

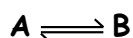
Chapter 13 – Fundamental Equilibrium Concepts

Chemical equilibrium can be defined two different ways: (i) It is the condition in which the concentrations of all reaction species do not change with time, or (ii) It is the condition of opposing reactions proceeding at the same rate. You saw this concept introduced briefly in Chapter 4 last semester (weak acids and bases), but it wasn't discussed in any detail. In one sense, the idea of equilibrium is a little unsettling. Why is it that a reaction starts and makes progress to making the products, then seemingly just stops and doesn't progress further. In this chapter, we will explore how and why chemical equilibria occur.

13.1 Chemical Equilibria

Before getting to the mathematical description of equilibrium, we should talk about its molecular basis. In a sense, that a reaction should go to completion or not start at all is fairly intuitive. If the products are more stable than the reactants the reaction proceeds, if they're not the reaction doesn't. That a reaction should go part way and apparently stop is a little surprising.

Consider an equilibrium between **A** and **B** in solution where each reaction is unimolecular. In each case, interconversion occurs when an **A** or **B** molecule undergoes a collision of sufficient force to provide the activation energy necessary for reaction. What if **A** and **B** are of nearly equal stability, with **B** just slightly more stable than **A**. Even though formation of **B** is favored, there will always be collisions that result in regeneration of **A**. The equilibrium results when the forward and reverse rates equalize.



$$\text{rate}(\text{forward}) = k_f[\mathbf{A}]$$

$$\text{rate}(\text{reverse}) = k_r[\mathbf{B}]$$

Another way of expressing this is looking at a plot of the activation energy of the reaction (Chapter

12). In Figure 1, we see that the activation energy of the forward reaction ($\mathbf{A} \rightarrow \mathbf{B}$) is nearly equal to the activation energy for the reverse reaction ($\mathbf{B} \rightarrow \mathbf{A}$). In this situation, there is enough background energy to allow both reactions proceed at an appreciable rate, so both materials are present in the reaction vessel at all times.

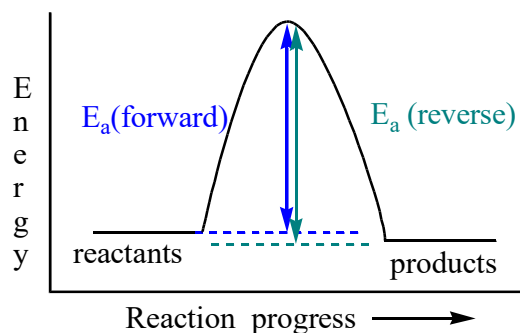


Figure 1

If we start with pure \mathbf{A} in a container, initially the forward rate will be large and the reverse rate zero. The forward rate will then slow (\mathbf{A} is used up) and the reverse rate will accelerate (\mathbf{B} is formed) until they become equal. If pure \mathbf{B} is used, then the “reverse” rate will be large and the “forward” rate will be zero. Likewise, the large rate will slow down and the small rate will increase until they equalize.

At equilibrium

$$k_f[\mathbf{A}] = k_r[\mathbf{B}]$$

The following graphs show representative plots for the change in concentration for two

