(*This assignment is *optional.* You lose no marks if it is not handed it in.)

1. This question refers to the chemical equilibrium of nitrogen tetroxide and nitrogen dioxide at 25 °C.

$$N_2O_4(g) \;=\; 2\,NO_2(g)$$
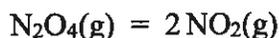
The equilibrium constant K for the reaction is 0.333 at 25 °C.

   a) One mole of pure N_2O_4 partially decomposes to NO_2 at 1.00 bar total pressure. Show 0.723 mol N_2O_4 and 0.555 mol NO_2 are present at equilibrium.

[8] **b)** Show the conversion of one mole of pure N_2O_4 to 0.723 mol pure N_2O_4 and 0.555 mol pure NO_2 at 1.00 bar *is not spontaneous.*

   c) Calculate ΔG_{mix} for the mixing of 0.723 mol N_2O_4 and 0.555 mol NO_2 at 25 °C and 1.00 bar.

   d) To indicate the importance of mixing in chemical reaction equilibrium, show the conversion of one mole of pure N_2O_4 to a mixture of 0.723 mol N_2O_4 + 0.555 mol NO_2 *is spontaneous.*

2. Equilibrium constant data for the reaction $2Ag_2O(s) = 4Ag(s) + O_2(g)$ from 0 °C to 100 °C:

$t\,/\,°C$	K
0.0	0.0000120
25.0	0.000119
50.0	0.000826
75.0	0.00434
100.0	0.0183

[9]

   a) Prepare a van't Hoff graph of the data by plotting $\ln K$ against $1/T$.

   b) Is the reaction exothermic? Justify your answer.

   c) Is $\Delta H°$ for the reaction independent of temperature? Explain.

   d) Calculate $\Delta G°$, $\Delta H°$ and $\Delta S°$ at 25 °C. (*Suggestion:* Use $\Delta G° = -RT\ln K = \Delta H° - T\Delta S°$)

   e) Use the reaction quotient Q to show solid Ag_2O is stable in air ($p_{O2} = 0.20$ bar) at 25 °C.

   f) Calculate the decomposition temperature of $Ag_2O(s)$ heated in air.

3. 1.00 mol N_2 and 4.00 mol H_2 react at 500 K and constant volume to form NH_3. The initial pressures are $p_{N2} = 2.00$ bar and $p_{H2} = 8.00$ bar. Calculate the number of moles of NH_3 at equilibrium.

[3]

   Data: the equilibrium constant K of the reaction $N_2(g) + 3H_2(g) = 2NH_3(g)$ is 10.1 at 500 K.

Chem 231   Assignment #8

(Q1) a) $N_2O_4(g)$ $\rightleftharpoons$ $2NO_2(g)$

initially: $P_{N_2O_4(i)} = 1.00\ bar$ $P_{NO_2(i)} = 0$

equilibrium: $P_{N_2O_4}$ P_{NO_2}
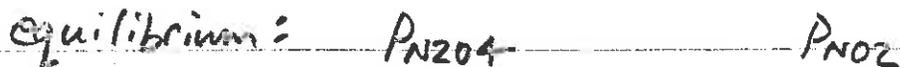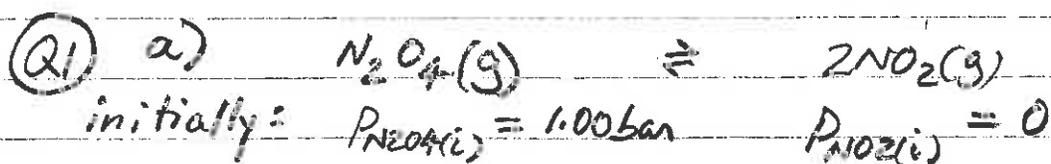
total pressure $p = 1.00\ bar = P_{N_2O_4} + P_{NO_2}$

$$K = 0.333 = \frac{P_{NO_2}^2}{P_{N_2O_4}} = \frac{P_{NO_2}^2}{1.00\,bar - P_{NO_2}}$$

$$K - K P_{NO_2} = P_{NO_2}^2 \implies P_{NO_2}^2 + K P_{NO_2} - K = 0$$

solve
quadratic $P_{NO_2} = \dfrac{-K \pm \sqrt{K^2 + 4K}}{2}$ $\left(\begin{array}{l}\text{only the}\\ \text{positive root}\\ \text{is acceptable}\end{array}\right)$

$$P_{NO_2} = \frac{-0.333 + \sqrt{0.333^2 + 4(0.333)}}{2} = 0.4341\ bar$$

$$P_{N_2O_4} = p - P_{NO_2} = 1.00\ bar - 0.4341\ bar$$

$P_{N_2O_4} = 0.5659\ bar$ $\left(\text{check}: \dfrac{(0.4341)^2}{0.5659} = 0.333\ = K\right)$

