

9.4: Pressure Dependence of K_p - Le Châtelier's Principle

Since the equilibrium constant K_p is a function of ΔG_{rxn}° which is defined for a specific composition (all reactants in their standard states and at unit pressure (or fugacity), changes in pressure have no effect on equilibrium constants for a fixed temperature. However, changes in pressure can have profound effects on the compositions of equilibrium mixtures.

To demonstrate the relationship, one must recall Dalton's law of partial pressures. According to this relationship, the partial pressure of a component of a gas-phase mixture can be expressed

$$p_i = \chi_i p_{tot}$$

It is the combination of mole fractions that describes the composition of the equilibrium mixture.

Substituting the above expression into the expression for K_p yields

$$K_p = \prod_i (\chi_i p_{tot})^{\nu_i}$$

This expression can be factored into two pieces – one containing the mole fractions and thus describing the composition, and one containing the total pressure.

$$K_p = \left(\prod_i \chi_i^{\nu_i} \right) \left(\prod_i p_{tot}^{\nu_i} \right)$$

The second factor is a constant for a given total pressure. If the first term is given the symbol K_x , the expression becomes

$$K_p = K_x (p_{tot})^{\sum_i \nu_i}$$

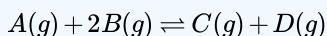
In this expression, K_x has the same form as an equilibrium constant

$$K_x = \prod_i \chi_i^{\sum_i \nu_i}$$

but is not itself a constant. The value of K_x will vary with varying composition, and will *need* to vary with varying total pressure (in most cases) in order to maintain a constant value of K_p .

✓ Example 9.4.1:

Consider the following reaction at equilibrium.



In which direction will the equilibrium shift if the volume of the reaction vessel is decreased?

Solution

A decrease in the volume will lead to an increase in total pressure. Since the equilibrium constant can be expressed as

$$K_p = \frac{p_C p_D}{p_A p_B^2} = \frac{\chi_C \chi_D}{\chi_A \chi_B^2} (p_{tot})^{-1}$$

An increase in pressure will lead to an increase in K_x to maintain a constant value of K_p . So the reaction will shift to form more of the products C and D .

Note: This should make some sense, since a shift to the side of the reaction with fewer moles of gas will lower the total pressure of the reaction mixture, and thus relieving the stress introduced by increasing the pressure. This is exactly what is expected according to Le Chatelier's principle.

It should be noted that there are several ways one can affect the total pressure of a gas-phase equilibrium. These include the introduction or removal of reactants or products (perhaps through condensation or some other physical process), a change in volume of the reaction vessel, or the introduction of an inert gas that does not participate in the reaction itself. (Changes in the temperature will be discussed in a later section.) The principle of Le Chatelier's can be used as a guide to predict how the equilibrium composition will respond to a change in pressure.

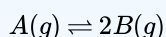
Le Chatelier's principle: When a stress is introduced to a system at equilibrium, the system will adjust so as to reduce the stress.

Le Chatelier's principle is fairly clear on how to think about the addition or removal of reactants or products. For example, the addition of a reactant will cause the system to shift to reduce the partial pressure of the reactant. It can do this by forming more products.

An important exception to the rule that increasing the total pressure will cause a shift in the reaction favoring the side with fewer moles of gas occurs when the total pressure is increased by introducing an inert gas to the mixture. The reason is that the introduction of an inert gas will affect the total pressures *and* the partial pressures of each individual species.

✓ Example 9.4.2:

A 1.0 L vessel is charged with 1.00 atm of A, and the following reaction is allowed to come to equilibrium at 298 K.



with $K_p = 3.10$.

- What are the equilibrium partial pressures and mole fractions of A and B?
- If the volume of the container is doubled, what are the equilibrium partial pressures and mole fractions of A and B?
- If 1.000 atm of Ar (an inert gas) is introduced into the system described in b), what are the equilibrium partial pressures and mole fractions of A and B once equilibrium is reestablished?