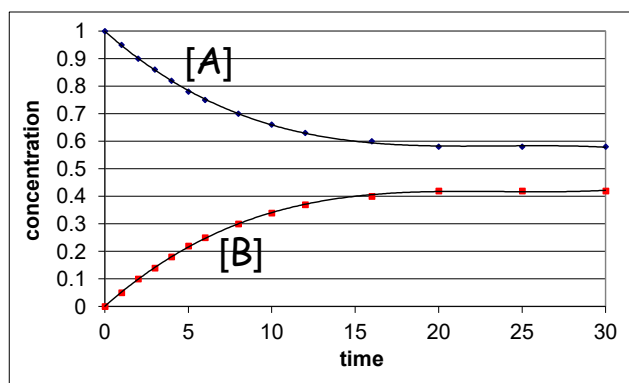


Figure 2

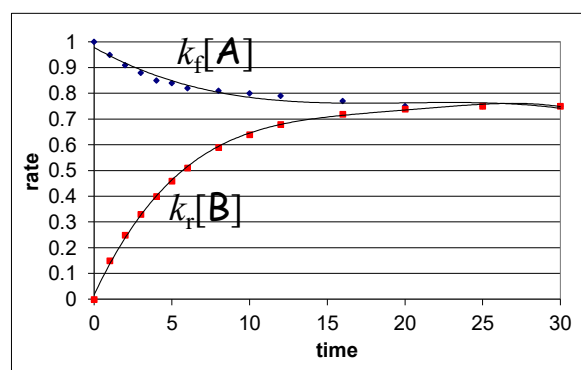


Figure 3

species with time (Figure 2) and the change in the rates of **A** disappearance and **B** appearance as the system approaches equilibrium (Figure 3).

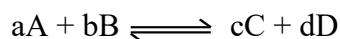
13.2 Equilibrium Constants

The previous equality can be rearranged to produce a useful equation.

$$\frac{k_f}{k_r} = \frac{[\mathbf{B}]}{[\mathbf{A}]} = K_{\text{eq}}$$

where K_{eq} is the equilibrium constant. Always remember that **equilibria are dynamic processes**, both the forward and reverse reactions are always occurring.

The previous equation can be generalized for any combination of materials in solution at equilibrium:

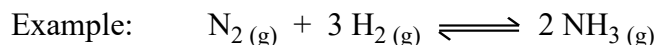


$$K_{\text{eq}} = \frac{[\mathbf{C}]^c[\mathbf{D}]^d}{[\mathbf{A}]^a[\mathbf{B}]^b}$$

If the same reactants were in the gas phase, the partial pressures of the gases are used in place of concentrations and the equilibrium constant becomes:

$$K_{\text{eq}} = \frac{P_{\mathbf{C}}^c P_{\mathbf{D}}^d}{P_{\mathbf{A}}^a P_{\mathbf{B}}^b}$$

It is important to use the “eq” as a subscript to help differentiate between the equilibrium and rate constants (handwriting sometimes makes distinguishing a capital K from a little k difficult).



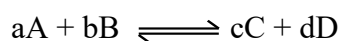
$$K_{\text{eq}} = \frac{P_{\text{NH}_3}^2}{P_{\text{N}_2} P_{\text{H}_2}^3}$$

Thus, the equilibrium constant expression depends only on the reaction stoichiometry.

Equilibrium constants have no units. They are temperature dependent (since rate constants are temperature dependent), so the temperature must be specified when an equilibrium constant is given. Since **equilibrium constants depend only on stoichiometry and temperature**, mechanism is irrelevant. This is important because catalysts change mechanisms (Chapter 12.7). As we will see at the end of this chapter, adding a catalyst causes the system to reach equilibrium more quickly, but the amounts of the various species aren't affected.

Prediction of the Direction of Reaction

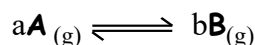
If a system is not at equilibrium, there are times it would be useful to determine in which direction the reaction would shift. For a non-equilibrium system



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

where Q is the reaction quotient. This is the same equation as on the third page of the notes for the equilibrium constant. Hence, the reaction quotient, Q , provides a number that is related to the equilibrium constant. When Q equals K_{eq} , the reaction is at equilibrium. When $Q \neq K_{eq}$, the reaction is moving towards equilibrium. If $Q < K_{eq}$, the reaction 'shifts right.' If $Q > K_{eq}$, the reaction 'shifts left.'

If you find this difficult to remember or are concerned you'll mix the two up, try the following method to remember these trends. Consider the equilibrium:



$$Q = \frac{P_B^b}{P_A^a}$$

Which way will the equilibrium shift if the reaction is begun with **A** but no **B**? To the right,

since there is no **B**, the reaction must try to produce some. In this case, $Q = 0$, which is less than K_{eq} no matter what the value of K or P_{A} are. Thus, if $Q < K_{\text{eq}}$, then the reaction shifts right.

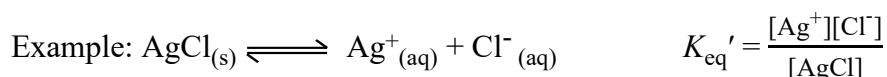
The other extreme occurs when the reaction starts with **B**, but no **A**. Then the reaction shifts left to produce some **A**. Here $Q = \infty$, which is greater than K no matter what the value of K_{eq} or P_{B} are. Thus, if $Q > K_{\text{eq}}$, then the reaction shifts left.

