# Reaction Equilibrium in the Gas Phase*

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## 1 Foundation

In beginning our study of the reactions of gases, we will assume a knowledge of the physical properties of gases as described by the **Ideal Gas Law** and an understanding of these properties as given by the postulates and conclusions of the **Kinetic Molecular Theory**. We assume that we have developed a dynamic model of phase equilibrium in terms of competing rates. We will also assume an understanding of the bonding, structure, and properties of individual molecules.

## 2 Goals

In performing stoichiometric calculations, we assume that we can calculate the amount of product of a reaction from the amount of the reactants we start with. For example, if we burn methane gas, $CH_4\,(g)$, in excess oxygen, the reaction

$$CH_4\,(g) + 2O_2\,(g) \rightarrow CO_2\,(g) + 2H_2O\,(g) \tag{1}$$

occurs, and the number of moles of $CO_2\,(g)$ produced is assumed to equal the number of moles of $CH_4\,(g)$ we start with.

From our study of phase transitions we have learned the concept of equilibrium. We observed that, in the transition from one phase to another for a substance, under certain conditions both phases are found to coexist, and we refer to this as phase equilibrium. It should not surprise us that these same concepts of equilibrium apply to chemical reactions as well. In the reaction (1), therefore, we should examine whether the reaction actually produces exactly one mole of $CO_2$ for every mole of $CH_4$ we start with or whether we wind up with an equilibrium mixture containing both $CO_2$ and $CH_4$. We will find that different reactions provide us with varying answers. In many cases, virtually all reactants are consumed, producing the stoichiometric amount of product. However, in many other cases, substantial amounts of reactant are still present when the reaction achieves equilibrium, and in other cases, almost no product is produced at equilibrium. Our goal will be to understand, describe and predict the reaction equilibrium.

An important corollary to this goal is to attempt to control the equilibrium. We will find that varying the conditions under which the reaction occurs can vary the amounts of reactants and products present at equilibrium. We will develop a general principle for predicting how the reaction conditions affect the amount of product produced at equilibrium.

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## 3 Observation 1: Reaction equilibrium

We begin by analyzing a significant industrial chemical process, the synthesis of ammonia gas, $NH_3$, from nitrogen and hydrogen:

$$N_2\left(g\right) + 3H_2\left(g\right) \rightarrow 2NH_3\left(g\right) \quad (2)$$

If we start with 1 mole of $N_2$ and 3 moles of $H_2$, the balanced equation predicts that we will produce 2 moles of $NH_3$. In fact, if we carry out this reaction starting with these quantities of nitrogen and hydrogen at 298K in a 100.0L reaction vessel, we observe that the number of moles of $NH_3$ produced is 1.91 mol. This "yield" is less than predicted by the balanced equation, but the difference is not due to a limiting reagent factor. Recall that, in stoichiometry, the limiting reagent is the one that is present in less than the ratio of moles given by the balanced equation. In this case, neither $N_2$ nor $H_2$ is limiting because they are present initially in a 1:3 ratio, exactly matching the stoichiometry. Note also that this seeming deficit in the yield is not due to any experimental error or imperfection, nor is it due to poor measurements or preparation. Rather, the observation that, at 298K, 1.91 moles rather than 2 moles are produced is completely reproducible: every measurement of this reaction at this temperature in this volume starting with 1 mole of $N_2$ and 3 moles of $H_2$ gives this result. We conclude that the reaction (2) achieves **reaction equilibrium** in which all three gases are present in the gas mixture. We can determine the amounts of each gas at equilibrium from the stoichiometry of the reaction. When $n_{NH_3} = 1.91\text{mol}$ are created, the number of moles of $N_2$ remaining at equilibrium is $n_{N_2} = 0.045\text{mol}$ and $n_{H_2} = 0.135\text{mol}$.

It is important to note that we can vary the relative amount of $NH_3$ produced by varying the temperature of the reaction, the volume of the vessel in which the reaction occurs, or the relative starting amounts of $N_2$ and $H_2$. We shall study and analyze this observation in detail in later sections. For now, though, we demonstrate that the concept of reaction equilibrium is general to all reactions.

Consider the reaction

$$H_2\left(g\right) + I_2\left(g\right) \rightarrow 2HI\left(g\right) \quad (3)$$

If we begin with 1.00 mole of $H_2$ and 1.00 mole of $I_2$ at 500K in a reaction vessel of fixed volume, we observe that, at equilibrium, $n_{HI} = 1.72\text{mol}$, leaving in the equilibrium mixture $n_{H_2} = 0.14\text{mol}$ and $n_{I_2} = 0.14\text{mol}$.

