Ch. 14 Discussion ?’s

- Concentration Units
  - Professor Nizkorodov Problem
- Equilibrium
  - Professor Nizkorodov Problem
- Equilibrium Constant
  - 14.15, 14.20, 14.21, 14.22, 14.30, 14.31
- Reaction Quotient
  - 14.40
- Concentration Calculations
  - 14.41, 14.42, 14.44
- Le Chatelier’s Principle
  - 14.56, 14.61
A small amount (0.44 grams) of dry ice is placed in a two liter bulb maintained at a room temperature (23°C). Calculate the CO₂ concentration in [mol/L] and partial pressure in [atm] after the dry ice sublimes.

**Answer:**
Assume complete sublimation & Ideal Gas Behavior
For g/L: calculate mol from g; L is given
For $P_{\text{CO}_2}$: Calculate P from $PV=NRT$
What processes are balanced in rates during the following equilibria:

a) Water vapor in equilibrium with liquid water

b) Gas-phase acetic acid in equilibrium with acetic acid dimer

c) A substance at its triple point

d) Blackbody radiator in equilibrium with its radiation field.
14.15 The equilibrium constant $K_c$ for the reaction: $2\text{HCl}_\text{(g)} \rightleftharpoons \text{H}_2\text{(g)} + \text{Cl}_2\text{(g)}$ is $4.17 \times 10^{-34}$ at 25°C. What is the equilibrium constant for the reaction $\text{H}_2\text{(g)} + \text{Cl}_2\text{(g)} \rightleftharpoons 2\text{HCl}_\text{(g)}$ at the same temperature?

**Answer:**

Reverse rxn: $K'_c = \frac{1}{K_c}$
14.20 A reaction vessel contains NH₃, N, and H₂ at equilibrium at a certain temperature. The equilibrium concentrations are [NH₃] = 0.25 M, [N₂] = 0.11 M, and [H₂] = 1.91 M. Calculate the equilibrium constant, $K_c$, if the reaction is represented as:

a) $N₂(g) + 3H₂(g) \rightleftharpoons 2NH₃(g)$

b) $\frac{1}{2} N₂(g) + \frac{3}{2} H₂(g) \rightleftharpoons NH₃(g)$

**Answer:**

For the reaction $aA + bB \rightleftharpoons cC$

$$K_c = \frac{[C]^c}{[A]^a[B]^b}$$
14.21 The equilibrium constant, $K_c$, for the reaction: $I_2(g) \rightleftharpoons 2I(g)$ is $3.8 \times 10^{-5}$ at 727°C. Calculate both $K_c$ and $K_p$ for the equilibrium $2I(g) \rightleftharpoons I_2(g)$ at the same temperature.

**Answer:**

Reverse rxn: $K'_c = \frac{1}{K_c}$

$K_p = K'_c (RT)^\Delta n$
At equilibrium, the pressure of the following reaction mixture

\[ \text{CaCO}_3 (s) \rightleftharpoons \text{CaO} (s) + \text{CO}_2 (g) \]

is 0.105 atm at 350°C. Calculate both \( K_c \) and \( K_p \) for this reaction.

**Answer:**

\[ K_p = \frac{\Pi P_{\text{products}}}{\Pi P_{\text{reactants}}} \]
14.30 Predict the equilibrium constant for the last reaction based on the information provided:

\[
\begin{align*}
\text{H}_2\text{C}_2\text{O}_4^{\text{(aq)}} & \rightleftharpoons \text{H}^+^{\text{(aq)}} + \text{HC}_2\text{O}_4^{-\text{(aq)}} & K'_c = 6.5 \times 10^{-2} \\
\text{HC}_2\text{O}_4^{-\text{(aq)}} & \rightleftharpoons \text{H}^+^{\text{(aq)}} + \text{C}_2\text{O}_4^{2-\text{(aq)}} & K''_c = 6.1 \times 10^{-5} \\
\text{H}_2\text{C}_2\text{O}_4^{\text{(aq)}} & \rightleftharpoons \text{C}_2\text{O}_4^{2-\text{(aq)}} + 2\text{H}^+^{\text{(aq)}} & K_c = ????
\end{align*}
\]

**Answer:**

Write \(K_c\) in terms of \(K'_c\) and \(K''_c\)

\[K_c = K'_c K''_c\]
14.31 Predict the equilibrium constant for the last reaction based on the information provided:

\[ \text{C} \,(s) + \text{CO}_2 \,(g) \rightleftharpoons 2\text{CO} \,(g) \quad K_p' = 1.3 \times 10^{14} \]
\[ \text{CO} \,(g) + \text{Cl}_2 \,(g) \rightleftharpoons \text{COCl}_2 \,(g) \quad K_p'' = 6.0 \times 10^{-3} \]
\[ \text{C} \,(s) + \text{CO}_2 \,(g) + 2\text{Cl}_2 \,(g) \rightleftharpoons 2\text{COCl}_2 \,(g) \quad K_p = ??? \]

**Answer:**

Write $K_p$ in terms of $K_p'$ and $K_p''$

\[ K_p = K_p' \times K_p''^2 \]
For the synthesis of ammonia

$\text{N}_2(g) + 3\text{H}_2(g) \rightleftharpoons 2\text{NH}_3(g)$

the equilibrium constant $K_c$ at $375^\circ C$ is $1.2$. Starting with $[\text{H}_2]_0 = 0.76 \text{ M}$, $[\text{N}_2]_0 = 0.60 \text{ M}$, and $[\text{NH}_3]_0 = 0.48 \text{ M}$, which gases will have increased/decreased in concentration when the mixture comes to an equilibrium?