Homogeneous and Heterogeneous Equilibria

Until now, all of the equilibria you have seen have been homogeneous equilibria.

Homogeneous equilibria are equilibria in which all reactants and products exist in the same phase.

A heterogeneous equilibrium is one in which reactants and products exist in at least two different phases.



This equilibrium constant presents us with a problem. How do we measure the concentration of a solid? Concentration has units of mol/L. These are similar to the units for density: g/mL. Dividing the density of a substance by its molecular weight gives the proper units.

$$\frac{\text{density}}{\text{MW}} = \frac{\text{g/cm}^3}{\text{g/mol}} = \frac{\text{mol}}{\text{cm}^3} = \frac{\text{mol}}{\text{mL}}$$

But the density of a solid is a constant, so its “concentration” is also a constant. From the end of the last section, we know all values are unitless and so this value is incorporated into the equilibrium constant. Thus, the equilibrium equation simplifies to:

$$K_{\text{eq}}' = \frac{[\text{Ag}^+][\text{Cl}^-]}{\text{constant}}$$

$$K_{\text{eq}} = K_{\text{eq}}'(\text{constant}) = [\text{Ag}^+][\text{Cl}^-] = 1.8 \times 10^{-10}$$

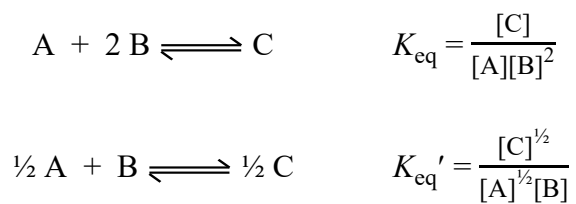
This means that if AgCl is placed in a sealed container, the $[Ag^+]$ and $[Cl^-]$ are the same whether an ounce or pound of AgCl is present. All that is required is that some be present.

This can be illustrated using a physical process with which you are familiar. Imagine an empty swimming pool on a dry, hot summer day. If you put a drop of water into the pool and covered it, the drop would completely evaporate. In this situation, the system would not be at equilibrium. Now imagine opening the cover, filling the pool with an inch of water, then recovering it. At this point some water would remain behind after evaporation. This is a physical equilibrium. After this point, adding water will NOT result in more water vapor. A chemical equilibrium works exactly the same way. If some silver(I) chloride is put in a sealed container and all of it dissolves, no equilibrium exists. If you add more silver(I) chloride and some is left after stirring, adding more won't change the amount of silver or chloride ions in the container.

The same is true for pure liquids too. An important generalization is that for any heterogeneous equilibrium involving gases; only the gases appear in the equilibrium expression. Again, while the amounts of pure solids and liquids present are not important, they must be there for the equilibrium to occur.

Coupled Equilibria

A short time ago, it was stated that equilibrium constants depend only on reaction stoichiometry. For this reason, it is convention to write out the stoichiometry using only whole numbers. Using fractions can change the equilibrium constant. For example:

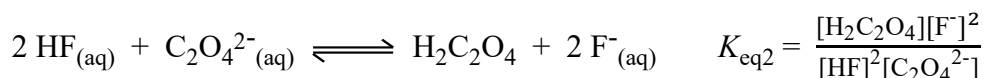
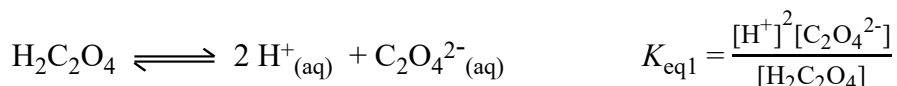
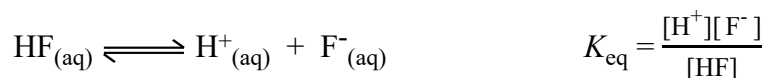