Similarly, consider the decomposition reaction

$$N_2O_4\left(g\right) \rightarrow 2NO_2\left(g\right) \quad (4)$$

At 298K in a 100.0L reaction flask, 1.00 mol of $N_2O_4$ partially decomposes to produce, at equilibrium, $n_{NO_2} = 0.64\text{mol}$ and $n_{N_2O_4} = 0.68\text{mol}$.

Some chemical reactions achieve an equilibrium that appears to be very nearly complete reaction. For example,

$$H_2\left(g\right) + Cl_2\left(g\right) \rightarrow 2HCl\left(g\right) \quad (5)$$

If we begin with 1.00 mole of $H_2$ and 1.00 mole of $Cl_2$ at 298K in a reaction vessel of fixed volume, we observe that, at equilibrium, $n_{HCl}$ is almost exactly 2.00 mol, leaving virtually no $H_2$ or $Cl_2$. This does not mean that the reaction has not come to equilibrium. It means instead that, at equilibrium, there are essentially no reactants remaining.

In each of these cases, the amounts of reactants and products present at equilibrium vary as the conditions are varied but are completely reproducible for fixed conditions. Before making further observations that will lead to a quantitative description of the reaction equilibrium, we consider a qualitative description of equilibrium.

We begin with a dynamic equilibrium description. We know from our studies of phase transitions that equilibrium occurs when the rate of the forward process (*e.g.* evaporation) is matched by the rate of reverse process (*e.g.* condensation). Since we have now observed that gas reactions also come to equilibrium, we postulate that at equilibrium the forward reaction rate is equal to the reverse reaction rate. For example, in the reaction here (4), the rate of decomposition of $N_2O_4$ molecules at equilibrium must be exactly matched by the rate of recombination (or **dimerization**) of $NO_2$ molecules.

To show that the forward and reverse reactions continue to happen at equilibrium, we start with the $NO_2$ and $N_2O_4$ mixture at equilibrium and we vary the volume of the flask containing the mixture. We observe that, if we increase the volume and the reaction is allowed to come to equilibrium, the amount of $NO_2$ at equilibrium is larger at the expense of a smaller amount of $N_2O_4$. We can certainly conclude that the amounts of the gases at equilibrium depend on the reaction conditions. However, if the forward and reverse reactions stop once the equilibrium amounts of material are achieved, the molecules would not "know" that the volume of the container had increased. Since the reaction equilibrium can and does respond to a change in volume, it must be that the change in volume affects the rates of both the forward and reverse processes. This means that both reactions must be occurring at equilibrium, and that their rates must exactly match at equilibrium.

This reasoning reveals that the amounts of reactant and product present at equilibrium are determined by the rates of the forward and reverse reactions. If the rate of the forward reaction (*e.g.* decomposition of $N_2O_4$) is faster than the rate of the reverse reaction, then at equilibrium we have more product than reactant. If that difference in rates is very large, at equilibrium there will be much more product than reactant. Of course, the converse of these conclusions is also true. It must also be the case that the rates of these processes depends on, amongst other factors, the volume of the reaction flask, since the amounts of each gas present at equilibrium change when the volume is changed.

## 4 Observation 2: Equilibrium constants

It was noted above that the equilibrium partial pressures of the gases in a reaction vary depending upon a variety of conditions. These include changes in the initial numbers of moles of reactants and products, changes in the volume of the reaction flask, and changes in the temperature. We now study these variations quantitatively.

Consider first the reaction here (4). Following on our previous study of this reaction, we inject an initial amount of $N_2O_4\,(g)$ into a 100L reaction flask at 298K. Now, however, we vary the initial number of moles of $N_2O_4\,(g)$ in the flask and measure the equilibrium pressures of both the reactant and product gases. The results of a number of such studies are given here (Table 1: Equilibrium Partial Pressures in Decomposition Reaction).

