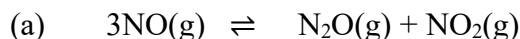


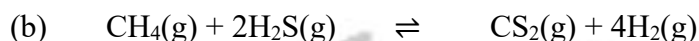
2018/2019 CH110 TUTORIAL SHEET 10 – CHEMICAL EQUILIBRIUM PH'S ANSWER KEY

COPPERBELT UNIVERSITY'S CHEMISTRY DEPARTMENT

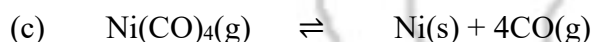
1. Write the expression for K_C for the following reactions. In each case indicate whether the reaction is homogeneous or heterogeneous.



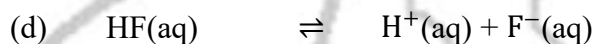
ANSWER: $K_C = \frac{[\text{N}_2\text{O}][\text{NO}_2]}{[\text{NO}]^3}$ **Homogeneous**



ANSWER: $K_C = \frac{[\text{CS}_2][\text{H}_2]^4}{[\text{CH}_4][\text{H}_2\text{S}]^2}$ **Homogeneous**



ANSWER: $K_C = \frac{[\text{CO}]^4}{[\text{Ni(CO)}_4]}$ **Homogeneous**

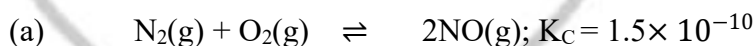


ANSWER: $K_C = \frac{[\text{H}^+][\text{F}^-]}{[\text{HF}]}$ **Homogeneous**

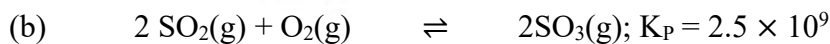


ANSWER: $K_C = \frac{[\text{Ag}^+]^2}{[\text{Zn}^{2+}]}$ **Heterogeneous**

2. When the following reactions come to equilibrium, does the equilibrium mixture contain mostly reactants or mostly products?



ANSWER: It contains mostly reactants because $K_C \ll 1$



ANSWER: It contains mostly products because $K_C \gg 1$

3. If $K_C = 0.042$ for $\text{PCl}_3\text{(g)} + \text{Cl}_2\text{(g)} \rightleftharpoons \text{PCl}_5\text{(g)}$ at 500 K, what is the value of K_P for this reaction at this temperature?

ANSWER: While $K_P = \frac{P_{\text{PCl}_5}}{P_{\text{PCl}_3}P_{\text{Cl}_2}}$, $K_C = \frac{[\text{PCl}_5]}{[\text{PCl}_3][\text{Cl}_2]}$

Since from the ideal gas law $[\text{PCl}_5] = \frac{n_{\text{PCl}_5}}{V} = \frac{P_{\text{PCl}_5}}{RT}$,

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$$[\text{PCl}_3] = \frac{n_{\text{PCl}_3}}{V} = \frac{P_{\text{PCl}_3}}{RT} \text{ and}$$

$$[\text{Cl}_2] = \frac{n_{\text{Cl}_2}}{V} = \frac{P_{\text{Cl}_2}}{RT}$$

Substituting the last term in the equation gives

$$K_C = \frac{[\text{PCl}_5]}{[\text{PCl}_3][\text{Cl}_2]} = K_P(RT)^{-\Delta n}$$

$$\text{where } \Delta n = \sum_{\text{products}} n - \sum_{\text{reactants}} n$$

Since $\sum_{\text{products}} n = 1$ and $\sum_{\text{reactants}} n = 2$ we see that

$$\Delta n = 1 - 2 = -1 \text{ so that } -\Delta n = +1 \text{ and}$$

$$K_C = K_P(RT)^{-\Delta n} = K_P(RT)$$

From the above equation, we see that

$$K_P = K_C(RT)^{\Delta n} \text{ or } K_C(RT)^{-1}$$

that is

$$K_P = 0.042 \left(\frac{1}{8.205 \times 10^{-2} \times 500} \right) = \left(\frac{4.2}{8.205 \times 5} \right) \times 10^{-2}$$

$$\underline{\underline{K_P = 1.0 \times 10^{-3}}}$$

4. At 1000 K, $K_P = 1.85$ for the reaction
 $\text{SO}_2(\text{g}) + \frac{1}{2}\text{O}_2(\text{g}) \rightleftharpoons \text{SO}_3(\text{g})$

- (a) What is the value of K_P for the reaction $\text{SO}_3(\text{g}) \rightleftharpoons \text{SO}_2(\text{g}) + \frac{1}{2}\text{O}_2(\text{g})$?