Now let $[A] = 2 M$, $[B] = 3 M$, and $[C] = 4 M$, then

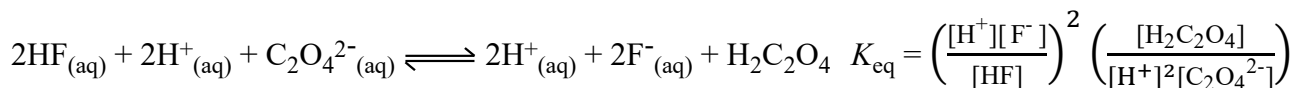
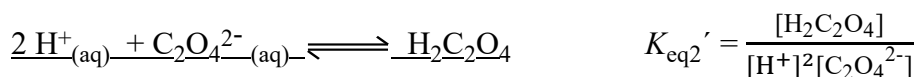
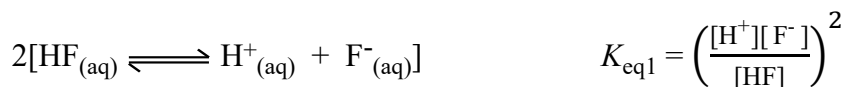
$$K_{\text{eq}} = \frac{4}{2(3)^2} = \frac{2}{9} = 0.222 \quad K_{\text{eq}}' = \frac{(4)^{1/2}}{(2)^{1/2}(3)} = \frac{2}{3\sqrt{2}} = 0.471$$

This is one of the reasons that you were told in CHM 211 to balance equations with only whole number coefficients (Section 4.1).

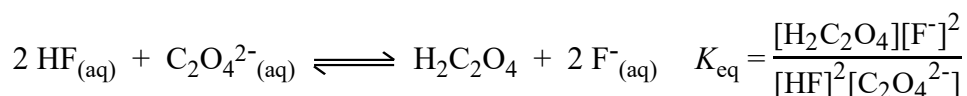
An interesting situation occurs when two equilibria occur in sequence (we'll see examples of this later). Consider the two weak acids HF_(aq) and H₂C₂O_{4(aq)} (oxalic acid) at 25 °C and a mixture of them.



The question is: “What is the relationship between the first two equations and the third?” We generate the third equation by reversing the second equilibrium and adding it to the first, which must be doubled to give the correct stoichiometry:



which simplifies the reaction and equilibrium expression we sought:



This example illustrates three facts about equilibria and their associated equations:

- 1) When an equilibrium is reversed, K_{eq} is inverted. i.e. $K_{\text{eq}}(\text{forward}) = \frac{1}{K_{\text{eq}}(\text{reverse})}$
- 2) When an equilibrium occurs more than once, the equilibrium constant is raised to that power.
- 3) When two equilibria are added, their equilibrium constants are multiplied.

The Magnitude of Equilibrium Constants

This is not in your book, but might make understanding chemical equilibria easier. There are 3 possible scenarios for the size of equilibrium constants: very large, very small, or close to one. When equilibrium constants are very large (e.g. >1000) reactions are essentially complete if the product can be removed quickly. If they are very small (e.g. <0.001), then essentially no product forms. It is only if the equilibrium constant is “near” one that an appreciable amount of all reactants and products exists. Let’s use the formation of phosgene as an example:



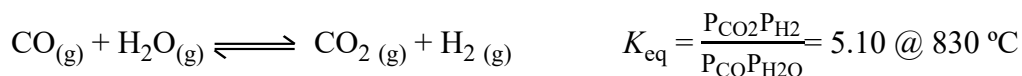
If $P_{\text{COCl}_2} = 1.00 \text{ atm}$ and $P_{\text{CO}} = P_{\text{Cl}_2}$, then what are the pressures of CO and Cl_2 ?

$$1.49 \times 10^8 = \frac{(1.00)}{x^2}$$

$$x = P_{\text{CO}} = P_{\text{Cl}_2} = 8.19 \times 10^{-5} \text{ atm}$$

As you can see, the pressures of CO and Cl_2 are about 0.001% that of COCl_2 . For all practical purposes, there is no reactant material left in the reaction vessel. Likewise, for reactions with extremely small equilibrium constants little product forms. In many situations, we can think of these reactions as either going to completion or never starting. Nevertheless, these small amounts of material can be important. Historical note: In World War I, phosgene was the major component of mustard gas.