$N_2O_4(g) = \quad 2NO_2(g)$
$1.000\,mol - y \qquad 2y$ $y = moles\ of\ N_2O_4\ reacted$

$NO_2\ mol$
$fraction = \dfrac{P_{NO_2}}{P} = 0.4341 = \dfrac{2y}{1-y+2y} = \dfrac{2y}{1+y}$

$y = 0.2772$ $moles\ N_2O_4 = 1-y = 0.723\ mol$
                    $moles\ NO_2 = 2y = 0.555\ mol$

(Q1 cont.)

b) 1.000 mol pure N_2O_4 $\xrightarrow[\text{1 bar}]{25°C}$ 0.723 mol pure N_2O_4
$+$
0.555 mol pure NO_2
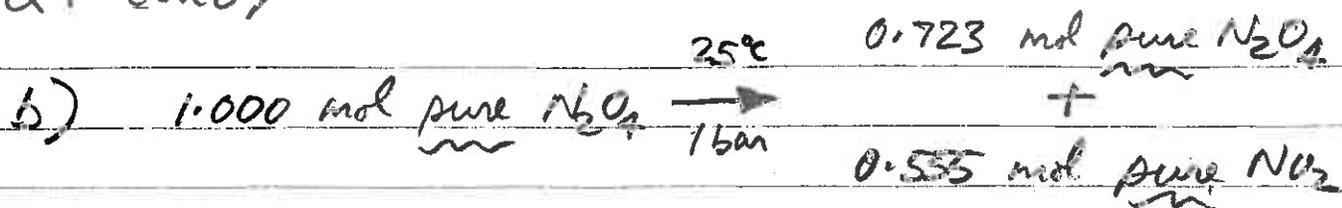
$$\Delta G_1 = (0.723 \text{ mol}) \Delta G_{fm}^{\circ}(N_2O_4, g) + 0.555 \text{ mol } \Delta G_{fm}^{\circ}(NO_2, g)$$

$$- (1.000 \text{ mol}) \Delta G_{fm}^{\circ}(N_2O_4, g)$$

$$= (-0.277 \text{ mol}) \Delta G_{fm}^{\circ}(N_2O_4, g) + (0.555 \text{ mol}) \Delta G_{fm}^{\circ}(NO_2, g)$$

$$= 0.277 \left[(-1 \text{ mol}) \Delta G_{fm}^{\circ}(N_2O_4, g) + (2 \text{ mol}) \Delta G_{fm}^{\circ}(NO_2, g) \right]$$

$$\Delta G_1 = 0.277 \, \Delta G_R^{\circ} \leftarrow \left(\begin{array}{l} \text{standard Gibbs energy change} \\ \text{for } N_2O_4(g) = 2 NO_2 \, g \end{array} \right)$$

$$= 0.277(-RT \ln K) = -0.277 (8.314 \tfrac{J}{K \cdot mol})(298.15 K) \ln(0.333)$$

$$\Delta G_1 = +755 \text{ J mol}^{-1} \qquad \underline{\text{not spontaneous}} \left(\begin{array}{l} \Delta G_1 > 0 \text{ at} \\ \text{fixed } T, p \end{array} \right)$$

c) Mix 0.723 mol pure N_2O_4 and 0.555 mol pure NO_2

$$\Delta G_{mix} = n_{N2O4} \, RT \ln \left(\frac{P_{N2O4}}{P} \right) + n_{NO2} \, RT \ln \left(\frac{P_{NO2}}{P} \right) \qquad \text{(from a)}$$

$$= (0.723 \text{ mol})(8.314 \tfrac{J}{K \cdot mol})(298.15 K) \ln(1 - 0.4341)$$

$$+ (0.555)(8.314)(298.15) \ln(0.4341)$$

$$= -1020 \text{ J} - 1148 \text{ J}$$

$$\Delta G_{mix} = -2170 \text{ J}$$

(Q1 cont.)