ANSWER:

$$\text{Since the reaction } \text{SO}_2(\text{g}) + \frac{1}{2}\text{O}_2(\text{g}) \rightleftharpoons \text{SO}_3(\text{g}) \text{ has } K_P = \frac{P_{\text{SO}_3}}{P_{\text{SO}_2} P_{\text{O}_2}^{1/2}}$$

$$\text{and the reaction } \text{SO}_3(\text{g}) \rightleftharpoons \text{SO}_2(\text{g}) + \frac{1}{2}\text{O}_2(\text{g}) \text{ has } K'_P = \frac{P_{\text{SO}_2} P_{\text{O}_2}^{1/2}}{P_{\text{SO}_3}}$$

It is clear that the latter reaction is reverse of the former and its equilibrium constant is the inverse of the former reaction so that

$$K'_P = \frac{P_{\text{SO}_2} P_{\text{O}_2}^{1/2}}{P_{\text{SO}_3}} = \frac{1}{K_P} \text{ or } K'_P = \left(\frac{1}{1.85} \right) = 0.54$$

- (b) What is the value of K_P for the reaction $2\text{SO}_2(\text{g}) + \text{O}_2(\text{g}) \rightleftharpoons 2\text{SO}_3(\text{g})$?

ANSWER:

$$\text{Since the reaction } \text{SO}_2(\text{g}) + \frac{1}{2}\text{O}_2(\text{g}) \rightleftharpoons \text{SO}_3(\text{g}) \text{ has } K_P = \frac{P_{\text{SO}_3}}{P_{\text{SO}_2} P_{\text{O}_2}^{1/2}}$$

$$\text{and the reaction } 2\text{SO}_2(\text{g}) + \text{O}_2(\text{g}) \rightleftharpoons 2\text{SO}_3(\text{g}) \text{ has}$$

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$$K'_P = \left(\frac{P_{SO_3}}{P_{SO_2}^{3/2} P_{O_2}^{1/2}} \right) \times \left(\frac{P_{SO_3}}{P_{SO_2} P_{O_2}^{1/2}} \right) \text{ or } K'_P = \left(\frac{P_{SO_3}}{P_{SO_2} P_{O_2}^{1/2}} \right)^2 = \frac{P_{SO_3}^2}{P_{SO_2}^2 P_{O_2}}$$

It is clear that the latter is doubling of the former and its equilibrium constant is the square of the former reaction so that

$$K'_P = \frac{P_{SO_3}^2}{P_{SO_2}^2 P_{O_2}} = K_P^2 \text{ or } K'_P = (1.85)^2 = 3.42$$

- (c) What is the value of K_C for the reaction in part (b)?

ANSWER:

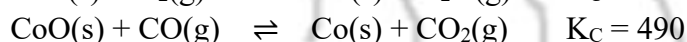
Since the relationship between K_P and K_C is $K_C = K_P(RT)^{-\Delta n}$

and $\Delta n = 2 - 3 = -1$, $K_C = K_P(RT)^{-(-1)} = K_P(RT)$

Substituting appropriate values in the latest equation gives

$$K_C = K_P(RT) = 3.42 \times 8.31 \times 1000 = 28441.$$

5. The following equilibria were attained at 823 K:



Based on these equilibria, calculate the equilibrium constant for



ANSWER:

The first two equations involve heterogeneous reactions whereas the third reaction is a homogeneous reaction. The mass action laws or the equilibrium constant equations are as follows:

For reaction $\text{CoO(s)} + \text{H}_2(\text{g}) \rightleftharpoons \text{Co(s)} + \text{H}_2\text{O(g)}$ we have

$$K_{C1} = \frac{[\text{H}_2\text{O}]}{[\text{H}_2]} = 67 \text{ with } \frac{1}{K_{C1}} = \frac{[\text{H}_2]}{[\text{H}_2\text{O}]} = \frac{1}{67}$$

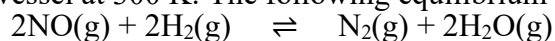
Similarly, for the reaction $\text{CoO(s)} + \text{CO(g)} \rightleftharpoons \text{Co(s)} + \text{CO}_2(\text{g})$ we have

$$K_{C2} = \frac{[\text{CO}_2]}{[\text{CO}]} = 490 \text{ with } \frac{1}{K_{C2}} = \frac{[\text{CO}]}{[\text{CO}_2]} = \frac{1}{490}$$

