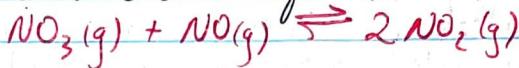


(7)

Week 2 Discussion Questions

1) The exothermic reaction  $\text{NO}_3(g) + \text{NO}(g) \rightleftharpoons 2\text{NO}_2(g)$  has a  $K_c$  of  $1.25 \times 10^{-3}$  at  $250^\circ\text{C}$ .

a) Balance the above chemical equation-



b) A rigid, 3.00 L flask is initially stocked with 0.600 mol of each reactant and product from this reaction at a temperature of  $250^\circ\text{C}$ . Once this reaction has reached equilibrium, how many grams of nitrogen monoxide gas will be present in the flask?

$$Q_c = \frac{[0.20\text{M}]^2}{[0.20\text{M}]^2} = 1 \quad K < Q \Rightarrow \text{shift left.}$$

	$\text{NO}_3(g)$	$+ \text{NO}(g)$	$\rightleftharpoons 2\text{NO}_2(g)$
I	0.20 M	0.20 M	0.20 M
C	$+x$	$+x$	$-2x$
E	$0.20+x$	$0.20+x$	$0.20-2x$

$$K_c = \frac{[\text{NO}_2]^2}{[\text{NO}_3][\text{NO}]} = \frac{(0.20-2x)^2}{(0.20+x)^2} = 1.25 \times 10^{-3}$$

$$\Rightarrow \frac{0.20-2x}{0.20+x} = 0.03536$$

$\Rightarrow 0.20-2x = (0.03536)(0.20+x)$ . Solve for x gives

$$\boxed{x = 0.0948 \text{M}}$$

$$[\text{NO}]_{\text{eq}} = 0.20+x = 0.2948 \text{M}$$

$$\Rightarrow 0.2948 \text{M} \times 3.00 \text{L} = 0.884 \text{ mol NO} \times \frac{30 \text{ g NO}}{1 \text{ mol NO}}$$

$$\boxed{= 26.5 \text{ g NO}}$$

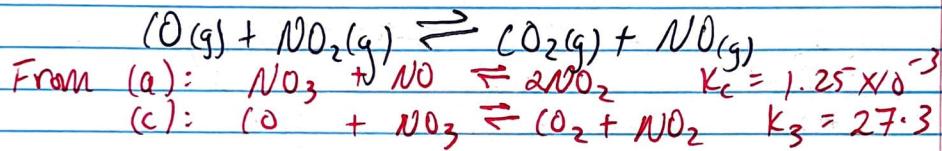
(8)

c) To increase the  $[NO_3]$  present in the flask at equilibrium, how would you adjust the reaction temperature? How will this impact the value of  $K_c$  for the reaction, if at all? Explain.

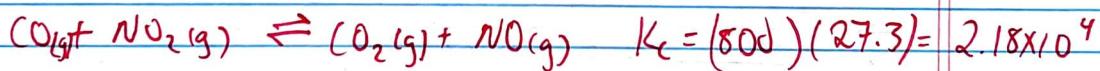
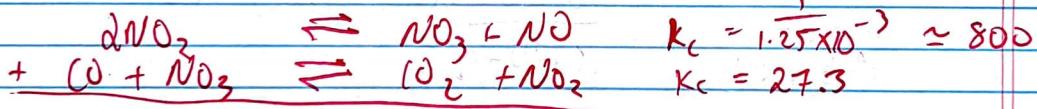
Rxn is exothermic, so increasing temp  $\Rightarrow$  too much heat product, this causes a reverse shift to form more  $NO_3$ .

Reverse shift will cause reactant concentrations to increase causing  $K_{eq}$  to be a smaller value.

d) At  $250.^\circ C$ , the reaction  $O(g) + NO_3(g) \rightleftharpoons CO_2(g) + NO_2(g)$  has a  $K_c = 27.3$ . Given this information, calculate  $K_p$  for the following reaction:



Reverse first rxn and add together gives:



$a+b-c-d=0$  in this case, hence  $\Delta n=0$ , and

$$K_c = K_p \Rightarrow [K_p = 2.18 \times 10^4]$$

2) A student sets up the reaction  $4Fe_3O_4(s) + O_2(g) \rightleftharpoons 6Fe_2O_3(s)$  with a  $Q_c$  of 4.00 at a certain temperature in a sealed, 3.00 L container. At equilibrium at that temperature, she finds the reaction to have a  $K_c$  of 100. Given that she isolated a mass of 10.0 g of  $Fe_3O_4(s)$  once the container reaches equilibrium, how many grams of  $Fe_3O_4(s)$  did she initially put into the container?