Solution

Part a:

First, we can use an ICE[1] table to solve part a).

	A	2 B
Initial	1.00 atm	0
Change	-x	+2x
Equilibrium	1.00 atm - x	2x

So (for convenience, consider K_p to have units of atm)

$$3.10 \text{ atm} = \frac{(2x)^2}{1.00 \text{ atm} - x}$$

Solving for x yields values of

$$x_1 = -1.349 \text{ atm}$$

$$x_1 = 0.574 \text{ atm}$$

Clearly, x_1 , while a solution to the mathematical problem, is not physically meaningful since the equilibrium pressure of B cannot be negative. So the equilibrium partial pressures are given by

$$p_A = 1.00 \text{ atm} - 0.574 \text{ atm} = 0.426 \text{ atm}$$

$$p_B = 2(0.574 \text{ atm}) = 1.148 \text{ atm}$$

So the mole fractions are given by

$$\chi_A = \frac{0.426 \text{ atm}}{0.426 \text{ atm} + 1.148 \text{ atm}} = 0.271$$

$$\chi_B = 1 - \chi_A = 1 - 0.271 = 0.729$$

Part b:

The volume is doubled. Again, an ICE table is useful. The initial pressures will be half of the equilibrium pressures found in part a).

	A	2 B
Initial	0.213 atm	0.574 atm
Change	-x	+2x
Equilibrium	0.213 atm - x	0.574 atm + 2x

So the new equilibrium pressures can be found from

$$3.10 \text{ atm} = \frac{(0.574 \text{ atm} + 2x)^2}{0.213 \text{ atm} - x}$$

And the values of x that solve the problem are

$$x_1 = -1.4077 \text{ atm}$$

$$x_1 = 0.05875 \text{ atm}$$

We reject the negative root (since it would cause both of the partial pressures to become negative. So the new equilibrium partial pressures are

$$p_A = 0.154 \text{ atm}$$

$$p_B = 0.0692 \text{ atm}$$

And the mole fractions are

$$\chi_A = 0.182$$

$$\chi_B = 0.818$$

We can see that the mole fraction of A decreased and the mole fraction B increased. This is the result expected by Le Chatlier's principle since the lower total pressure favors the side of the reaction with more moles of gas.

Part c:

We introduce 1.000 atm of an inert gas. The new partial pressures are

$$p_A = 0.154 \text{ atm}$$

$$p_B = 0.692 \text{ atm}$$

$$p_{Ar} = 1.000 \text{ atm}$$

And because the partial pressures of A and B are unaffected, the equilibrium does not shift! What is affected is the composition, and so the mole fractions will change.

$$\chi_A = \frac{0.154 \text{ atm}}{0.154 \text{ atm} + 0.692 \text{ atm} + 1.000 \text{ atm}} = 0.08341$$

$$\chi_B = \frac{0.692 \text{ atm}}{0.154 \text{ atm} + 0.692 \text{ atm} + 1.000 \text{ atm}} = 0.08341$$

$$\chi_{Ar} = \frac{1.000 \text{ atm}}{0.154 \text{ atm} + 0.692 \text{ atm} + 1.000 \text{ atm}} = 0.08341$$

And since

$$K_p = K_x(p_{tot})$$

$$\frac{(0.3749)^2}{0.08342}(1.846 \text{ atm}) = 3.1$$

Within round-off error, the value obtained is the equilibrium constant. So the conclusion is that the introduction of an inert gas, even though it increases the total pressure, does not induce a change in the partial pressures of the reactants and products, so it does not cause the equilibrium to shift.

[1] ICE is an acronym for “Initial, Change, Equilibrium”. An ICE table is a tool that is used to solve equilibrium problems in terms of an unknown number of moles (or something proportional to moles, such as pressure or concentration) will shift for a system to establish equilibrium. See (Tro, 2014) or a similar General Chemistry text for more background and information.

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