Chemistry 231 **Assignment #7** (due Tuesday 17 November, in class)

1. This question refers to a **heat engine** operating with $T_H = 293$ K and $T_C = 263$ K.

a) Calculate the minimum amount of heat q_H that must be absorbed by the engine to perform 1.00 MJ work on the surroundings.

b) This engine is inefficient compared to modern heat engines. Why?

[4] **c)** If the engine in run in reverse as a **heat pump**, calculate the minimum amount of work required to "pump" 1.00 MJ of heat into the warm reservoir.

d) Part **c** shows that inefficient engines run in reverse can provide heat much more cheaply than electric resistive heaters. Explain briefly.

2. **a)** Starting with $dH = TdS + Vdp$, use a suitable Maxwell relation to show

$$\left(\frac{\partial H}{\partial p}\right)_T = V(1-\beta T)$$

[2] **b)** Use the equation derived in part **a** to prove $(\partial H/\partial p)_T = 0$ for ideal gases.

3. This question refers to the **de-mixing** of 100.0 moles of air at 300 K and 1.00 bar to produce 80.0 moles of pure N_2 and 20.0 moles of pure O_2.

[6] **a)** Calculate q, w, ΔU, ΔH, ΔS and ΔG assuming ideal-gas behavior.

b) Prove the de-mixing process is impossible in an isolated system.

c) Calculate the minimum amount of work that must be provided to produce 80.0 moles of pure N_2 and 20.0 moles of pure O_2 from 100.0 moles of air.

d) The availability of pure N_2 and pure O_2 has important practical applications. Name two.

4. Huge amounts of energy (*and time and money*!) must be spent to purify chemicals using fractional distillation, recrystallization, chromatography, and other separation techniques. Why?
[1] Give a very brief (one or two lines) thermodynamic explanation.

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5. Show:

a) liquid water and water vapor are in equilibrium at 100 °C and 1.00 bar.

$$H_2O(l) = H_2O(g,)$$

[3] **b)** $H_2O(l) \rightarrow H_2O(g)$ is spontaneous at 1.00 bar and temperatures higher than 100 °C.

c) $H_2O(g) \rightarrow H_2O(l)$ is spontaneous at 1.00 bar and temperatures lower than 100 °C.

Hint: $(\partial G/\partial T)_p = -S$ and therefore $(\partial \Delta G/\partial T)_p = -\Delta S$

Data at 100 °C: $\Delta H_{vap,m}^{o} = 40.65$ kJ mol^{-1}
$S_m^{o}(H_2O, l) = 86.54$ J K^{-1} mol^{-1}
$S_m^{o}(H_2O, g) = 195.48$ J K^{-1} mol^{-1}

6. A reactor for the **synthesis of ammonia**

$$N_2(g) + 3H_2(g) = 2NH_3(g)$$

contains N_2 at 20.0 bar, H_2 at 12.0 bar and NH_3 at 110.0 bar at 500 K. Assuming ideal gas behavior:

a) Show the gases in the reactor are not at chemical equilibrium.

b) To reach chemical equilibrium, should more NH_3 be produced? Justify your answer.

[4$^+$] **c)** For a **bonus point**, give the equilibrium partial pressures of N_2, H_2 and NH_3 in the reactor.

d) For a higher yield of ammonia, should the pressure in the reactor be increased? Explain.

e) For a higher yield of ammonia, should the temperature in the tank be increased? Explain.

Data at 500 K: $\Delta H_{fm}^{o}(NH_3, g) = -49.8$ kJ mol^{-1}
$\Delta G_{fm}^{o}(NH_3, g) = 4.80$ kJ mol^{-1}

Chem 231 **Assignment #7** $\left(w_{engine} = -w_{surr}\right)$

Q1 a) maximum engine efficiency $\varepsilon_{max} = 1 - \frac{T_C}{T_H} = \frac{-w_{max}}{q_H}$

$(w = -1.00\ MJ)$ $-$ engine work

maximum work done on the surroundings $= (+1.00\ MJ)$ $-w_{max} = \left(1 - \frac{T_C}{T_H}\right) q_H$

$\left(\text{max. efficiency } 1 - \frac{T_C}{T_H} = 0.102\right)$ $+1.00\ MJ = \left(1 - \frac{263\ K}{293\ K}\right) q_H$

$$\boxed{q_H = +9.77\ MJ}$$

b) The 10.2 % efficiency of the engine is relatively low compared to modern heat engines operating with much **higher T_H values** (up to about 1600 K for gas turbines!)