d) 1.000 mol pure N_2O_4 $\rightarrow$ 0.723 mol N_2O_4 + 0.555 mol NO_2 mixed
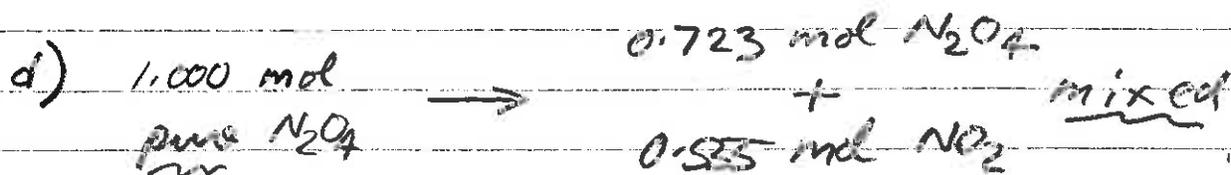
$$\Delta G_{total} = \Delta G \left(\begin{array}{c} chemical \\ reaction \\ only \end{array} \right) + \Delta G_{mix} \left(\begin{array}{c} mixing \\ only \end{array} \right)$$

$$= \Delta G \,(part\ b) + \Delta G \,(part\ c)$$

$$= +755\ J + (-2170\ J)$$

$$\Delta G_{total} = -1420\ J \qquad < 0 \qquad overall\ process \left(\begin{array}{c} react \\ + \\ mix \end{array} \right)$$
$$\qquad\qquad\qquad\qquad is\ spontaneous$$

(Q2) a) $2Ag_2O(s) = 4Ag(s) + O_2(g)$
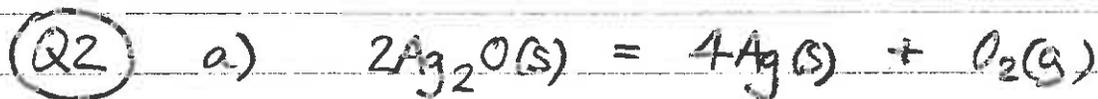
Plot $\ln K$ against $\frac{1}{T}$ (see attached graph)

linear regression gives

$$\ln K = \underset{(intercept)}{16.017} - \underset{(slope)}{(7470.0\ K)} \frac{1}{T}$$

b) $\dfrac{d\ln K}{d\frac{1}{T}} = -7470.0\ K = -\dfrac{\Delta H_R^0}{R}$

$$\Delta H_R^0 = R(7470.0\ K) = (8.314\ J\,K^{-1}mol^{-1})(7470\ K)$$

$$\Delta H_R^0 = 62105\ J\ mol^{-1} \quad \left(>0, endothermic \right)$$
$$\qquad\qquad\qquad\qquad\quad system\ absorbs\ heat$$

Q2 a)