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$$Q_C = \frac{1}{[O_2]_i} \Rightarrow 4.00 = \frac{1}{[O_2]_i} \Rightarrow [O_2]_i = 0.25 \text{ M}$$

$$K_C = \frac{1}{[O_2]_{eq}} \Rightarrow 100 = \frac{1}{[O_2]_{eq}} \Rightarrow [O_2]_{eq} = 0.01 \text{ M}$$

$$\begin{array}{l} I \\ C \quad -x \\ E \quad 0.01 \text{ M} \end{array} \left\{ \Rightarrow x = 0.24 \text{ M } O_2 \text{ used up.} \right.$$

$$0.24 \text{ M } O_2 \times 3.00 \text{ L} = 0.72 \text{ mol } O_2 \times \frac{4 \text{ mol } Fe_3O_4}{1 \text{ mol } O_2} = 2.88 \text{ mol } Fe_3O_4$$

$$2.88 \text{ mol } Fe_3O_4 \times 231.55 \text{ g } Fe_3O_4 = 667 \text{ g } Fe_3O_4$$

$$\begin{array}{l} 10.0 \text{ g } Fe_3O_4 \text{ left over} \\ 667 \text{ g } Fe_3O_4 \text{ used up} \end{array} \left\{ \Rightarrow \boxed{667 \text{ g } Fe_3O_4 \text{ initially in cylinder}} \right.$$

3) Calculate  $\Delta S_{corr}^\circ$  for the following reaction at 298 K, given  
 $\Delta S_{rxn}^\circ = 162.7 \text{ J/mol}\cdot\text{K}$ ,  $K_{eq} = 9.2 \times 10^4$

$$\Delta G^\circ = \Delta H^\circ - T \Delta S^\circ$$

$$-RT \ln K = \Delta H^\circ - T \Delta S^\circ$$

$$-(8.314 \frac{\text{J}}{\text{mol}\cdot\text{K}})(298 \text{ K}) \ln(1.2 \times 10^4) = \Delta H^\circ - (298 \text{ K})(162.7 \frac{\text{J}}{\text{mol}\cdot\text{K}})$$

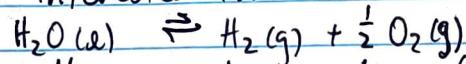
$$\Rightarrow \Delta H^\circ = +25.2 \text{ kJ/mol}$$

$$\Delta S_{corr}^\circ = \frac{-\Delta H_{sys}^\circ}{T} = \frac{-(25.2 \text{ kJ/mol})}{298 \text{ K}} = \boxed{-84.6 \frac{\text{J}}{\text{mol}\cdot\text{K}}}$$

This question should look familiar to one from last quarter.

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4) You are interested in



Experimentally, you have  $K_{\text{eq}}$  for 2 temperatures.  
Determine  $\Delta H^\circ$  and  $\Delta S^\circ$ .

Convert  $K_{\text{eq}} \rightarrow \ln K_{\text{eq}}$

$$T \rightarrow \frac{1}{\text{Temp}}$$

$\frac{1}{T}$	$\ln K_{\text{eq}}$
<del>5.000</del> $\times 10^{-4}$	-13.2
$6.667 \times 10^{-4}$	-5.83
$4.348 \times 10^{-4}$	

$$\ln K_{\text{eq}} = -\frac{\Delta H^\circ}{R} \frac{1}{T} + \frac{\Delta S^\circ}{R}$$

So, take slope of line to get  $-\frac{\Delta H^\circ}{R}$ .

$$m = \frac{-5.83 + 13.2}{4.348 \times 10^{-4} - 6.667 \times 10^{-4}}$$

$$= -31597.1 \text{ K} = -\frac{\Delta H^\circ}{R}$$

$$\begin{aligned} \text{So } \Delta H^\circ &= (31597.1 \text{ K}) \left( 8.3145 \frac{\text{J}}{\text{mol} \cdot \text{K}} \right) \\ \boxed{\Delta H^\circ = 263 \frac{\text{kJ}}{\text{mol}}} \end{aligned}$$

Recall from point-slope form

$$y - y_1 = m(x - x_1)$$

$$\Rightarrow y = mx - mx_1 + y_1$$

$$\text{So } y\text{-intercept is } y_1 - mx_1 = \frac{\Delta S^\circ}{R}$$

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$$S_0 - 5.83 - (-31597.1 \text{ k})(9.348 \times 10^{-4} \frac{1}{\text{K}}) = \frac{\Delta S^\circ}{R}$$

$$\Rightarrow 7.91 = \frac{\Delta S^\circ}{R}$$

$$\Rightarrow \left( 8.3145 \frac{\text{J}}{\text{mol} \cdot \text{K}} \right) (7.91) = \Delta S^\circ$$

$$\boxed{\Delta S^\circ = 65.8 \frac{\text{J}}{\text{mol} \cdot \text{K}}}$$

- 5) Solution A has  $A = 0.653$  at 587 nm. If you dilute solution A 5-fold to obtain solution B, what is the absorbance for solution B at 587 nm? ~~assume~~ Both solutions A & B contain the same chemical species.

$$\frac{A_1}{A_2} = \frac{c_1}{c_2} \Rightarrow \text{if } c_2 = \frac{1}{5} c_1$$

$$\text{Then } A_1 = \frac{c_1}{c_2} A_2 = \frac{c_1}{\frac{1}{5} c_1} = 5A_2$$

$$\Rightarrow \frac{A_1}{5} = A_2 \Rightarrow \underline{\underline{0.131}} = \underline{\underline{0.653 / 5 = A_2}}$$

- 6) Use the color wheel shown to answer the following:

- a) Explain why a blue solution has an optimum wavelength around 615 nm.