c) "pumping" 1.00 MJ heat into the T_H reservoir means the heat pump "loses" 1.00 MJ heat at T_H

$$q_H = -1.00\ MJ$$

from $1 - \frac{T_C}{T_H} = \frac{-w_{max}}{q_H}$ get $w_{max} = -\left(1 - \frac{T_C}{T_H}\right) q_H$

$$w_{max} = -\left(1 - \frac{263\ K}{293\ K}\right)(-1.00\ MJ) = \boxed{0.102\ MJ}$$

d) For an electric resistive heater, 0.102 MJ of electric work gives 0.102 MJ heat. For the reversible heat pump, 0.102 MJ electric work gives 1.00 MJ heat (≈ 10 times larger)

(Q2) a) $dH = TdS + Vdp$ ÷ dp at constant T

$$\left(\frac{\partial H}{\partial P}\right)_T = T\left(\frac{\partial S}{\partial P}\right)_T + V\cancel{\left(\frac{\partial P}{\partial P}\right)_T}^{\,1}$$

but what is $\left(\frac{\partial S}{\partial P}\right)_T$? (not experimentally convenient)

independent variables P, T suggest looking at

$$dG = -S\underset{\equiv}{dT} + V\underset{\equiv}{dP}$$

with the Maxwell relation $\left(\frac{\partial S}{\partial P}\right)_T = -\left(\frac{\partial V}{\partial T}\right)_P$

substitute

$$\left(\frac{\partial H}{\partial P}\right)_T = T\left(\frac{\partial S}{\partial P}\right)_T + V = -T\left(\frac{\partial V}{\partial T}\right)_P + V$$

$$= -TV\beta + V$$

$$\left(\frac{\partial H}{\partial P}\right)_T = V(1-\beta T)$$

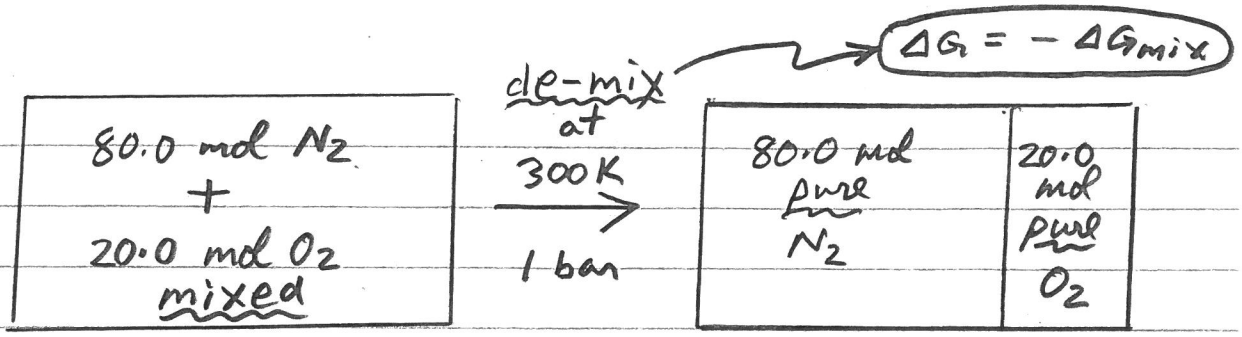
(recall $\beta = \frac{1}{V}\left(\frac{\partial V}{\partial T}\right)_P$ (volumetric thermal expansivity))

b) for an ideal gas: $\beta = \frac{1}{T}$

and $\left(\frac{\partial H}{\partial P}\right)_T = V\left(1 - \frac{1}{T}T\right) = 0$

H depends only on T

(Q3)



a) isothermal (constant T) ideal gases:

$$\boxed{\Delta U = \Delta H = 0}$$

$$\boxed{q = \Delta H = 0} \text{ (constant pressure)}$$

$$\Delta U = q + w \Rightarrow 0 = 0 + w \qquad \boxed{w = 0}$$ (no volume change)

$$\Delta G = -\Delta G_{mix} = -\left(n_{N2} RT \ln x_{N2} + n_{O2} RT \ln x_{O2}\right)$$

$$= -(80.0)(8.314)(300)\ln(0.800) - (20.0)(8.314)(300)\ln(0.200)$$

$$\Delta G = (44525 + 80285)\,J = \boxed{\Delta G \quad 125\ kJ}$$

$$\Delta G = \Delta(H - TS) = \overset{0}{\Delta H} - \Delta(TS) = -T\Delta S$$

$$\Delta S = -\Delta G/T = -(125000\,J)/300K = \boxed{\Delta S \quad -416\ J\,K^{-1}}$$

b) The entropy decreases for an isolated system ($q = w = 0$)
$\Rightarrow$ impossible

c) $-w' \leq -\Delta G_{T,P} \Rightarrow w' \geq \Delta G_{TP}$ $\quad w' \geq 125\ kJ$

minimum work required to purify the air is $\boxed{125\ kJ}$

d) pure N_2 used to make NH_3 (mostly for fertilizers to help feed the world)

pure O_2 used to make high-quality steel

(Q4) De-mixing to produce pure chemicals is nonspontaneous ⇒ requires energy input