If the equilibrium constant is closer to 1, as in the next reaction, there may be a significant amount of each substance present.



If, at equilibrium, $P_{\text{CO}} = P_{\text{H}_2\text{O}} = P_{\text{CO}_2} = 1.00$ atm, then $P_{\text{H}_2} = 5.10$ atm.

If $K_{\text{eq}} < 1$, the equilibrium favors the reactants (“lies to the left”).

If $K_{\text{eq}} > 1$, the equilibrium favors the products (“lies to the right”).

Since equilibria can be approached from either side, the way the reaction is written is somewhat arbitrary. When an equilibrium is reversed, K_{eq} is inverted. For the previous example, if the equation is written in the opposite direction the following results are obtained.



13.3 Shifting Equilibria: Le Châtelier’s Principle

In this section we examine what happens when a system that is at equilibrium is disturbed in some way. For example, what happens if reagents are added or the temperature or pressure is changed? Le Châtelier’s principle states that if a stress is applied to a system at equilibrium, the system will adjust so as to partially relieve the stress. The word “stress” here means any disturbances to an equilibrium, such as the ones just mentioned. One thing you must remember as you go through this section is that Le Châtelier’s principle does not cause anything. It is an observation about systems, not a physical explanation of why things occur the way they do.

Changes in Reactant or Product Concentrations

When a reactant or product is added to a system at equilibrium, the system will shift so as to remove some of the added material. If a reaction component is removed from an equilibrium mixture, the system will shift so as to replace some of it.

Why does this happen? Consider our generic equilibrium $\mathbf{A} \rightleftharpoons \mathbf{B}$ where the forward and

reverse steps are elementary steps. Then, at equilibrium,

$$k_f[\mathbf{A}] = k_r[\mathbf{B}]$$

If some **B** is added, then

$$k_f[\mathbf{A}] > k_r[\mathbf{B}]$$

In the Figures below, **A** is added 5 minutes into the reaction causing an upward spike in its concentration. As time goes by, **[A]** will decrease and **[B]** will increase (Figure 4) until the ratio of their rates returns to the original value (Figure 5). At that time, the equilibrium will be reestablished. In the new equilibrium, there will be more of both **A** and **B** than in the original equilibrium (Figure 4). But the real reason the equilibrium shifts is because the reaction rate increases. Adding more **A** means there are more reactant molecules and hence more collisions per unit time. Since there are no more **B** molecules (at the instant the extra **A** is added) this rate cannot increase until the additional reactions of **A** molecules produce **B** products.