**Answer:**

Compare $Q$ to $K_c$

$$aA + bB \rightleftharpoons cC$$

$$Q = \frac{[C]^c}{[A]^a[B]^b}$$

$Q > K_c \rightarrow$ products small, so shift to left for equilibrium
14.41 For the reaction,

\[ \text{H}_2 (g) + \text{CO}_2 (g) \rightleftharpoons \text{H}_2\text{O} (g) + \text{CO} (g) \]

at 700°C, \( K_c = 0.534 \). Calculate the number of moles of \( \text{H}_2 \) that will be present at equilibrium if a mixture of 0.300 mole of \( \text{CO} \) and 0.300 mole of \( \text{H}_2\text{O} \) is allowed to equilibrate at 700°C in a 10.0-L container.

**Answer:**

Write \( K_c \) equation

Make an ICE (initial, change, and equilibrium conc.) table to write and expression for the equilibrium conc. Hint: make the change in conc. \( x \)

Plug into \( K_c \) equation and solve for \( x \).
14.42 At 1000 K, a sample of pure NO₂ decomposes according to the reaction:

$$2 \text{NO}_2 \ (g) \rightleftharpoons 2\text{NO} \ (g) + \text{O}_2 \ (g)$$

The equilibrium constant $K_p$ is 158. The partial pressure of O₂ turns out to be 0.25 atm at equilibrium. What are equilibrium pressure of NO and NO₂ under the same conditions?

**Answer:**

Write $K_p$ equation

<table>
<thead>
<tr>
<th></th>
<th>2NO₂ (g)</th>
<th>2NO(g)</th>
<th>O₂(g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Initial</td>
<td>$P_{\text{NO}_2 \text{initial}}$</td>
<td>0 atm</td>
<td>0 atm</td>
</tr>
<tr>
<td>Change</td>
<td>-0.50 atm</td>
<td>+0.50 atm</td>
<td>+0.25 atm</td>
</tr>
<tr>
<td>Equilibrium</td>
<td>$P_{\text{NO}_2}$</td>
<td>0.50 atm</td>
<td>0.25 atm</td>
</tr>
</tbody>
</table>

Plug into $K_p$ equation and solve for $P_{\text{NO}_2}$
Molecular iodine dissociate at high temperatures as follows:

\[
I_2 (g) \rightleftharpoons 2I(g)
\]

At 1000K, the equilibrium constant \( K_c \) is 3.80 \( \times \) 10\(^{-5} \). Starting with 0.0456 mole of pure \( I_2 \) in a 2.30-L flask maintained at 1000K calculate the equilibrium concentrations of \( I \) and \( I_2 \).

**Answer:**

Write \( K_c \) equation

Make an ICE table

Plug equilibrium conc. expressions into \( K_c \) equation and solve for \( x \);

*Hint: use quadratic equation*

\[
x = \frac{-b \pm \sqrt{b^2 - 4ac}}{2a}
\]
14.56 What effect does an increase in pressure have on each of the following systems at equilibrium? Assume that the system is contained in cylinder with a movable piston maintained at a constant temperature:

\[
\begin{align*}
A_{(s)} & \rightleftharpoons 2B_{(s)} \\
2A_{(l)} & \rightleftharpoons B_{(l)} \\
A_{(s)} & \rightleftharpoons B_{(g)} \\
A_{(g)} & \rightleftharpoons B_{(g)} \\
A_{(g)} & \rightleftharpoons 2B_{(g)}
\end{align*}
\]

**Answer:**

Le Chatelier’s Principle

Changes in Pressure affects the conc. of gases from \( PV = nRT \), i.e. \( P \) is proportional to \( \frac{N}{V} \) aka molarity
14.61 Consider the gas-phase reaction in a closed container: \( \text{O}_2 (g) + 2\text{CO}(g) \rightleftharpoons 2\text{CO}_2 (g) \)

Predict the shift in the equilibrium position when inert helium gas is added to the system:

a) At constant pressure
b) At constant volume

Assume that the addition of helium has no effect on the temperature of the container.

**Answer:**

a) If add gas but \( P=\text{constant} \) then the \( V \) must change causing the partial pressures to decrease; Predict shift with Le Chatelier’s Principle

b) If \( V=\text{constant} \) then partial pressures=constant; i.e. no change in \( Q \)