Blue solution absorbs light in wavelength that corresponds to complementary color. Complement of blue is orange, which is between 580-620. Hence 615 makes sense for optimal wavelength of absorbance.

- b) Explain why a red solution has an optimum wavelength around 575 nm.

Same reason as (a), but just different complementary color.

- 7) The molar absorptivity coefficient of an inorganic compound X in water ~~is~~ is  $5.00 \times 10^3 \text{ cm}^{-1} \text{ M}^{-1}$  near its max absorbance at 456 nm.

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- a) A student prepares a compound X solution that is 0.0300% (w/v) in concentration. This is labeled solution 1. Calculate the molarity of solution 1. The molar mass of X is 300.00 g/mol.

$$0.0300\%(\text{w/v}) = 0.0300 \times \frac{1000 \text{ mL}}{100 \text{ mL}} \times \frac{1 \text{ mol}}{300.00 \text{ g}}$$

$$= 1.00 \times 10^{-3} \text{ M}$$

- b) Serial dilution using 10mL volumetric pipet and added to 100mL volumetric flask. This is labeled solution 2. Calculate molarity of solution 2.

$$M_1 V_1 = M_2 V_2 \Rightarrow M_2 = \frac{M_1 V_1}{V_2} = \frac{(1.00 \times 10^{-3} \text{ M})(10.00 \text{ mL})}{100.00 \text{ mL}}$$

$$= 1.00 \times 10^{-4} \text{ M}$$

1:10 dilution?

- c) Using molar absorptivity coefficient and a 1.00 cm cuvette, calculate the absorbance of solution 1:2.

$$A_1 = (5.00 \times 10^3 \text{ cm}^{-1} \text{ M}^{-1})(1.00 \text{ cm})(1.00 \times 10^{-3} \text{ M}) = 5.00$$

$$A_2 = (5.00 \times 10^3 \text{ cm}^{-1} \text{ M}^{-1})(1.00 \text{ cm})(1.00 \times 10^{-4} \text{ M}) = 0.500$$

- d) Compute the ratio of  
i) Molarities of solution 2 to 1.

$$\frac{1.00 \times 10^{-4} \text{ M}}{1.00 \times 10^{-3} \text{ M}} = .100 = \frac{1}{10}$$

- ii) Absorbance of solution 2 to 1

$$\frac{0.500}{5.00} = .100 = \frac{1}{5}$$

They should be the same!

- 8) For the following reaction, calculate  $\Delta G^\circ$  and  $K_{eq}$  at 298K. Write the equilibrium constant expression.

At equilibrium  $\Delta G^\circ = RT \ln K$

$$\Delta G_{rxn}^\circ = \sum_i n_i G_{f,i}^\circ - \sum_j n_j G_{f,j}^\circ$$

$$= 2(86.55 \text{ kJ/mol}) - 2(51.71) = 69.68 \text{ kJ}$$

$$\boxed{\Delta G_{rxn}^\circ = 69.68 \text{ kJ}}$$

Then  $-69.680 \text{ J} = 8.3145 \frac{\text{J}}{\text{mol}\cdot\text{K}} (298 \text{ K}) \ln K$   
 $\Rightarrow K = e^{-28.1}$

$$\boxed{K_{eq} = 6.12 \times 10^{-13} = \frac{(P_{NO})^2 (P_{Cl_2})}{(P_{NOCl})^2}}$$

- 9) At  $T = 1200^\circ\text{C}$  the following reaction has an equilibrium constant  $K_{eq} = 0.612$
- $$P_4(g) \rightleftharpoons 2P_2(g)$$

a) Suppose the initial partial pressure of  $P_4$  is 5.00 atm and that of  $P_2$  is 2.00 atm. Calculate  $Q$  and state whether the reaction proceeds to the right or left at equilibrium is approached.

$$Q_o = \frac{P_{P_2}^2}{P_{P_4}} = \frac{2.00^2}{5.00} = \boxed{10.800}$$

$Q_o > K = 0.612$ , shifts to the left

- b) Calculate the partial pressures at equilibrium.

$$10 = \frac{(2.00 - 2x)^2}{5.00 + x} = 0.612$$

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We can solve this via the quadratic formula (or using any of your preferred numerical solver, or [wolframalpha](#))  
 to find

$$x \approx 0.115$$

Then  $\boxed{P_{P_2} = 1.77 \text{ atm} \quad P_{P_4} = 5.12 \text{ atm}} \text{ at equilibrium}$

c) If the volume of the system is then increased, will there be a net formation or dissociation of  $P_4$ ?

Net dissociation of  $P_4$ . Wants more gas molecules to fill larger volume and maintain same pressure.

- 10) a) ~~Shifts towards products~~ shifts towards products  
 b) Shifts towards products  
 c) Shifts towards reactants  
 d) No shift  
 e) Shift towards reactants