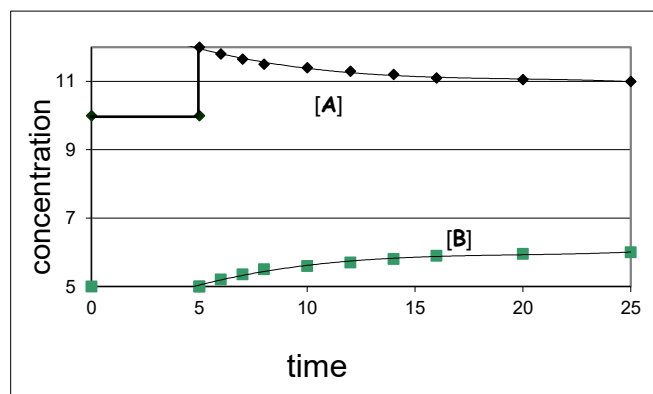


Figure 4

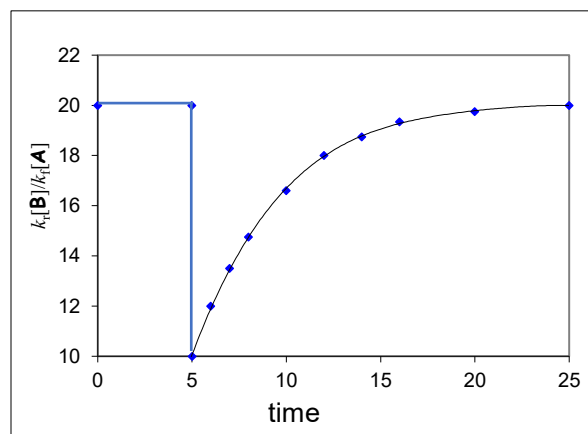


Figure 5

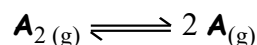
A somewhat more complicated example would be the equilibrium: $\mathbf{A}_{(g)} + \mathbf{C}_{(g)} \rightleftharpoons \mathbf{B}_{(g)}$. If some **A** is added, once again the forward rate increases for the same reasons described in the above paragraph. However, this time while there is more **A** and **B** in the new equilibrium, there is less **C**. This is because some of the existing **C** must be used to convert the added **A** to **B**. Since no extra **C**

was added, the amount of it must decrease.

Effects of Volume and Pressure Changes

For a gaseous equilibrium, changing the pressure by altering the container volume causes the equilibrium to shift so as to partially restore the original pressure. To understand why a pressure change (caused by a volume change) can affect an equilibrium consider the following situation.

Imagine the equilibrium of a dimer with its monomer:



Suppose we have 50 \mathbf{A}_2 molecules and 50 \mathbf{A} molecules at equilibrium and that the forward and reverse reactions are elementary steps. What happens if we halve the volume of the container (i.e. double the pressure)? The reduced volume means that collisions will happen twice as frequently. Since the forward reaction is unimolecular, its rate won't change initially, but the reverse reaction, which is bimolecular, will occur at a faster rate. The result is the reaction will shift to the left. Other systems have more complicated explanations, but follow similar logic.

The same prediction can be generated mathematically using the ideal gas equation. Recall that the ideal gas equation can be rearranged:

$$PV = nRT \Rightarrow \frac{n}{V} = \frac{P}{RT}$$

$$\text{For } \mathbf{A}_{(g)} \rightleftharpoons \mathbf{B}_{(g)} \quad K_{\text{eq}} = \frac{P_{\mathbf{B}}}{P_{\mathbf{A}}} = \frac{\left(\frac{n_{\mathbf{B}}RT}{V}\right)}{\left(\frac{n_{\mathbf{A}}RT}{V}\right)} = \frac{n_{\mathbf{B}}}{n_{\mathbf{A}}}$$

$$\text{For } \mathbf{A}_{(g)} \rightleftharpoons 2\mathbf{B}_{(g)} \quad K_{\text{eq}} = \frac{P_{\mathbf{B}}^2}{P_{\mathbf{A}}} = \frac{\left(\frac{n_{\mathbf{B}}RT}{V}\right)^2}{\left(\frac{n_{\mathbf{A}}RT}{V}\right)} = \left(\frac{n_{\mathbf{B}}^2RT}{n_{\mathbf{A}}}\right) \frac{1}{V}$$

As you can see, if there are equal numbers of gas molecules on either side of the equilibrium the volume terms divide away and pressure has no effect on the equilibrium. If they are different,

then the volume change affects the position of the equilibrium. Further, if pressure is increased by decreasing volume, the number of moles of **B** gas must drop as well to maintain the equilibrium. This is the same prediction made by Le Chatelier's principle.

If the pressure is increased by adding a non-reactive gas, there is no effect on equilibrium. This is because the rate of reactive collisions (e.g. **A** bumping into another **A**) doesn't change. If small amounts of a participant gas are added concentration effects (*vide supra*) are usually more important than pressure effects.

Effect of Temperature Changes

Unlike the previous two stresses, a change in temperature usually results in a change in the value of the equilibrium constant. Remember that rate constants are temperature dependent and that equilibrium constants are a ratio of rate constants. Nevertheless, there is a convenient rule here. If the temperature of an equilibrium mixture is increased, the equilibrium shifts in the direction that absorbs heat (endothermic). Remember that when a reaction is reversed, the sign of ΔH reverses. Thus, in an equilibrium, the magnitude of ΔH is the same in each direction, only the sign changes.

In the book example, $\text{N}_2\text{O}_4 \rightleftharpoons 2 \text{NO}_2$, $\Delta H = 57.2 \text{ kJ}$. Warming the reaction results in a shift to the right. Does this seem reasonable? In the right-hand direction, a nitrogen-nitrogen bond is broken. The added thermal energy causes this to happen.