(Q5) a) at 100 °C and 1.00 bar (p°)

$H_2O(l) = H_2O(g)$

for 1.00 mol H_2O: $\Delta H_m = \Delta H^\circ_{vap,m} = 40.65\ kJ\ mol^{-1}$

$\Delta S_m = S^\circ_m(H_2O, g) - S^\circ_m(H_2O, l)$

$= (195.48 - 86.54)\ J\ K^{-1}\ mol^{-1}$

$\Delta S_m = 108.94\ J\ K^{-1}\ mol$

$\Delta G_m = \Delta(H_m - TS_m) = \Delta H_m - \Delta(TS_m) = \Delta H_m - T\Delta S_m$ (fixed T)

$= 40650\ J\ K^{-1}\ mol^{-1} - (373.15\ K)(108.94\ J\ K^{-1}\ mol^{-1})$

$= (40650 - 40650)\ J\ mol^{-1}$

$\boxed{\Delta G_m = 0 \text{ at fixed } T, p}$

∴ reversible

b) $\Delta G = 0$ at 100 °C, 1.00 bar and

$\left(\frac{\partial \Delta G}{\partial T}\right) = -\Delta S = -108.94\ J\ K^{-1}$ ΔG decreases with T

∴ $\boxed{\Delta G < 0 \text{ above } 100\ ^\circ C}$ for $H_2O(l) \rightarrow H_2O(g)$ and evaporation is spontaneous

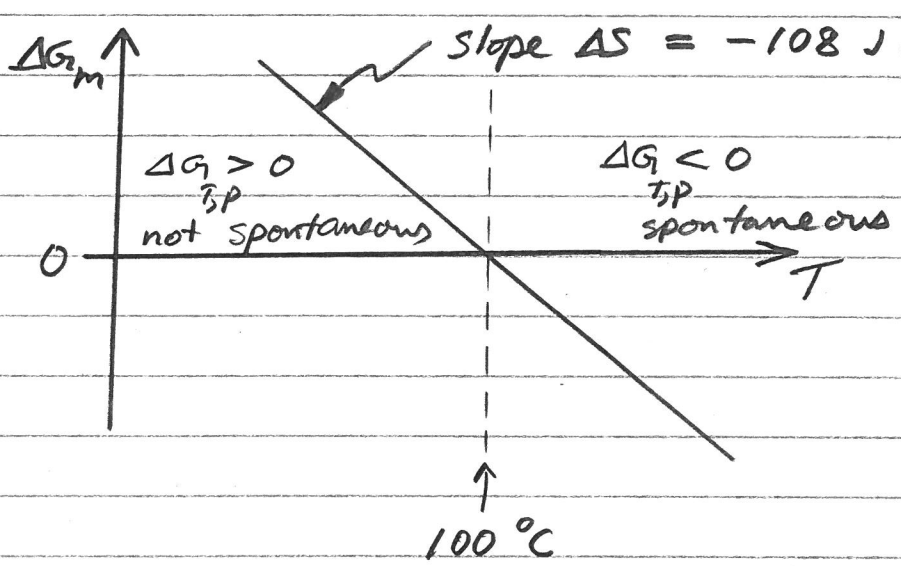
(Q5 cont.)

c) similarly, $H_2O(\ell) \rightarrow H_2O(g)$

has $\Delta G = 0$ at 100 °C, 1.00 bar

and $(\partial \Delta G / \partial T)_p < 0$ (ΔG decreases with T)

$\therefore$ $\boxed{\Delta G > 0 \text{ below } 100\ ^\circ C}$ and
water evaporation is not spontaneous at 1.00 bar



(Q6) $N_2(g) + 3H_2(g) = 2NH_3(g)$

equilibrium constant $K = \dfrac{P_{NH3}^2}{P_{N2}\, P_{H2}^3} = \exp(-\Delta G^\circ / RT)$

