

16.5: Heterogenous Equilibria - Reactions Involving Solids and Liquids

Learning Objectives

- To understand how different phases affect equilibria.

When the products and reactants of an equilibrium reaction form a single phase, whether gas or liquid, the system is a homogeneous equilibrium. In such situations, the concentrations of the reactants and products can vary over a wide range. In contrast, a system whose reactants, products, or both are in more than one phase is a heterogeneous equilibrium, such as the reaction of a gas with a solid or liquid.

As noted in the previous section, the equilibrium constant expression is actually a ratio of activities. To simplify the calculations in general chemistry courses, the activity of each substance in the reaction is often approximated using a ratio of the molarity of a substance compared to the standard state of that substance. For substances that are liquids or solids, the standard state is just the concentration of the substance within the liquid or solid. Because the molar concentrations of pure liquids and solids normally do not vary greatly with temperature, the ratio of the molarity to the standard state for substances that are liquids or solids always has a value of 1. For example, for a compound such as $\text{CaF}_2(\text{s})$, the term going into the equilibrium expression is $[\text{CaF}_2]/[\text{CaF}_2]$ which cancels to unity. Thus, when the activities of the solids and liquids (including solvents) are incorporated into the equilibrium expression, they do not change the value.

Consider the following reaction, which is used in the final firing of some types of pottery to produce brilliant metallic glazes:



The glaze is created when metal oxides are reduced to metals by the product, carbon monoxide. The equilibrium constant expression for this reaction is as follows:

$$K = \frac{a_{\text{CO}}^2}{a_{\text{CO}_2} a_{\text{C}}} = \frac{[\text{CO}]^2}{[\text{CO}_2][1]} = \frac{[\text{CO}]^2}{[\text{CO}_2]} \quad (16.5.2)$$

The equilibrium constant for this reaction can also be written in terms of the partial pressures of the gases:

$$K_p = \frac{(P_{\text{CO}})^2}{P_{\text{CO}_2}} \quad (16.5.3)$$

Incorporating all the constant values into K' or K_p allows us to focus on the substances whose concentrations change during the reaction.

Although the activities of pure liquids or solids are not written explicitly in the equilibrium constant expression, these substances must be present in the reaction mixture for chemical equilibrium to occur. Whatever the concentrations of CO and CO_2 , the system described in Equation 16.5.1 will reach chemical equilibrium only if a stoichiometric amount of solid carbon or excess solid carbon has been added so that some is still present once the system has reached equilibrium. As shown in Figure 16.5.1, it does not matter whether 1 g or 100 g of solid carbon is present; in either case, the composition of the gaseous components of the system will be the same at equilibrium.

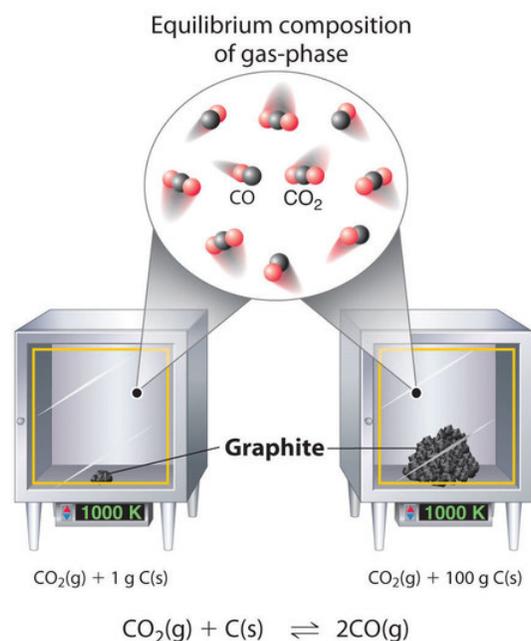


Figure 16.5.2: Effect of the Amount of Solid Present on Equilibrium in a Heterogeneous Solid–Gas System. In the system, the equilibrium composition of the gas phase at a given temperature, 1000 K in this case, is the same whether a small amount of solid carbon (left) or a large amount (right) is present.

✓ Example 16.5.1

Write each expression for K , incorporating all constants, and K_p for the following equilibrium reactions.

- $\text{PCl}_3(\text{l}) + \text{Cl}_2(\text{g}) \rightleftharpoons \text{PCl}_5(\text{s})$
- $\text{Fe}_3\text{O}_4(\text{s}) + 4 \text{H}_2(\text{g}) \rightleftharpoons 3 \text{Fe}(\text{s}) + 4 \text{H}_2\text{O}(\text{g})$

Given: balanced equilibrium equations.

Asked for: expressions for K and K_p .

Strategy:

Find K by writing each equilibrium constant expression as the ratio of the concentrations of the products and reactants, each raised to its coefficient in the chemical equation. Then express K_p as the ratio of the partial pressures of the products and reactants, each also raised to its coefficient in the chemical equation.

Solution

This reaction contains a pure solid (PCl_5) and a pure liquid (PCl_3). Their activities are equal to 1, so when incorporated into the equilibrium constant expression, they do not change the value. So

$$K = \frac{1}{(1)[\text{Cl}_2]}$$

and

$$K_p = \frac{1}{(1)P_{\text{Cl}_2}}$$

This reaction contains two pure solids (Fe_3O_4 and Fe), which are each assigned a value of 1 in the equilibrium constant expressions:

$$K = \frac{(1)[\text{H}_2\text{O}]^4}{(1)[\text{H}_2]^4}$$

and

$$K_p = \frac{(1)(P_{H_2O})^4}{(1)(P_{H_2})^4}$$

? Exercise 16.5.1

Write the expressions for K and K_p for the following reactions.

- $\text{CaCO}_3(\text{s}) \rightleftharpoons \text{CaO}(\text{s}) + \text{CO}_2(\text{g})$
- $\text{C}_6\text{H}_{12}\text{O}_6(\text{s}) + 6 \text{O}_2(\text{g}) \rightleftharpoons 6 \text{CO}_2(\text{g}) + 6 \text{H}_2\text{O}(\text{g})$
glucose

Answer a

$$K = [\text{CO}_2] \text{ and } K_p = P_{\text{CO}_2}$$

Answer b

$$K = \frac{[\text{CO}_2]^6 [\text{H}_2\text{O}]^6}{[\text{O}_2]^6} \text{ and } K_p = \frac{(P_{\text{CO}_2})^6 (P_{\text{H}_2\text{O}})^6}{(P_{\text{O}_2})^6}$$

For reactions carried out in solution, the solvent is assumed to be pure, and therefore is assigned an activity equal to 1 in the equilibrium constant expression. The activities of the solutes are approximated by their molarities. The result is that the equilibrium constant expressions appear to only depend upon the concentrations of the solutes.

The activities of pure solids, pure liquids, and solvents are defined as having a value of '1'. Often, it is said that these activities are "left out" of equilibrium constant expressions. This is an unfortunate use of words. The activities are not "left out" of equilibrium constant expressions. Rather, because they have a value of '1', they do not change the value of the equilibrium constant when they are multiplied together with the other terms. The activities of the solutes are approximated by their molarities.

Summary

An equilibrated system that contains products and reactants in a single phase is a homogeneous equilibrium; a system whose reactants, products, or both are in more than one phase is a heterogeneous equilibrium.

Contributors and Attributions

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