The Effect of Catalysts

First, recall what a catalyst does: A catalyst increases the rate of a reaction without itself being permanently changed. How does it do this? By changing the reaction path to one with a lower activation energy.

If the activation energy is lower, it is lower in both directions. The net effect is that the reaction accelerates in both directions. Thus, the position of the equilibrium does not change, but

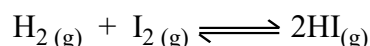
the speed at which equilibrium is reached increases.

13.4 Equilibrium Calculations

Calculation of an Equilibrium Constant

A mixture of 5.000×10^{-3} mol H_2 and 1.000×10^{-2} mol I_2 is placed in a 5.000 L container @ 448 °C. At equilibrium, the pressure of HI is 0.1106 atm. Calculate K_{eq} at 448 °C.

The first thing you need is the balanced equation (this is always the case):



Now convert the units of all substances to get initial pressures:

$$P_{\text{H}_2\text{i}} = \left(\frac{5.000 \times 10^{-3} \text{ mol}}{5.000 \text{ L}} \right) \left(0.08205 \frac{\text{L}\cdot\text{atm}}{\text{mol}\cdot\text{K}} \right) (721 \text{ K}) = 0.05916 \text{ atm}$$

Note the subscript "i."
Using it makes solving the problem easier.

$$P_{\text{I}_2\text{i}} = \left(\frac{1.000 \times 10^{-2} \text{ mol}}{5.000 \text{ L}} \right) \left(0.08205 \frac{\text{L}\cdot\text{atm}}{\text{mol}\cdot\text{K}} \right) (721 \text{ K}) = 0.1183 \text{ atm}$$

$$P_{\text{HIi}} = 0 \text{ atm}$$

You are given the equilibrium pressure of HI as 0.1106 atm. How much H_2 and I_2 were required to form that much HI? To answer this, you must remember that pressure and the number of moles of gas are directly proportional ($P \propto n$). This simplifies the math. Below the subscript "c" means *consumed* and the subscript "e" means *equilibrium*.

$$P_{\text{H}_2\text{c}} = (0.1106 \text{ atm}) \left(\frac{1 \text{ mol}_{\text{H}_2}}{2 \text{ mol}_{\text{HI}}} \right) = 0.05531 \text{ atm}_{\text{H}_2}$$

$$P_{\text{I}_2\text{c}} = (0.1106 \text{ atm}) \left(\frac{1 \text{ mol}_{\text{I}_2}}{2 \text{ mol}_{\text{HI}}} \right) = 0.05531 \text{ atm}_{\text{I}_2}$$

$$P_{\text{H}_2\text{e}} = P_{\text{H}_2\text{i}} - P_{\text{H}_2\text{c}} = (0.05916 \text{ atm}) - (0.05531 \text{ atm}) = 0.00384 \text{ atm}$$

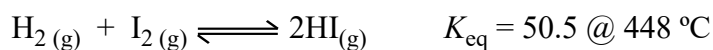
$$P_{\text{I}_2\text{e}} = P_{\text{I}_2\text{i}} - P_{\text{I}_2\text{c}} = (0.1183 \text{ atm}) - (0.05531 \text{ atm}) = 0.0630 \text{ atm}$$

Now that you have all three equilibrium pressures, the equilibrium constant can be calculated.

$$K_{\text{eq}} = \frac{(0.1106)^2}{(0.00384)(0.0630)} = 50.6$$

Calculation of Equilibrium Concentrations

What are the equilibrium concentrations of all species for



when $P_{\text{H}_2\text{i}} = P_{\text{I}_2\text{i}} = 0.100 \text{ atm}$ and $P_{\text{HIi}} = 0 \text{ atm}$

- 1) Which way does the equilibrium shift? $Q = 0 < K \Rightarrow$ right
- 2) What are the equilibrium pressures?

$$P_{\text{H}_2\text{i}} = 0.100 \text{ atm} \quad P_{\text{H}_2\text{e}} = (0.100 - x) \text{ atm}$$

$$P_{\text{I}_2\text{i}} = 0.100 \text{ atm} \quad P_{\text{I}_2\text{e}} = (0.100 - x) \text{ atm}$$

$$P_{\text{HIi}} = 0 \text{ atm} \quad P_{\text{HIe}} = 2x \text{ atm}$$

The reason why x is subtracted from the H_2 and I_2 pressures, while P_{HI} increases by $2x$ is reaction stoichiometry. For each molecule of H_2 or I_2 consumed, 2 molecules of HI are produced. Forgetting this is a common mistake when working problems.

