

CHM 3400 – Fundamentals of Physical Chemistry

Second Hour Exam (Version C – Answers for all versions are at the end of the exam).

March 25, 2020

There are five problems on the exam. Do all of the problems. Show your work. Note that the exam must be turned in by 5:00pm on Thursday, March 26th. You do not need to submit a copy of the exam, as I will have that information. Also note that different students will have different questions.

$$R = 0.082057 \text{ L}\cdot\text{atm}/\text{mole}\cdot\text{K}$$

$$R = 0.083145 \text{ L}\cdot\text{bar}/\text{mole}\cdot\text{K}$$

$$R = 8.3145 \text{ J}/\text{mole}\cdot\text{K}$$

$$F = 96485. \text{ C}/\text{mol}$$

$$N_A = 6.022 \times 10^{23}$$

$$1 \text{ L}\cdot\text{atm} = 101.3 \text{ J}$$

$$1 \text{ atm} = 1.013 \text{ bar} = 1.013 \times 10^5 \text{ N}/\text{m}^2$$

$$1 \text{ atm} = 760 \text{ torr}$$

$$(1 \text{ volt})\cdot(1 \text{ Coulomb}) = 1 \text{ Joule}$$

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:

a) $\Delta H_{\text{vap}}^\circ$, the enthalpy of vaporization for the liquid.

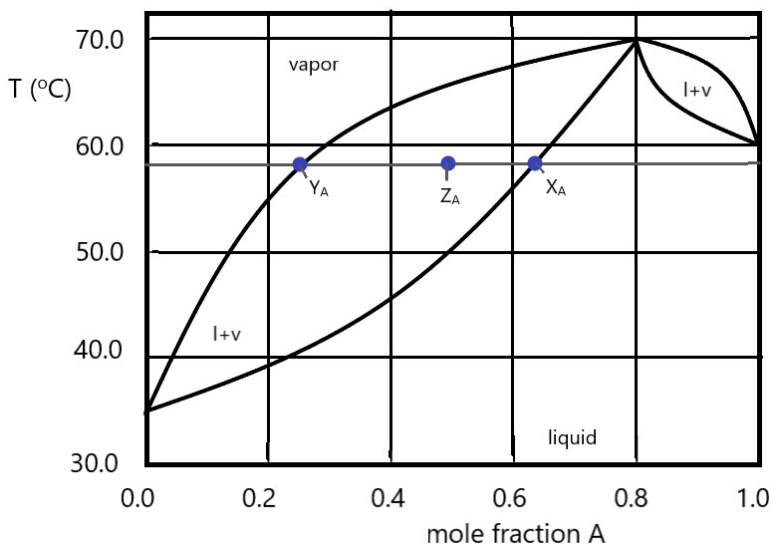
b) T_{vap}° , the normal boiling point for the liquid.

2. (24 points) A phase diagram for a solution of two pure chemical substances 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.

a) What are $T_{A,\text{vap}}^\circ$ and $T_{B,\text{vap}}^\circ$, the normal boiling point for pure A and pure B?

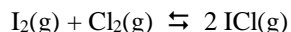
b) Do A and B form an azeotrope? If your answer is yes, give the mole fraction of A and the normal boiling point for the azeotrope.

c) 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. (16 points) A solution is prepared by dissolving 0.3648 g of a nonvolatile solid in cyclohexane (C_6H_{12} , MW = 84.16 g/mol). The final volume of the solution is $V = 100.0 \text{ mL}$. The osmotic pressure exerted by the solution, measured at $T = 30.0 \text{ }^\circ\text{C}$, is $\Pi = 463. \text{ torr}$. Based on this information, find the molecular weight of the nonvolatile solid.

4. (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

5. (16 points) Because of the difficulty in carrying out direct measurements, the solubility products for rare earth fluorides are often determined by electrochemical measurement. The solubility products can then be used to selectively precipitate particular rare earth ions from aqueous solution.

Using the data below, find the numerical value for K_{sp} , the solubility product for erbium III fluoride ($\text{ErF}_3(\text{s})$), at $T = 25.0 \text{ }^\circ\text{C}$, the temperature at which the data are given.

Reduction half-reaction	E° (v)	Free energy data
$\text{Er}^{3+}(\text{aq}) + 3 \text{e}^- \rightarrow \text{Er}(\text{s})$	- 2.331	$\Delta G^\circ_f(\text{ErF}_3(\text{s})) = - 1638. \text{ kJ/mol}$
$\text{F}_2(\text{g}) + 2 \text{e}^- \rightarrow 2 \text{F}^-(\text{aq})$	+ 2.866	$\Delta G^\circ_f(\text{Er}(\text{s})) = \Delta G^\circ_f(\text{F}_2(\text{g})) = 0.00 \text{ kJ/mol}$

Solutions.

