \text{ J/K}$$

$$\Delta S_2 = -92.4 \text{ J/K}$$

$$\Delta S = 14.8 \text{ J K}^{-1} > 0 \text{ spontaneous}$$

<u>part (b)</u> <u>final temp. T_f</u>

again $\Delta U = 0$; heat balance

$$q_H = -q_{fusion} - q_C$$

(heat to melt ice at 273.15 K)

$$n_H C_m^{water} (T_H - \underset{\text{unknown}}{T_f}) = n_C \Delta H_m^{fus} - n_C C_m^{water} (T_C - T_0)$$

solve for T_f:

$$T_f = \frac{1}{(n_C + n_H)} \left(n_C T_C + n_H T_H - \frac{n_C \Delta H_m^{fus}}{C_m^{water}} \right)$$

use n_C, n_H from part (a) (or again m_C, m_H)

$$T_f = 289 \text{ K} = 15.8 \,^\circ C$$

Entropy

(1) reversibly melt ice at 0°C
(2) reversibly heat cold water to T_f } similar to (a)
(3) " cool hot " " " } (but different ΔT)

$$\Delta S_1 = \frac{q_{rev}}{T} = \frac{n_c \Delta H_m^{fus}}{T}$$ const T ; n_c from (a)

$= 177(4)$ J/K

$\Delta S_2 = 34.1$ J/K

$\Delta S_3 = -176(3)$ J/K

$\Delta S = 35.$ J/K

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(2) adiabatic: $q = 0 \Rightarrow \Delta S = 0$

$C_{V,m} = \frac{3}{2}R \Rightarrow C_{p,m} = C_{V,m} + R = \frac{5}{2}R$ (ideal gas)

and $\gamma = 5/3$

adiabat: $p_1 V_1^\gamma = p_2 V_2^\gamma$

$$V_1 = \frac{nRT_1}{p_1} = 0.0218 \text{ m}^3$$

$V_2 =$ ~~0.0331 m³~~ 0.0331 m^3

$$T_2 = \frac{p_2 V_2}{nR} = 295.5 \text{ K} = 296 \text{ K}$$

$\Delta U = n C_{V,m} \Delta T = -1.77$ kJ

$\Delta H = n C_{p,m} \Delta T = -2.95$ kJ

(Q3)

$$\Delta G = \Delta H - T\Delta S \quad (\text{const } T)$$

(a) 300 K $\quad \Delta G = -34.1\ \text{kJ mol}^{-1}$

600 K $\quad 16.9\ \text{kJ mol}^{-1}$

1000 K $\quad 85.0\ \text{kJ mol}^{-1}$

(b) $\Delta G = 0 \Rightarrow T = \dfrac{\Delta H}{\Delta S} = 501\ \text{K}$

(Q4) (a) isothermal, ideal gas: $\Delta U = 0 \quad (T = 294.15\ \text{K})$

$$q_{rev} = -w_{rev} = \int_{V_1}^{V_2} P\,dV = nRT \ln\frac{V_2}{V_1} = -424\ \text{J}$$

$V_1 = 6.00\ \text{L}$

$V_2 = 3.00\ \text{L}$

$$\Delta S_{syst} = \frac{q_{rev}}{T} \quad (\text{const } T)$$

$$= nR \ln\frac{V_2}{V_1} = -1.44\ \text{J/K}$$

reversible: $\Delta S_{surr} = -\Delta S_{syst} = 1.44\ \text{J/K}$

$$\Delta G = \underbrace{\Delta H}_{0 \text{ ideal gas, isothermal}} - T\Delta S \quad (\text{const } T)$$

$$\Delta G = -T\Delta S = -q_{rev} = w_{rev}$$

(b) final state of the system is the same as in (a). Hence, all state functions of the system are the same, i.e.

$\Delta U = \Delta H = 0$

$\Delta G = 424\ \text{J}$

$\Delta S_{syst} = -1.44\ \text{J/K}$

Surr: We need $q_{surr} = -q_{syst}$:

$$\Delta U = 0 = q_{syst} + w_{syst}$$

$$-q_{surr} = q_{syst} = -w_{syst} = \int P\,dV$$

integral for the irreversible process

$$= P\Delta V$$

const P

$$= 3\,atm * (-3.00\,L)$$

$$= -912\,J = -q_{surr}$$

{ Work done on system is larger than in part (a)

$$\Delta S_{surr} = \frac{q_{surr}}{T} = 3.10\,J/K$$

(Q5) From lecture: $\left(\frac{\partial U}{\partial V}\right)_T = -P + T\left(\frac{\partial P}{\partial T}\right)_V$

v. d. Waals: $P = \frac{nRT}{V-nb} - \frac{n^2a}{V^2}$

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

Hence $\left(\frac{\partial U}{\partial V}\right)_T = \underbrace{-\frac{nRT}{V-nb} + \frac{n^2a}{V^2}}_{-P} + T\frac{nR}{V-nb}$

$$\boxed{= \frac{n^2a}{V^2}}$$

P6

Q6 (from midterm 2, 2011)

1. Free energy calculation **5 marks**

(a) Calculate ΔG for 1.00 mole of liquid water as the external pressure is increased from 1.00 bar to 2.00 bar at a constant temperature of 298.0K. *You may need some or all of the following information: molar mass of water: 18.015 g mol^{-1}; density at 25.0°C: 997.05 kg m^{-3}.*

(b) Calculate ΔG for 1.00 mole of an ideal gas as the external pressure is increased from 1.00 bar to 2.00 bar at a constant temperature of 298.0K.

Gibbs eq'n $dG = VdP - SdT$ const T, $dT = 0$; $\left(\frac{\partial G}{\partial P}\right)_T = V \Rightarrow$

$dG = VdP$

1 $\int dG = \Delta G = \int V dP$

2 (a) V of l does not change over this pressure range (i.e. constant):

$\Delta G = V\int dP = V\Delta P$

$V = n\frac{M}{\rho} = 1.807 * 10^{-5} m^3 \Rightarrow \Delta G = 1.81 J$

2 (b) gas: V does change: $V = \frac{nRT}{P}$

$\Delta G = \int \frac{nRT}{P} dP = nRT\int \frac{dP}{P} = nRT \ln \frac{P_2}{P_1}$

$= 1.72 kJ$