vant' Hoff plot of $\ln K$ against $1000/T$ for the reaction

$$2\,Ag_2O(s) \;=\; 4\,Ag(s) \;+\; O_2(g)$$

slope against $1000/T \;=\; -7.470$ K

slope against $T \;=\; -7{,}470.$ K

$\Delta H^o \;=\; -Rd\ln K/d(1/T)$

$\;=\; -R(-7{,}470\ K) \;=\; 62{,}100\ J\ mol^{-1}$

ln$K$

$1000/T\ /\ (K^{-1})$
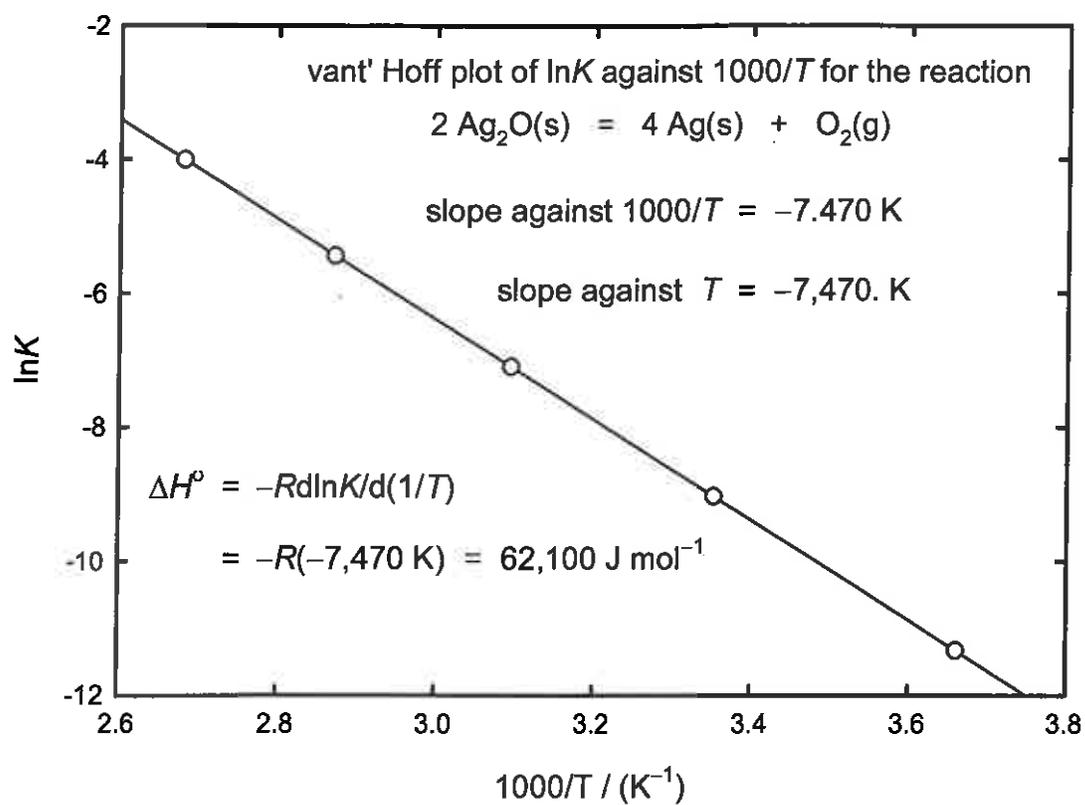
(Q2 cont.)

c) slope of $\ln K$ against $\frac{1}{T}$ = $-\frac{\Delta H_R^0}{R}$

slope appears to be constant (a "straight-line" graph)
suggests ΔH_R^0 is constant

d) at 25 °C $K = 0.000119$

$\Delta G_R^0 = -RT \ln K = -(8.314\ J\ K^{-1}\ mol^{-1})(298.15)\ln(0.000119)$

$$\boxed{\Delta G_R^0 = 22400\ J\ mol^{-1}} = \Delta(H_R^0 - TS_R^0)$$ (T fixed)

$\Delta G_R^0 = \Delta H_R^0 - T\Delta S_R^0$ $\Delta S_R^0 = \dfrac{\Delta H_R^0 - \Delta G_R^0}{T}$

$$\boxed{\Delta H_R^0 = 62105\ J\ mol^{-1}}$$ (from b)

$\Delta S_R^0 = \dfrac{62105 - 22400}{298.15}\ \dfrac{1}{K} = 133.2\ \dfrac{J}{K}$

e) air: $Q = P_{O_2} = 0.20\ bar$
   $K = 0.000119$ at 25°C $Q > K$
   backs reaction favorable $2Ag_2O(s) \longleftarrow 4Ag(s) + O_2(g)$
   $Ag_2O(s)$ is stable

f) $Ag_2O(s)$ decomposes in air when $Q = K = 0.20\ bar$

$\ln K = \ln(0.20) = 16.017 - (7470K)\dfrac{1}{T_{decomp}}$ $= -1.609$

$T_{decomp} = 424\ K$ $(151°c)$

(Q3) 1.00 mol N_2 at 2.00 bar } react at constant
4.00 mol H_2 at 8.00 bar } volume to form NH_3

$$N_2(g) + 3H_2(g) = 2NH_3(g)$$
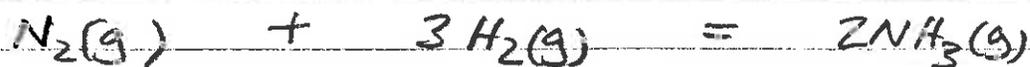
initially: 2.00 bar   8.00 bar   0 bar

at equilibrium: 2.00 bar $-y$ 8.00 bar $-3y$ $2y$

(at constant volume $p_i = n_i \frac{RT}{V}$ is proportional to n_i)

$$K = \frac{p_{NH_3}^2}{p_{N2}\, p_{H2}^3} = \frac{(2y)^2}{(2.00-y)(8.00-3y)^3} = 10.1$$

cubic equation in y not easily to solve analytically

suggestion: plot values of the function $f(y)$ against y

$$f(y) = \frac{(2y)^2}{(2.00-y)(8.00-3y)^3} - 10.1 \qquad (0 \le y \le 2.00)$$

find the y value that gives $f(y) = 0$

attached graph gives $y = 1.889$

$$p_{NH_3} = 2y = 2(1.889 \text{ bar}) = 3.778 \text{ bar}$$
(2.00 bar $N_2 \Rightarrow$ 1.00 mol N_2 initially)
$$\text{moles } NH_3 = \frac{1}{2} \, 3.778 \text{ mol} = 1.889 \text{ mol}$$

