

CHM 3400 – Fundamentals of Physical Chemistry
 Second Hour Exam
 March 25, 2020

There are five problems on the exam. Do all of the problems. Show your work.

$R = 0.082057 \text{ L}\cdot\text{atm}/\text{mole}\cdot\text{K}$
 $R = 0.083145 \text{ L}\cdot\text{bar}/\text{mole}\cdot\text{K}$
 $R = 8.3145 \text{ J}/\text{mole}\cdot\text{K}$
 $F = 96485. \text{ C}/\text{mol}$

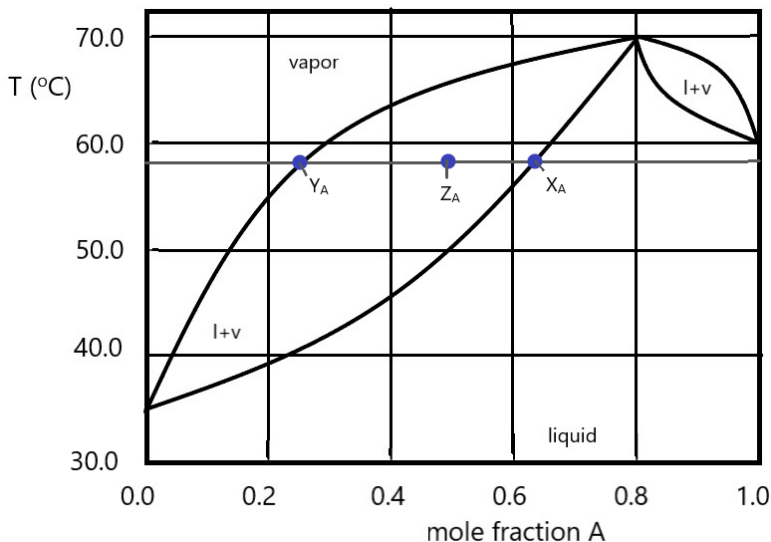
$N_A = 6.022 \times 10^{23}$
 $1 \text{ L}\cdot\text{atm} = 101.3 \text{ J}$
 $1 \text{ atm} = 1.013 \text{ bar} = 1.013 \times 10^5 \text{ N}/\text{m}^2$
 $1 \text{ atm} = 760 \text{ torr}$
 $(1 \text{ volt})\cdot(1 \text{ Coulomb}) = 1 \text{ Joule}$

1. (20 points) The vapor pressure of an unknown pure organic liquid is $p = 288.1 \text{ torr}$ at $T = 45.0 \text{ }^\circ\text{C}$ and $p = 605. \text{ torr}$ at $T = 70.0 \text{ }^\circ\text{C}$. Find the following:

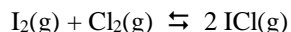
- $\Delta H_{\text{vap}}^\circ$, the enthalpy of vaporization for the liquid.
- T_{vap}° , the normal boiling point for the liquid.

2. (24 points) A phase diagram for a solution of two volatile liquids A and B is given below, at a pressure $p = 1.00 \text{ atm}$. Use the information in the phase diagram to answer the following questions.

- What are $T_{A,\text{vap}}^\circ$ and $T_{B,\text{vap}}^\circ$, the normal boiling point for pure A and pure B?
- Do A and B form an azeotrope? If your answer is yes, give the mole fraction of A and the normal boiling point for the azeotrope.
- Consider a system containing 2.148 moles of A and 2.252 moles of B, at a temperature $T = 58.0 \text{ }^\circ\text{C}$. At this temperature the mole fraction of A in the liquid phase is $X_A = 0.638$ and the mole fraction of A in the vapor phase is $Y_A = 0.248$. Based on this information, find n_l , the total number of moles in the liquid phase.



3. (24 points) There is interest in the gas phase reaction of elemental halogens to form interhalogen compounds. As an example, consider the following reaction:



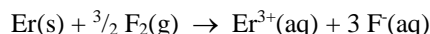
- Write the expression for K , the equilibrium constant for the above reaction, in terms of the activities of the reactants and products.
- Give the expression for K , the equilibrium constant for the above reaction, assuming ideal behavior.
- Find the numerical value for K for the above reaction at $T = 25.0 \text{ }^\circ\text{C}$.
- Find the numerical value for K for the above reaction at $T = 60.0 \text{ }^\circ\text{C}$.

NOTE: Use the data given below (at $T = 25.0 \text{ }^\circ\text{C}$) to answer part c and d of this problem.

