CHEM 1032 Key **Week 6**

EQUILIBRIUM

This worksheet should help you identify how we can use equilibrium to understand chemical reactions. It is intended for you to work through it in order. *(Don't skip ahead.)* The double headed arrow ($\rightleftharpoons$) indicates equilibrium.

Consider three different chemical reactions that involve CO_2:

A. $(4\ COF_{2\,(g)} \rightleftharpoons 2\ CO_{2\,(g)} + 2\ CF_{4\,(g)}) \times \frac{1}{2}$	$(K_c = 4.4 \times 10\text{-}6)^{\wedge 1/2}$
B. $CO_{2\,(g)} + C_{(s)} \rightleftharpoons 2\ CO_{(g)}$ flip..	$K_c = 1.9$ $1/1.9$
C. $CO_{(g)} + H_2O_{(g)} \rightleftharpoons CO_{2\,(g)} + H_{2\,(g)}$ no change	$K_c = ???$

Write out the equilibrium expression for the three reactions, so that each produces 1 mole of CO_2.

$2\ COF_{2\,(g)} \rightleftharpoons CO_{2\,(g)} + CF_{4\,(g)}$ $\quad K = 0.0021 = \frac{[CO_2][CF_4]}{[COF_2]^2}$

$2\ CO_{(g)} \rightleftharpoons CO_{2\,(g)} + C_{(s)}$ $\quad K = 0.5263 = \frac{[CO_2]}{[CO]^2}$

$CO_{(g)} + H_2O_{(g)} \rightleftharpoons CO_{2\,(g)} + H_{2\,(g)}$ $\quad K = ? = \frac{[CO_2][H_2]}{[CO][H_2O]}$

USE THESE EQUILIBRIUM EXPERSSIONS FOR THE REST OF THE WORKSHEET

What is the equilibrium constant of **Reaction C** if the equilibrium concentrations are:

$[CO] = 0.011$ M $\quad [H_2O] = 0.011$ M $\quad [CO_2] = 0.109$ M $\quad [H_2] = 0.109$ M

$$K = \frac{[CO_2][H_2]}{[CO][H_2O]} = \frac{(0.109)(0.109)}{(0.011)(0.011)} = 98.2$$

What is the value of K_p for each reaction (25 °C)?

$$K_p = K_c (RT)^{\Delta n}$$

A. $\Delta n = 0 \quad \therefore \quad K_p = K_c$

B. $\Delta n = 1 - 2 = -1$

$$K_p = (0.5263)\left((0.08206 \tfrac{L \cdot atm}{mol \cdot K})(298\ K)\right)^{-1}$$

$$K_p = 0.0215$$

we can't really cancel these units but we're going conc (M) → pressure (atm) so we use this not 8.314 J/mol·K.

C. $\Delta n = 0 \quad \therefore \quad K_p = K_c$

What is the value of $\Delta G°_{rxn}$ for each reaction (25 °C)?

$$\Delta G°_{rxn} = -RT \ln K$$

(answers are converted from J to kJ by dividing by 1000)

A. $\Delta G°_{rxn} = -(8.314\ J/mol \cdot K)(298\ K) \ln(0.0021) = +15.28\ kJ/mol$

B. $\Delta G°_{rxn} = -(8.314\ J/mol\ K)(298\ K) \ln(0.5263) = +1.59\ kJ/mol$

C. $\Delta G°_{rxn} = -(8.314\ J/mol\ K)(298\ K) \ln(98.2) = -11.36\ kJ/mol$

Which reaction is the most spontaneous at 25 °C? Why?

Reaction C is the only one that has a (−) $\Delta G°_{rxn}$ value so it is the only reaction which is spontaneous. Reactions A & B both have (+) values so they are nonspontaneous at standard conditions.

