

CHM 3400 – Fundamentals of Physical Chemistry

Second Hour Exam

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

$$R = 0.08206 \text{ L}\cdot\text{atm}/\text{mole}\cdot\text{K}$$

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

$$R = 0.08314 \text{ L}\cdot\text{bar}/\text{mole}\cdot\text{K}$$

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

$$R = 8.314 \text{ J}/\text{mole}\cdot\text{K}$$

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

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

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

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

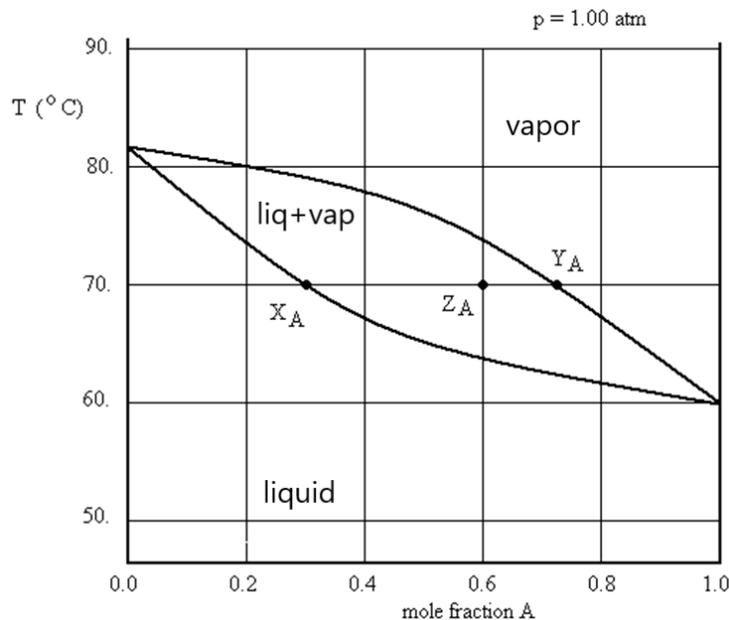
1. (24 points) A phase diagram for two volatile liquids A and B is given below, and may be used to answer the following questions. Note that in this problem $p = 1.00 \text{ atm}$.

a) What are the values for T_A° (normal boiling point of A) and T_B° (normal boiling point of B).

b) Does the above solution form any azeotropes? If your answer is yes, give the location (temperature and mole fraction) of each azeotrope that forms.

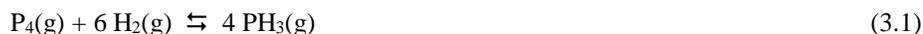
c) A closed system contains a solution of A and B at low temperature, with $n_A = 3.00$ moles and $n_B = 2.00$ moles (and so $Z_A = 0.600$). The solution is slowly heated. At what temperature (in $^\circ\text{C}$) will the solution first begin to boil.

d) We continue heating the solution until we reach a temperature $T = 70.0 \text{ }^\circ\text{C}$. At this point, $X_A = 0.308$ and $Y_A = 0.724$. How many moles of A are in the vapor phase at this temperature?



2. (16 points) The vapor pressure of pure water (H_2O , $M = 18.02 \text{ g}/\text{mol}$) at $T = 30.0 \text{ }^\circ\text{C}$ is 31.824 torr. When 1.084 g of a nonvolatile and nonionizing solute is dissolved in 200.0 g of water, the vapor pressure of the solution, again measured at $30.0 \text{ }^\circ\text{C}$, is 0.037 torr lower than the vapor pressure of pure water at the same temperature. What is M , the molecular mass of the solute?

3. (24 points) Phosphine (PH₃) is the phosphorus analogue of ammonia (NH₃). It plays a role in the biochemical cycling of phosphorus in the biosphere. In the gas phase, phosphine exists in equilibrium with phosphorus (P₄) and hydrogen (H₂).



a) Give the expression for K, the equilibrium constant for the above reaction, in terms of reactant and product activities.

b) Find the numerical value for the equilibrium constant for the above reaction at T = 298. K.

c) Find the numerical value for the equilibrium constant for the above reaction at T = 400. K.

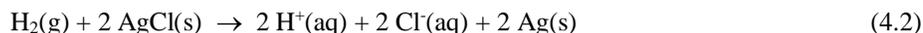
Thermochemical data of use in doing this problem are given below at T = 298. K.

Substance	ΔH°_f (kJ/mol)	ΔG°_f (kJ/mol)	S° (J/mol·K)
H ₂ (g)	0.0	0.0	130.68
P ₄ (g)	58.91	24.44	279.98
PH ₃ (g)	5.4	13.4	210.23

4. (16 points) Consider the following galvanic cell.



The balanced net cell reaction corresponding to this galvanic cell is



Data for the standard cell potential for the above galvanic cell have been obtained at several temperatures, and fit to the following formula

$$E^\circ_{\text{cell}} = 0.2220 \text{ V} - (6.5 \times 10^{-4} \text{ V/K}) (T - 298. \text{ K}) \quad (4.3)$$

Using eq 4.3, find E°_{cell} and $\Delta G^\circ_{\text{rxn}}$ for the above galvanic cell at T = 298.

5. (20 points) The gas phase reaction



is an example of a second order heterogeneous reaction, with the rate of the reaction given by the expression

$$\text{Rate} = - \frac{d[\text{F}_2]}{dt} = k[\text{NO}_2][\text{F}_2] \quad (5.2)$$

where $k = 38. \text{ L/mol}\cdot\text{s}$ at T = 27. °C

In a particular experiment (at T = 27. °C) the initial concentrations of reactants are $[\text{NO}_2]_0 = 2.0 \times 10^{-4} \text{ mol/L}$ and $[\text{F}_2]_0 = 5.0 \times 10^{-5} \text{ mol/L}$. No NO₂F is initially present in the system.

a) What is R₀, the initial rate of reaction, for the above conditions.

b) What will be the rate of reaction in this experiment when the concentration of NO₂F in the system reaches the value $[\text{NO}_2\text{F}] = 3.0 \times 10^{-5} \text{ mol/L}$?