Finally, for the reaction $\text{H}_2(\text{g}) + \text{CO}_2(\text{g}) \rightleftharpoons \text{CO(g)} + \text{H}_2\text{O(g)}$ we have

$$K_{C3} = \frac{[\text{H}_2\text{O}][\text{CO}]}{[\text{H}_2][\text{CO}_2]} = \left(\frac{[\text{H}_2\text{O}]}{[\text{H}_2]} \right) \left(\frac{[\text{CO}]}{[\text{CO}_2]} \right) = K_{C1} \left(\frac{1}{K_{C2}} \right) = \frac{67}{490} = 0.14$$

6. A mixture of 0.10 mol of NO, 0.050 mol of H₂, and 0.10 mol of H₂O is placed in a 1.0 L vessel at 300 K. The following equilibrium is established:



At equilibrium $[\text{NO}] = 0.062 \text{ M}$.

- (a) Calculate the equilibrium concentrations of H₂, N₂, and H₂O.

ANSWER: Completing the ICE table below, gives

Moles	2NO(g) +	2H ₂ (g)	\rightleftharpoons	N ₂ (g) +	2H ₂ O(g)
Initial	0.10	0.050		0.00	0.10
Change	-2x	-2x		+x	+2x
Equilibrium	0.10 - 2x	0.050 - 2x		+x	0.10 + 2x

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Since we are given that at equilibrium $[\text{NO}] = 0.062 \text{ M}$ and $V=1.0 \text{ L}$, then

$$n_{\text{NO}} = 0.062 \text{ mol/L} \times 1.0 \text{ L} = 0.062 \text{ mol.}$$

We can thus use this numbers of moles to determine the value for x by solving the equation

$$0.10 - 2x = 0.062 \text{ or } 2x = 0.10 - 0.062 \text{ or}$$

$$2x = 0.10 - 0.062 = 0.038 \text{ so that } x = \frac{0.038}{2} = 0.019 \text{ moles}$$

Thus, the H_2 moles and concentration are $0.050 - 0.038 = 0.012 \text{ mol}$ and **0.012 M**, respectively;

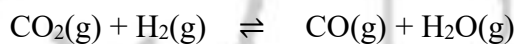
Similarly, N_2 moles and concentration are 0.019 mol and **0.019 M**, respectively while H_2O moles and concentration are $0.10 + 2x$ or $(0.10 + (2 \times 0.019)) = 0.138 \text{ mol}$ and **0.138 M**, respectively.

- (b) Calculate K_c .

ANSWER: The mass action law gives

$$K_c = \frac{[\text{N}_2][\text{H}_2\text{O}]^2}{[\text{NO}]^2[\text{H}_2]^2} = \frac{(0.019) \times (0.138)^2}{(0.062)^2 \times (0.012)^2} = 580.1$$

7. A mixture of 0.2000 mol of CO_2 , 0.1000 mol of H_2 , and 0.1600 mol of H_2O is placed in a 2.000 L vessel. The following equilibrium is established at 500 K:



- (a) Calculate the initial partial pressures of CO_2 , H_2 , and H_2O .

ANSWER: Table completion with $R = 8.205 \times 10^{-2} \text{ L atm K}^{-1} \text{ mol}^{-1}$ and $T = 500 \text{ K}$ so that $RT = 8.205 \times 10^{-2} \text{ L atm K}^{-1} \text{ mol}^{-1} \times 500 \text{ K}$ i. e. **41.025 L atm mol⁻¹** final row of required partial pressures.

Moles	$\text{CO}_2(\text{g}) +$	$\text{H}_2(\text{g})$	\rightleftharpoons	$\text{CO}(\text{g}) +$	$\text{H}_2\text{O}(\text{g})$
Initial moles (n_i)	0.2000	0.1000		0.0000	0.1600
Concentration Equation $C_i = \frac{n_i}{V}$ in mol L ⁻¹	$\frac{0.2000}{2.000}$	$\frac{0.100}{2.000}$		-	$\frac{0.16000}{2.000}$
Concentration value C_i	0.1000	0.0500		-	0.0800
Partial Pressure Equation $P_i = \frac{n_i}{V}RT$ or $P_i = C_iRT$	0.1000×41.025	0.0500×41.025		-	0.0800×41.025
Partial Pressure in atm	4.10 atm	2.05 atm		-	3.28 atm

- (b) At equilibrium $P_{\text{H}_2\text{O}} = 3.51 \text{ atm}$. Calculate the equilibrium partial pressures of CO_2 , H_2 , and CO .