(Q3)   Plot of f(y)
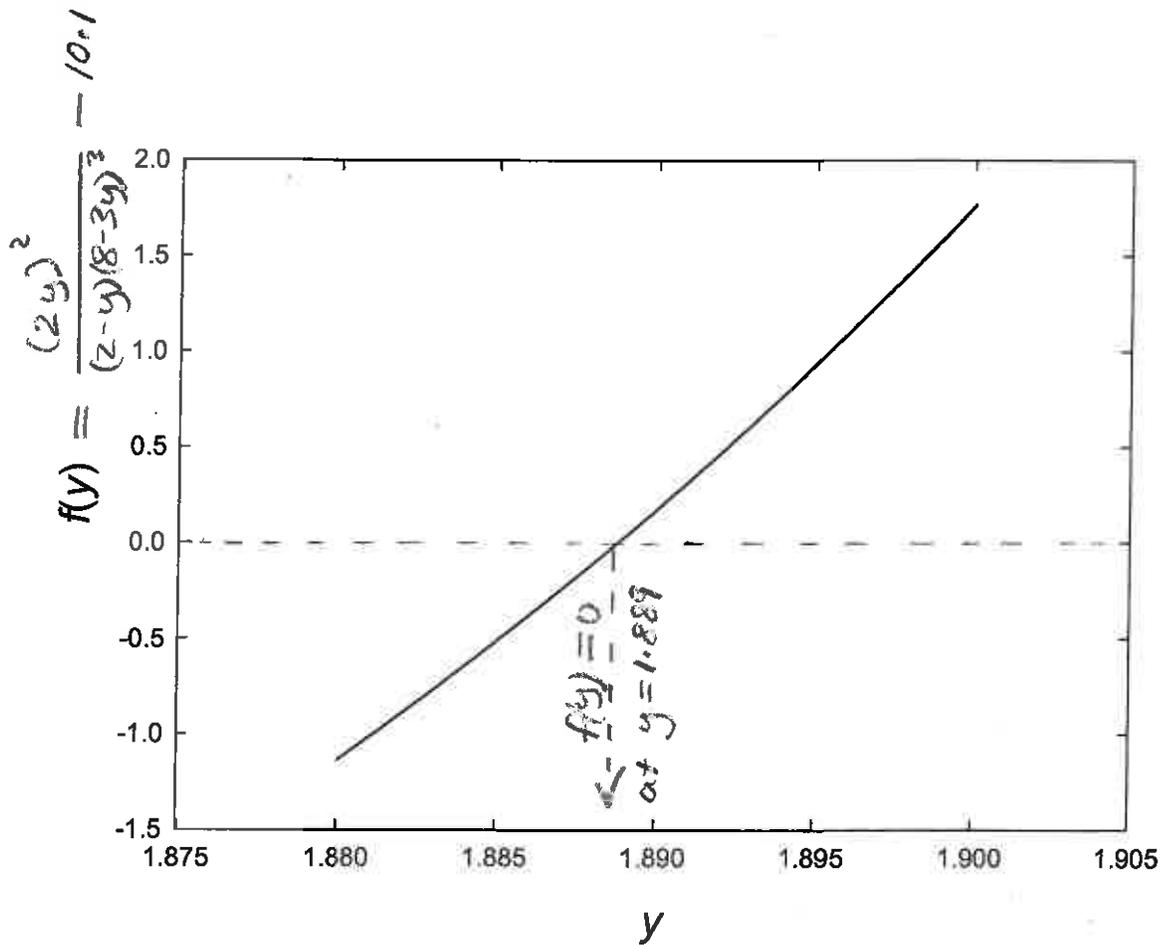
$$f(y) = \frac{(2y)^2}{(2-y)(8-3y)^3} - 10.1$$

$$\frac{(2y)^2}{(2-y)(8-3y)^3} = 10.1 \quad \text{when} \quad y = 1.889$$