MIDTERM 2B SOLUTIONS

Name: _____

Midterm 2b, ECH152, Spring 2023 — Student Number: _____

Exam, Form: A — TA: _____

Date: _____

Short Answers (10 questions, 20 points total)

Please write short and to the point answers. Only use the space provided below the question.

1. Most databases list ethalpy of formation (H_{fi}) and absolute entropies (S_i) of chemical species. How can we use this information to calculate the equilibrium constant?

$K_{eq} = \exp\left(-\frac{\Delta G^\circ}{RT}\right)$, $\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ$

$\Delta H^\circ = \sum_i \nu_i H_{fi}$ & $\Delta S^\circ = \sum_i \nu_i S_i$ } H_{fi} & S_i values are for species 'i' at temperature 'T'.

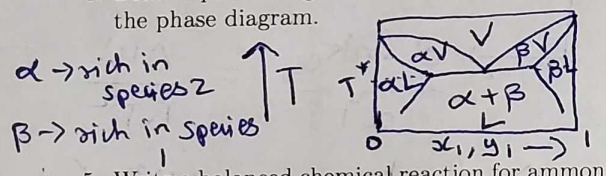
2. What is the criteria for chemical equilibrium in terms of the chemical potential for a reaction of type $\sum \nu_i A_i = 0$?

$$\sum_i \nu_i \mu_i = 0$$ as $dG = 0$

3. What is the extent of reaction? What are it's units?

Extent of reaction, ξ is the degree to which a reaction has taken place. Its units are moles.

4. Draw a phase diagram for two liquids in equilibrium with a vapor phase (VLLE). Label all regions of the phase diagram.



T-xy diagram at constant P for a binary system exhibiting VLLE

5. Write a balanced chemical reaction for ammonia (NH_3) combustion to yield NO_2 and H_2O. Assuming we start with stoichiometric amounts of NH_3 and O_2, write an expression for the equilibrium constant in terms of the extent of reaction.

$2NH_3 + \frac{7}{2}O_2 \longrightarrow 2NO_2 + 3H_2O$

$\nu = \sum_i \nu_i = 2 + 3 - 2 - 3.5 = -0.5$

$n_0 = \sum_i n_{i0} = 2 + 3.5 + 0 + 0 = 5.5$

$y_{NH_3} = \frac{2(1-\xi)}{5.5 - 0.5\xi}$, $y_{O_2} = \frac{3.5(1-\xi)}{5.5-0.5\xi}$, $y_{NO_2} = \frac{2\xi}{5.5-0.5\xi}$, $y_{H_2O} = \frac{3\xi}{5.5-0.5\xi}$

6. Write the equilibrium constant expression for the liquid phase reaction of $A + B \rightarrow C + D$, where A, B, C, and D form an non-ideal solution.

$$K_{eq} = \frac{y_{NO_2}^2 \cdot y_{H_2O}^3}{y_{NH_3}^2 \cdot y_{O_2}^{3.5}} \left(\frac{P^\circ}{P}\right)^{0.5}$$

$P^\circ = 1$ bar

$K_{eq} = \prod_i \left(\hat{f}_i / f_i^\circ\right)^{\nu_i} = \frac{f_A^\circ}{\hat{f}_A} \cdot \frac{f_B^\circ}{\hat{f}_B} \cdot \frac{\hat{f}_C}{f_C^\circ} \cdot \frac{\hat{f}_D}{f_D^\circ}$, $\hat{f}_i = \gamma_i x_i f_i$

f_i → fugacity of pure liquid 'i' at equilibrium T & P

f_i° → fugacity of pure liquid 'i' at temperature T & 1 bar.

$$K_{eq} = \left(\frac{\gamma_C \gamma_D}{\gamma_A \gamma_B}\right)\left(\frac{x_C x_D}{x_A x_B}\right)\frac{f_A^\circ}{f_A}\cdot\frac{f_B^\circ}{f_B}\cdot\frac{f_C}{f_C^\circ}\cdot\frac{f_D}{f_D^\circ}$$

$\left(\frac{G^E}{RT}\right)$ increases with increase in 'A' & A increases initially with increasing 'T' & then A decreases.

7. I have a mixture of two components that form a single liquid phase. As I increase the temperature, I observe phase separation. What can you tell me about how the exess Gibbs free energy changes with temperature? Assuming Margules one parameter model ($\gamma_1 = exp(Ax_2^2)$) is valid, how does A depend on temperature?