Consider **Reaction B**: The initial concentrations are [CO_2] = 0.00 M, [CO] = 0.215 M, and 10.4 g C. The equilibrium concentration of [CO] = 0.180 M. What is the equilibrium concentration of CO_2?

$$2\,CO_{(g)} \rightleftharpoons CO_{2\,(g)} + C_{(s)} \qquad K = 0.5263$$

	$2\,CO_{(g)}$	$CO_{2\,(g)}$	$C_{(s)}$
I	0.215	0.00	—
C	$-2x$	$+0.0175$	—
E	0.180	0.0175	—

$$0.215 - 2x = 0.180$$
$$-2x = -0.035$$
$$x = 0.0175$$

$$[CO_2] = 0.0175\,M$$

Consider **Reaction A**: When 1.12 mole of COF_2 is placed in a 2.00 L container, what is the concentration of CO_2 at equilibrium?

$$\frac{1.12\,mol}{2\,L} = 0.56\,M$$

$$2\,COF_{2\,(g)} \rightleftharpoons CO_{2\,(g)} + CF_{4\,(g)}$$

	$2\,COF_{2\,(g)}$	$CO_{2\,(g)}$	$CF_{4\,(g)}$
I	0.56	0	0
C	$-2x$	$+x$	$+x$
E	$0.56-2x$	x	x

$$K = \frac{[CO_2][CF_4]}{[COF_2]^2}$$

$$0.0021 = \frac{(x)(x)}{(0.56-2x)^2}$$

$$\sqrt{0.0021} = \sqrt{\frac{x^2}{(0.56-2x)^2}}$$

$$0.0458 = \frac{x}{0.56-2x}$$

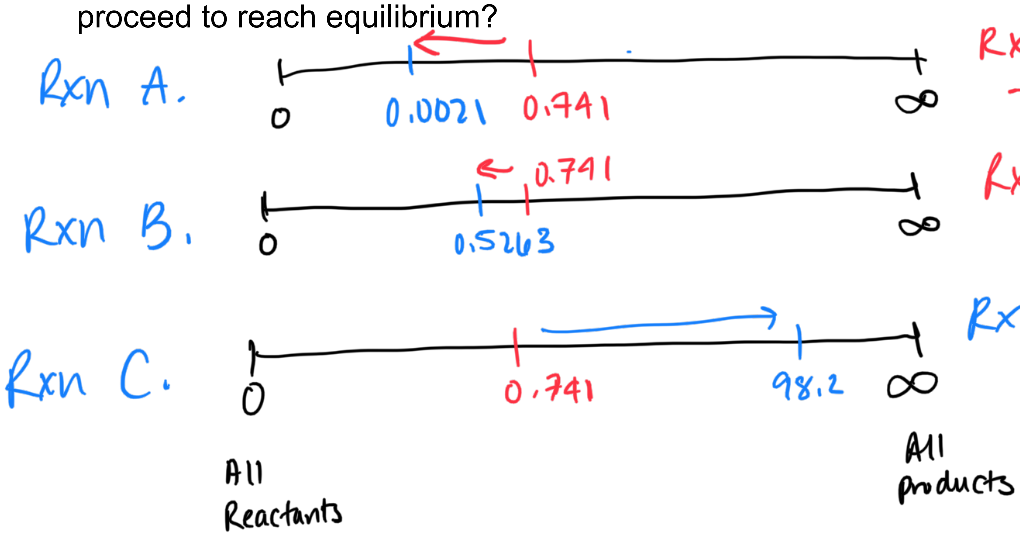
$$0.0256 - 0.0916x = x$$
$$0.0256 = 1.0916x$$
$$0.0234 = x$$

$$[CO_2] = 0.0234\,M$$

Assuming all three reactions have been optimized to have the same theoretical yield of CO_2, which reaction will produce the most CO_2 before it reaches equilibrium? Why? Is this consistent with your ΔG°_{rxn} values?

Based on our previous answers we see that Reaction B produced more than Reaction A. However we know that Reaction C is the most spontaneous of the 3, so it will produce the most CO_2. We also see it has the largest K value... so it will produce the most products.

At some point in each reaction, Q is found to be 0.741. What direction would each reaction proceed to reach equilibrium?



Rxn shifts back!

Rxn shifts back!

Rxn shifts forward!

When each reaction is at equilibrium, CO(g) is added to the mixture. How will each reaction respond?

Rxn A. $CO_{(g)}$ is not a part of the reaction, so no effect

Rxn B. $CO_{(g)}$ is a reactant, reaction will shift forward.

Rxn C. $CO_{(g)}$ is a reactant, reaction will shift forward.