- (c) **ANSWER:** Completing the ICE table below using pressures instead of concentrations gives,

Substance	$\text{CO}_2(\text{g}) +$	$\text{H}_2(\text{g})$	\rightleftharpoons	$\text{CO}(\text{g}) +$	$\text{H}_2\text{O}(\text{g})$
Initial (atm)	4.10	2.05		0.00	3.28
Change	$-x$	$-x$		$+x$	$+x$
Equilibrium	$4.10 - x$	$2.05 - x$		$+x$	$3.28 + x$

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Since we are given that at equilibrium $P_{\text{H}_2\text{O}} = 3.51 \text{ atm}$, then

$$P_{\text{H}_2\text{O}} = 3.51 = 3.28 + x \text{ or } x = 3.51 - 3.28 = 0.23 \text{ atm}$$

We can thus use this value for x by solving the P_{CO_2} equation as

$$P_{\text{CO}_2} = 4.10 - 0.23 = 3.87 \text{ atm}$$

And

$$P_{\text{CO}} = x = 0.23 \text{ atm}$$

8. At 100°C the equilibrium constant for the reaction $\text{COCl}_2(\text{g}) \rightleftharpoons \text{CO}(\text{g}) + \text{Cl}_2(\text{g})$ has the value $K_c = 2.19 \times 10^{-10}$. Are the following mixtures of COCl_2 , CO , and Cl_2 at 100°C at equilibrium? If not, indicate the direction that the reaction must proceed to achieve equilibrium.

a) $[\text{COCl}_2] = 2.00 \times 10^{-3} \text{ M}$, $[\text{CO}] = 3.3 \times 10^{-6} \text{ M}$, $[\text{Cl}_2] = 6.62 \times 10^{-6} \text{ M}$;

(b) $[\text{COCl}_2] = 4.50 \times 10^{-2} \text{ M}$, $[\text{CO}] = 1.1 \times 10^{-7} \text{ M}$, $[\text{Cl}_2] = 2.25 \times 10^{-6} \text{ M}$;

(c) $[\text{COCl}_2] = 0.0100 \text{ M}$, $[\text{CO}] = [\text{Cl}_2] = 1.48 \times 10^{-6} \text{ M}$

ANSWER: Key to this question is to compare the reaction quotient, Q , to the equilibrium constant K_c . If $Q \neq K_c$ the system is not at equilibrium. If $Q = K_c$ then the system is at equilibrium.

a) $[\text{COCl}_2] = 2.00 \times 10^{-3} \text{ M}$, $[\text{CO}] = 3.3 \times 10^{-6} \text{ M}$, $[\text{Cl}_2] = 6.62 \times 10^{-6} \text{ M}$;

$$Q = \frac{[\text{CO}][\text{Cl}_2]}{[\text{COCl}_2]} = \frac{(3.3 \times 10^{-6})(6.62 \times 10^{-6})}{2.00 \times 10^{-3}} = 1.09 \times 10^{-8}$$

Since $K_c = 2.19 \times 10^{-10}$ we easily see that $K_c < Q$ and the system is not at equilibrium.

(b) $[\text{COCl}_2] = 4.50 \times 10^{-2} \text{ M}$, $[\text{CO}] = 1.1 \times 10^{-7} \text{ M}$, $[\text{Cl}_2] = 2.25 \times 10^{-6} \text{ M}$;

$$Q = \frac{[\text{CO}][\text{Cl}_2]}{[\text{COCl}_2]} = \frac{(1.1 \times 10^{-7})(2.25 \times 10^{-6})}{4.50 \times 10^{-2}} = 5.50 \times 10^{-10}$$

Since $K_c = 2.19 \times 10^{-10}$ we easily see that $K_c < Q$ and the system is not at equilibrium.

(c) $[\text{COCl}_2] = 0.0100 \text{ M}$, $[\text{CO}] = [\text{Cl}_2] = 1.48 \times 10^{-6} \text{ M}$

$$Q = \frac{[\text{CO}][\text{Cl}_2]}{[\text{COCl}_2]} = \frac{(1.48 \times 10^{-6})(1.48 \times 10^{-6})}{1.00 \times 10^{-2}} = 2.21 \times 10^{-10}$$

Since $K_c = 2.19 \times 10^{-10}$ we easily see that $K_c \approx Q$ and the system is at equilibrium.

9. (a) At 1285°C , the equilibrium constant for the reaction $\text{Br}_2(\text{g}) \rightleftharpoons 2\text{Br}(\text{g})$ is $K_c = 1.04 \times 10^{-3}$. A 0.200 L vessel containing an equilibrium mixture of the gases has $0.245 \text{ g Br}_2(\text{g})$ in it. What is the mass of $\text{Br}(\text{g})$ in the vessel?