Now substitute into the equilibrium equation:

$$50.5 = \frac{(2x)^2}{(0.100 - x)(0.100 - x)} = \frac{(2x)^2}{(0.100 - x)^2}$$

$$7.10 = \frac{2x}{0.100 - x}$$

$$2x = (7.10)(0.100 - x)$$

$$x = 0.0780 \text{ atm}$$

$$P_{\text{H}_2\text{e}} = P_{\text{I}_2\text{e}} = 0.100 \text{ atm} - 0.0780 \text{ atm} = 0.0220 \text{ atm}$$

$$P_{\text{HIe}} = 2(0.0780 \text{ atm}) = 0.156 \text{ atm}$$

As a check it is a good habit to plug your answers back into the equilibrium equation to verify

you get back K_{eq} .

$$\frac{(0.156)^2}{(0.0220)(0.0220)} = 50.3 \approx K_{\text{eq}}$$

A more challenging set of initial conditions for the same reaction follows.

$$P_{\text{H}_2\text{i}} = 6.23 \times 10^{-2} \text{ atm} \quad P_{\text{I}_2\text{i}} = 4.14 \times 10^{-3} \text{ atm} \quad P_{\text{HIi}} = 2.24 \times 10^{-3} \text{ atm}$$

Now calculate the reaction quotient and direction of equilibrium shift.

$$Q = \frac{(2.24 \times 10^{-3})^2}{(6.23 \times 10^{-2})(4.14 \times 10^{-3})} = 19.4 < K_{\text{eq}} \text{ reaction shifts right}$$

$$P_{\text{H}_2\text{e}} = (6.23 \times 10^{-2} - x) \text{ atm} \quad P_{\text{I}_2\text{e}} = (4.14 \times 10^{-3} - x) \text{ atm} \quad P_{\text{HIe}} = (2.24 \times 10^{-3} + 2x) \text{ atm}$$

Note: If Q had been greater than K_{eq} , then x would have been added to H_2 & I_2 and subtracted from HI .

Substitute into the equilibrium expression.

$$50.5 = \frac{(2.24 \times 10^{-3} + 2x)^2}{(6.23 \times 10^{-2} - x)(4.14 \times 10^{-3} - x)}$$

Expand and collect terms

$$x^2 - (1.32 \times 10^{-2})x + (1.72 \times 10^{-5}) = 0$$

This requires the quadratic equation

$$x = \frac{-b \pm \sqrt{b^2 - 4ac}}{2a}$$

Plugging in and solving yields

$$x_1 = 1.47 \times 10^{-3} \text{ atm} \quad \text{and} \quad x_2 = 1.17 \times 10^{-2} \text{ atm}$$

But $x_2 > P_{\text{H}_2\text{i}}$ and $P_{\text{I}_2\text{i}}$ and so must be discarded. Substitute back into the expressions to calculate the equilibrium concentrations.

$$P_{\text{H}_2\text{e}} = (6.23 \times 10^{-2} \text{ atm}) - (1.47 \times 10^{-3} \text{ atm}) = 4.76 \times 10^{-2} \text{ atm}$$

$$P_{\text{I}_2\text{e}} = (4.14 \times 10^{-3} \text{ atm}) - (1.47 \times 10^{-3} \text{ atm}) = 2.67 \times 10^{-3} \text{ atm}$$

$$P_{\text{HIe}} = (2.24 \times 10^{-2} \text{ atm}) + 2(1.47 \times 10^{-3} \text{ atm}) = 2.53 \times 10^{-2} \text{ atm}$$

$$\text{Check: } \frac{(2.53 \times 10^{-2})}{(4.76 \times 10^{-3})(2.67 \times 10^{-3})} = 50.4 \approx K_C$$

In general, one solution to the quadratic equation will always be physically impossible.

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