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

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

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

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

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

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

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

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

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

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

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

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

3) For osmotic pressure, $\Pi = [B]RT$, and so

$$[B] = \frac{\Pi}{RT} = \frac{463 \text{ torr} (1 \text{ atm}/760 \text{ torr})}{(0.082057 \text{ L}\cdot\text{atm}/\text{mol}\cdot\text{K}) (303.15 \text{ K})} = 2.449 \times 10^{-2} \text{ mol/L}$$

Since there are 100.0 mL of solution, the number of moles of compound is

$$n = (0.1000 \text{ L}) (2.449 \times 10^{-2} \text{ mol/L}) = 2.449 \times 10^{-3} \text{ mol}$$

$$\text{and so } MW = \frac{0.3648 \text{ g}}{2.449 \times 10^{-3} \text{ mol}} = 149.0 \text{ g/mol}$$

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

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

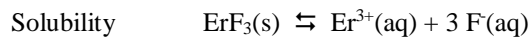
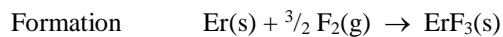
d) At $T = 60.0 \text{ }^\circ\text{C} = 333.15 \text{ K}$

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

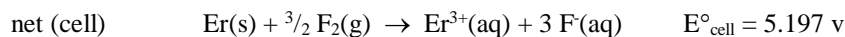
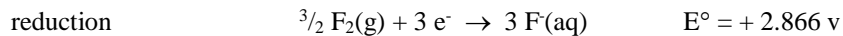
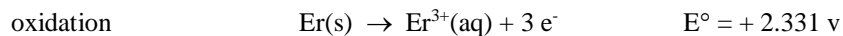
Taking the inverse logarithm of both sides of this relationship gives

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

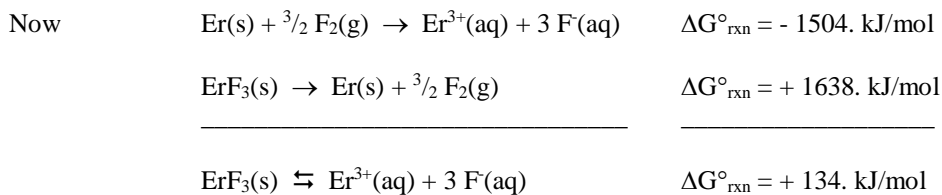
5) It is useful to recall both the solubility reaction and the formation reaction for ErF_3 .



Using the half-cell data, we may say



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



So $\ln(K) = -\frac{\Delta G^\circ_{\text{rxn}}}{RT} = -\frac{(134000. \text{ J/mol})}{(8.3145 \text{ J/mol}\cdot\text{K})(298.15 \text{ K})} = -54.05$
 $K = e^{-54.05} = 3.3 \times 10^{-24}$

Note that since I did not give all the information to do this problem, I did not grade problem 5. Instead, I multiplied your points on problems 1-4 by 100/84 to adjust to 100 points.

The answers to each version of the exam are given below:

- | | | | | | | | |
|----|--------------------------|--|----------------------------------|----------------------------------|------------|------------|---------------------|
| 1a | ΔH_{vap} | A 33.24 kJ/mol
D 34.42 kJ/mol | B 32.14 kJ/mol
E 31.07 kJ/mol | C 26.94 kJ/mol
F 28.28 kJ/mol | | | |
| 1b | T°_{vap} | A 348.9 K
D 343.7 K | B 348.5 K
E 340.8 K | C 351.6 K
F 341.8 K | | | |
| 2 | $T_A^\circ_{\text{vap}}$ | A 70 °C | B 80 °C | C 60 °C | D 60 °C | E 80 °C | F 70 °C |
| | $T_B^\circ_{\text{vap}}$ | A 46 °C | B 56 °C | C 36 °C | D 36 °C | E 56 °C | F 46 °C |
| | Azeotrope | A,F 0.80, 80 °C B,E 0.80 90 °C C,D 0.80, 70 °C | | | | | |
| | n_ℓ | A 1.80 mol | B 1.49 mol | C 2.71 mol | D 2.03 mol | E 1.72 mol | F 2.70 mol |
| 3 | MW | A 142.2 g/mol
D 160.4 g/mol | B 153.7 g/mol
E 132.7 g/mol | C 149.0 g/mol
F 169.7 g/mol | | | |
| 4c | K | A,B 420. | C,F 2.0×10^5 | | D,E 7.82 | | |
| 4d | K' | A 200. | B 260. | C 6.4×10^4 | D 7.03 | E 7.28 | F 3.8×10^4 |