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ANSWER: Completing the ICE table below using pressures instead of concentrations gives,

Substance	Br ₂ (g)	⇌	2Br(g) +
Initial (atm)	y		0
Change	-x		+2x
Equilibrium	y - x		+2x

Given $K_c = 1.04 \times 10^{-3}$, $V=0.200$ L and $m_{Br_2} = 0.245$ g

y is moles of Br₂ or $n_{Br_2} = \frac{m_{Br_2}}{M_{Br_2}}$.

Since $M_{Br_2} = 79.9 \times 2 = 159.8 \frac{g}{mol}$,

Then $y = n_{Br_2} = \frac{0.245}{159.8} = 0.00153$ mol

Now $K_c = \frac{[Br]^2}{[Br_2]}$ and $[Br_2] = \frac{n_{Br_2}}{V} = \frac{0.0015}{0.200} = 0.0076$ M

So that $K_c = \frac{[Br]^2}{[Br_2]}$ with appropriate substitution becomes

$$K_c = \frac{(2x)^2}{7.6 \times 10^{-3}}$$

This on substituting value of K_c becomes the equation

$$1.04 \times 10^{-3} = \frac{4x^2}{7.6 \times 10^{-3}} \text{ or}$$

$$1.04 \times 10^{-3} = \frac{x^2}{1.9 \times 10^{-3}}$$

Making x the subject gives $x^2 = 1.04 \times 10^{-3} \times 1.9 \times 10^{-3}$

Solving for x gives $x = \sqrt{1.04 \times 1.9 \times 10^{-3}} = 1.41 \times 10^{-3}$

- (b) For the reaction $H_2(g) + I_2(g) \rightleftharpoons 2HI(g)$, $K_c = 55.3$ at 700 K. In a 2.00 L flask containing an equilibrium mixture of the three gases, there are 0.056 g H₂ and 4.36 g I₂. What is the mass of HI in the flask?

- (d) **ANSWER:** We first need to determine the moles and concentrations of the given substances followed by completing the ICE table.

Since $m_{H_2} = 0.056$ g and $M_{H_2} = 1.01 \times 2 = 2.02 \frac{g}{mol}$

$$n_{H_2} = \frac{0.0056}{2.02} = 0.0277 \text{ mol}$$

So, the concentration of is

$$C_{H_2} = \frac{0.0277}{2.00} = 0.01385 \text{ mol/L}$$

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And since $m_{I_2} = 4.36 \text{ g}$ and $M_{I_2} = 126.90 \times 2 = 253.8 \frac{\text{g}}{\text{mol}}$

$$n_{I_2} = \frac{4.36}{253.8} = 0.0172 \text{ mol and } C_{I_2} = \frac{0.0172}{2.00} = 0.0086 \text{ mol/L}$$

Substance	$H_2(g) +$	$I_2(g)$	\rightleftharpoons	$2HI(g) +$
Initial	-	-		-
Change	-	-		-
Equilibrium	0.01385	0.0086		x

Writing the equilibrium equation gives us

$$K_c = \frac{[HI]^2}{[H_2][I_2]} \text{ or } 55.3 = \frac{x^2}{(1.385 \times 10^{-2}) \times (8.6 \times 10^{-3})}$$

Solving for x gives

$$x = \sqrt{5.53 \times 1.385 \times 8.6 \times 10^{-2}} = 8.1 \times 10^{-2}$$

From this concentration, the moles of HI is

$$n_{HI} = C_{HI} \times V = 8.1 \times 10^{-2} \times 2.00 = 0.162 \text{ mol}$$

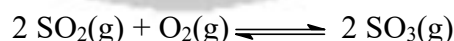
The mass of HI is give by the expression

$$m_{HI} = n_{HI} \times M_{HI}$$

Substituting the appropriate values where $M_{HI}=126.90+1.01=127.91 \text{ g/mol}$, we have

$$m_{HI} = 0.162 \times 127.91 = 20.72 \text{ g}$$

10. For the reaction $I_2 + Br_2(g) \rightleftharpoons 2 IBr(g)$, $K_c = 280$ at 150°C . Suppose that 0.500 mol IBr in a 1.00- L flask is allowed to reach equilibrium at 150°C . What are the equilibrium concentrations of IBr, I_2 , and Br_2 ?
11. Consider the following equilibrium, for which $\Delta H < 0$



How will each of the following changes affect an equilibrium mixture of the three gases?

- $O_2(g)$ is added to the system;
- the reaction mixture is heated;
- the volume of the reaction vessel is doubled;

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- (d) a catalyst is added to the mixture;
- (e) the total pressure of the system is increased by adding a noble gas;
- (f) $\text{SO}_3(\text{g})$ is removed from the system.