Substance	ΔH°_f (kJ/mol)	S° (J/mol·K)	ΔG°_f (kJ/mol)
$\text{Cl}_2(\text{g})$	0.0	223.1	0.0
$\text{I}_2(\text{g})$	62.4	260.7	19.3
$\text{ICl}(\text{g})$	17.8	247.6	- 5.5

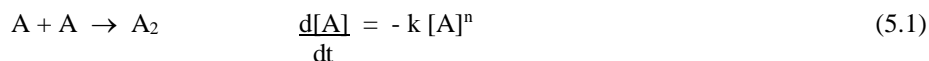
4. (16 points) Because of their use in the electronics industry there is interest in the electrochemical properties of rare earth metals and their chemical compounds.

Using the data below, find E°_{cell} , and $\Delta G^\circ_{\text{rxn}}$, the standard cell potential and change in free energy, for the reaction



Reduction half-reaction	E° (v)
$\text{Er}^{3+}(\text{aq}) + 3 \text{e}^- \rightarrow \text{Er}(\text{s})$	- 2.331
$\text{F}_2(\text{g}) + 2 \text{e}^- \rightarrow 2 \text{F}^-(\text{aq})$	+ 2.866

5. (16 points) In a sample of pure molecules of A and an inert gas, with $p_A \ll p_{\text{inertgas}}$, the following irreversible chemical reaction is found to occur.



where n , the order of reaction, is either 1 or 2.

In a particular experiment, the initial concentration of A is $[\text{A}]_0 = 4.18 \times 10^{-3} \text{ mol/L}$. After 100.0 s, the concentration of A is found to be $[\text{A}] = 2.74 \times 10^{-3} \text{ mol/L}$.

- Based on this information, and assuming the reaction is first order homogeneous, find the value for the rate constant for the reaction, including correct units.
- Based on this information, and assuming the reaction is second order homogeneous, find the value for the rate constant for the reaction, including correct units.

Solutions.

1) a) $\ln(p_2/p_1) = -(\Delta H^\circ_{\text{vap}}/R) \{ (1/T_2) - (1/T_1) \}$

So $\Delta H^\circ_{\text{vap}} = - \frac{R \ln(p_2/p_1)}{\{ (1/T_2) - (1/T_1) \}} = - \frac{(8.3145 \text{ J/mol}\cdot\text{K}) \ln(605./288.1)}{\{ (1/343.15 \text{ K}) - (1/318.15 \text{ K}) \}} = 26.94 \text{ kJ/mol}$

b) We can use the same equation as in part a. If we solve for $1/T_2$, we get

$$(1/T_2) = (1/T_1) - \frac{R \ln(p_2/p_1)}{\Delta H^\circ_{\text{vap}}}$$

We now know the value for $\Delta H^\circ_{\text{vap}}$. We can pick either data point for p_1 , T_1 (so we will pick 605. torr and 343.15 K), and 760 torr for p_2 . So

$$(1/T_2) = (1/343.15 \text{ K}) - \frac{(8.3145 \text{ J/mol}\cdot\text{K}) \ln(760./605.)}{26940. \text{ J/mol}} = 2.844 \times 10^{-3} \text{ K}^{-1}$$

$$T_2 = \frac{1}{2.985 \times 10^{-3} \text{ K}^{-1}} = 335.1 \text{ K} = 61.9 \text{ }^\circ\text{C}$$

2) a) $T_{A,\text{vap}}^\circ = 60.0 \text{ }^\circ\text{C}$ $T_{B,\text{vap}}^\circ = 36.0 \text{ }^\circ\text{C}$

b) Yes. The azeotrope is at $X_A = 0.80$, $T = 70.0 \text{ }^\circ\text{C}$

c) $n = n_A + n_B = 2.148 \text{ mol} + 2.252 \text{ mol} = 4.400 \text{ mol}$

$$Z_A = \frac{n_A}{n} = \frac{2.148}{4.400} = 0.4882$$

By the lever rule $\frac{n_g}{n_\ell} = \frac{X_A - Z_A}{Z_A - Y_A} = \frac{(0.638 - 0.4882)}{(0.4882 - 0.248)} = 0.6236$; so $n_g = 0.6236 n_\ell$

$$n = n_\ell + n_g = n_\ell + 0.6236 n_\ell = 1.6236 n_\ell$$

$$n_\ell = \frac{n}{1.6236} = \frac{4.400 \text{ mol}}{1.6236} = 2.710 \text{ mol}$$