$\Delta G^\circ = 2\Delta G_{fm}^\circ(NH_3, g) = 2(4.80\ kJ\ mol^{-1})$
$= 9600\ kJ\ mol^{-1}$

$K = \exp[-9600/(8.314)500] =$ $\boxed{K = 0.0993}$

(Q6 cont.)

a) $P_{N2} = 20.0$ bar
$P_{H2} = 12.0$ bar
$P_{NH3} = 110.0$ bar

given $Q = \dfrac{P_{NH3}^2}{P_{N2} P_{H2}^3} =$ **Q = 0.350**

($K = 0.0993$)

$Q > K$

the gas mixture is not at chemical equilibrium
(too much product, not enough reactants)

b) the back reaction $N_2 + 3H_2 \leftarrow 2NH_3$ is spontaneous

c) the reaction takes place in a "reactor" (a tank) at fixed volume

under these conditions $p_i = \dfrac{n_i RT}{V}$

so the partial pressure of gas i is proportional to its partial pressure p_i

	N_2	+	$3H_2$	=	$2NH_3$
initial:	20.0 bar		12.0 bar		110.0 bar
at equilibrium	$20.0 + x$		$12.0 + 3x$		$110.0 - 2x$

Solve $K = \dfrac{(110.0 - 2x)^2}{(20.0 + x)(12.0 + 3x)^3} = 0.0993$ for x

(Q6 c) cont.)

define $f(x) = \dfrac{(110.0 - x)^2}{(20.0 + x)(12.0 + 3x)^2}$

plot $f(x)$ against x and locate the value of x that gives $f(x) = K = 0.0993$

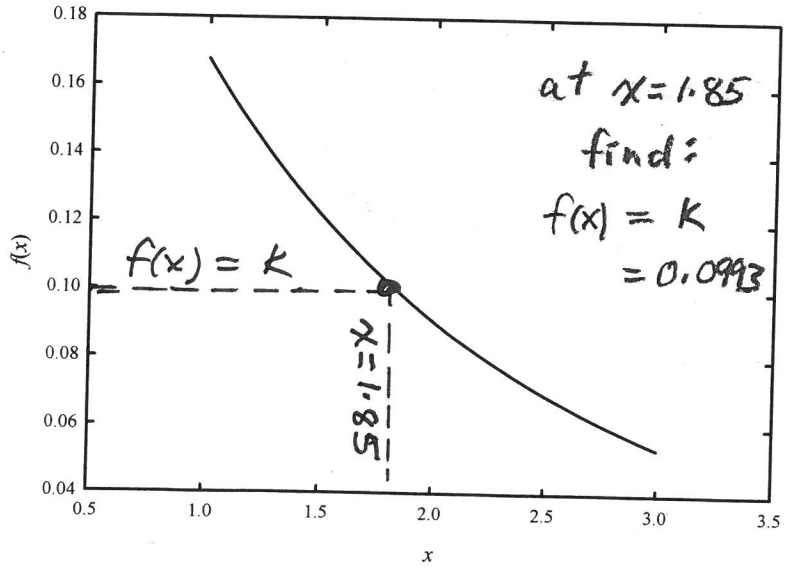
find $x = 1.846$

$P_{N2,eq} = 20.0 + 1.846 = 21.8$ bar

$P_{H2,eq} = 12.0 + 3(1.846) = 17.5$ bar

$P_{NH3,eq} = 110.0 - 1.846 = 108.1$ bar

(check $\left(\dfrac{P_{NH3}^2}{P_{N2}\,P_{H2}^2}\right)_{eq} = \dfrac{108.1^2}{21.8(17.5^3)} = 0.100$ ✓)



e) $N_2(g) + 3H_2(g) = 2NH_3(g)$

$\Delta H^\circ = 2\Delta H_{fm}(NH_3, g)$

$= 2(-49.8\ kJ\ mol^{-1})$

$\Delta H^\circ = -99.6\ kJ\ mol^{-1} < 0$ exothermic

$$\frac{d \ln K(T)}{dT} = \frac{\Delta H^\circ}{RT^2} < 0$$

$K(T)$ and the yield of the NH_3 product decrease with the temperature

reduce the temperature for a higher equilibrium NH_3 yield
(the back reaction is endothermic, opposing the temperature increase)

d) 4 moles of gas → 2 moles of gas

$N_2(g) + 3H_2(g) = 2NH_3(g)$

If the pressure is increased, the system responds by trying to oppose the change by shifting to the product side which has a smaller volume than the reactant side