$\frac{G^E}{RT} = Ax_1x_2 = A(1-x_1)x_1 = Ax_1 - Ax_1^2$ $\Rightarrow \frac{d^2}{dx_1^2}\left(\frac{G^E}{RT}\right) = -2A$

stability criterion, $\frac{d^2}{dx_1^2}\left(\frac{G^E}{RT}\right) > \frac{-1}{x_1x_2} \Rightarrow 2A < \frac{1}{x_1x_2}$

$\Rightarrow$ A > 2 for phase separation

8. Write an equation for the equilibrium constant for the gas-phase $A + B \rightarrow C + D$, where A, B, C and D form an ideal solution. Additionally, A and B are non-ideal gases, while C and D can be assumed as being ideal gases.

ideal solution, $\hat{\phi}_i \rightarrow \phi_i$

$K_{eq} = \prod_i (y_i\phi_i)^{\nu_i} = (y_A\phi_A)^{-1}(y_B\phi_B)^{-1}(y_C\phi_C)^{1}(y_D\phi_D)^{1}$

$\nu = 1+1-1-1$ C + D $\rightarrow$ ideal $\Rightarrow \phi_C = \phi_D = 1$ $\Rightarrow K_{eq} = \left(\frac{1}{\phi_A\phi_B}\right)\left(\frac{y_Cy_D}{y_Ay_B}\right)$

$\nu = 0$

9. We are given a mixture of ammonia (NH_3), hydrazine (N_2H_4), and oxygen (O_2) as reactants. The products of the combustion reaction are NO, NO_2 and H_2O. We know the initial moles of each reactant species. I'd like to calculate the equilibrium composition as a function of temperature. What do I do? Dervie a set of independent reactions.

$\frac{1}{2}N_2 + \frac{3}{2}H_2 \rightarrow NH_3 \rightarrow$ (A) C − A $\Rightarrow \frac{1}{2}O_2 - \frac{3}{2}H_2 \rightarrow NO - NH_3 \Rightarrow NH_3 + \frac{1}{2}O_2 \rightarrow NO + \frac{3}{2}H_2$ → (F)

$N_2 + 2H_2 \rightarrow N_2H_4 \rightarrow$ (B) D − A $\Rightarrow O_2 - \frac{3}{2}H_2 \rightarrow NO_2 - NH_3 \Rightarrow NH_3 + O_2 \rightarrow NO_2 + \frac{3}{2}H_2$ → (G)

$\frac{1}{2}N_2 + \frac{1}{2}O_2 \rightarrow NO \rightarrow$ (C) 2C − B $\Rightarrow O_2 - 2H_2 \rightarrow 2NO - N_2H_4 \Rightarrow N_2H_4 + O_2 \rightarrow 2NO + 2H_2$ → (H)

$\frac{1}{2}N_2 + O_2 \rightarrow NO_2 \rightarrow$ (D) 2D − B $\Rightarrow 2O_2 - 2H_2 \rightarrow 2NO_2 - N_2H_4 \Rightarrow N_2H_4 + 2O_2 \rightarrow 2NO_2 + 2H_2$ → (I)

$H_2 + \frac{1}{2}O_2 \rightarrow H_2O \rightarrow$ (E)

10. How does the equilibrium constant depend on the reaction temperature? How does it depend on the total pressure?

F + $\frac{3}{2}$E $\Rightarrow NH_3 + \frac{5}{4}O_2 \rightarrow NO + \frac{3}{2}H_2O$

G + $\frac{3}{2}$E $\Rightarrow NH_3 + \frac{7}{4}O_2 \rightarrow NO_2 + \frac{3}{2}H_2O$

H + 2E $\Rightarrow N_2H_4 + 2O_2 \rightarrow 2NO + 2H_2O$

I + 2E $\Rightarrow N_2H_4 + 3O_2 \rightarrow 2NO_2 + 2H_2O$

↳ 4 independent reactions

$\frac{d\ln K_{eq}}{dT} = \frac{\Delta H^\circ}{RT^2}$

$\Rightarrow \ln\frac{K_{eq}}{K_{eq}'} = \frac{-\Delta H^\circ}{R}\left(\frac{1}{T} - \frac{1}{T'}\right)$

If $\Delta H^\circ < 0 \Rightarrow K_{eq} \downarrow$ as $T \uparrow$

If $\Delta H^\circ > 0 \Rightarrow K_{eq} \uparrow$ as $T \uparrow$

$K_{eq} = \left(\frac{P}{P^\circ}\right)^{\nu} \prod_i (y_i\hat{\phi}_i)^{\nu_i}$

where $\nu = \sum_i \nu_i$

If $\nu > 0 \Rightarrow K_{eq} \uparrow$ as $P \uparrow$

If $\nu < 0 \Rightarrow K_{eq} \downarrow$ as $P \uparrow$

If $\nu = 0 \Rightarrow$ no dependence of P on K_{eq}