3) a) $K = \frac{(a_{\text{ICl}})^2}{(a_{\text{I}_2})(a_{\text{Cl}_2})}$

b) For ideal behavior, $K = \frac{(p_{\text{ICl}})^2}{(p_{\text{I}_2})(p_{\text{Cl}_2})}$

To do parts c and d we need to find $\Delta G^\circ_{\text{rxn}}$ and $\Delta H^\circ_{\text{rxn}}$.

$$\begin{aligned} \Delta G^\circ_{\text{rxn}} &= [2 \Delta G^\circ_f(\text{ICl}(\text{g}))] - [\Delta G^\circ_f(\text{I}_2(\text{g})) + \Delta G^\circ_f(\text{Cl}_2(\text{g}))] \\ &= [2(-5.5)] - [(19.3) + (0.0)] = -30.3 \text{ kJ/mol} \end{aligned}$$

$$\begin{aligned} \Delta H^\circ_{\text{rxn}} &= [2 \Delta H^\circ_f(\text{ICl}(\text{g}))] - [\Delta H^\circ_f(\text{I}_2(\text{g})) + \Delta H^\circ_f(\text{Cl}_2(\text{g}))] \\ &= [2(17.8)] - [(62.4) + (0.0)] = -26.8 \text{ kJ/mol} \end{aligned}$$

c) At $T = 25.0\text{ }^\circ\text{C} = 298.15\text{ K}$

$$\ln(K) = - \frac{\Delta G^\circ_{\text{rxn}}}{RT} = - \frac{(-30300. \text{ J/mol})}{(8.3145 \text{ J/mol}\cdot\text{K})(298.15 \text{ K})} = 12.22 \quad \text{so } K = e^{12.22} = 2.0 \times 10^5$$

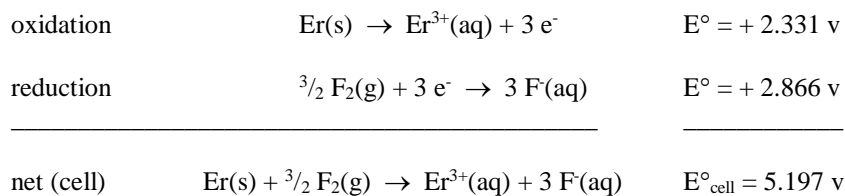
d) At $T = 60.0\text{ }^\circ\text{C} = 333.15\text{ K}$

$$\begin{aligned} \ln(K_2/K_1) &= -(\Delta H^\circ_{\text{rxn}}/R) \{ (1/T_2) - (1/T_1) \} \\ &= - [(-26800. \text{ J/mol}) / (8.3145 \text{ J/mol}\cdot\text{K})] \{ (1/333.15 \text{ K}) - (1/298.15 \text{ K}) \} = -1.136 \end{aligned}$$

Taking the inverse logarithm of both sides of this relationship gives

$$\frac{K_2}{K_1} = e^{-1.136} = 0.321 \quad K_2 = 0.321 K_1 = 0.321 (2.0 \times 10^5) = 6.4 \times 10^4$$

4) Using the half-cell data, we may say



and so $\Delta G^\circ_{\text{rxn}} = -nFE^\circ_{\text{cell}} = - (3) (96485. \text{ C/mol}) (+5.197 \text{ v}) = -1504. \text{ kJ/mol}$

5) a) If the reaction is first order homogeneous, then

$$\ln[A]_t = \ln[A]_0 - kt$$

Rearranging gives

$$k = \frac{\ln([A]_0/[A]_t)}{t} = \frac{\ln(4.18 \times 10^{-3} \text{ mol/L} / 2.74 \times 10^{-3} \text{ mol/L})}{100 \text{ s}} = 4.22 \times 10^{-2} \text{ s}^{-1}$$

b) If the reaction is second order homogeneous, then

$$\frac{1}{[A]_t} - \frac{1}{[A]_0} = kt$$

Rearranging gives

$$\begin{aligned} k &= (1/t) [(1/[A]_t) - (1/[A]_0)] = (1/100.0 \text{ s}) [(1/2.74 \times 10^{-3} \text{ mol/L}) - (1/4.18 \times 10^{-3} \text{ mol/L})] \\ &= 1.257 \text{ L/mol}\cdot\text{s} \end{aligned}$$