**Equilibrium Partial Pressures in Decomposition Reaction**

| **Initial** $n_{N_2O_4}$ | $P_{N_2O_4}$ **(atm)** | $P_{NO_2}$ **(atm)** |
|---|---|---|
| 0.1 | 0.00764 | 0.033627 |
| 0.5 | 0.071011 | 0.102517 |
| 1 | 0.166136 | 0.156806 |
| 1.5 | 0.26735 | 0.198917 |
| 2 | 0.371791 | 0.234574 |
| 2.5 | 0.478315 | 0.266065 |
| 3 | 0.586327 | 0.294578 |
| 3.5 | 0.695472 | 0.320827 |
| 4 | 0.805517 | 0.345277 |
| 4.5 | 0.916297 | 0.368255 |
| 5 | 1.027695 | 0.389998 |

**Table 1**

We might have expected that the amount of $NO_2$ produced at equilibrium would increase in direct proportion to increases in the amount of $N_2O_4$ we begin with. Table 1: Equilibrium Partial Pressures in Decomposition Reaction shows that this is not the case. Note that when we increase the initial amount of $N_2O_4$ by a factor of 10 from 0.5 moles to 5.0 moles, the pressure of $NO_2$ at equilibrium increases by a factor of less than 4.

The relationship between the pressures at equilibrium and the initial amount of $N_2O_4$ is perhaps more easily seen in a graph of the data in Table 1: Equilibrium Partial Pressures in Decomposition Reaction, as shown in Figure 1 (Equilibrium Partial Pressures in Decomposition Reaction). There are some interesting features here. Note that, when the initial amount of $N_2O_4$ is less than 1 mol, the equilibrium pressure of $NO_2$ is greater than that of $N_2O_4$. These relative pressures reverse as the initial amount increases, as the $N_2O_4$ equilibrium pressure keeps track with the initial amount but the $NO_2$ pressure falls short. Clearly, the equilibrium pressure of $NO_2$ does not increase proportionally with the initial amount of $N_2O_4$. In fact, the increase is slower than proportionality, suggesting perhaps a square root relationship between the pressure of $NO_2$ and the initial amount of $N_2O_4$.

**Equilibrium Partial Pressures in Decomposition Reaction**

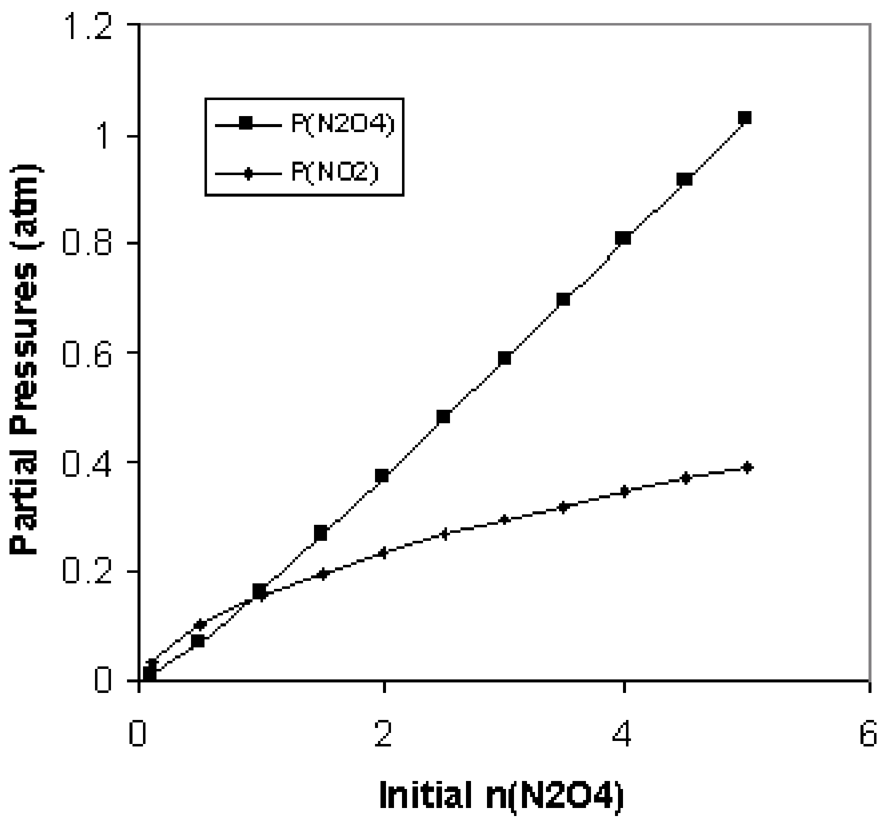


**Figure 1**

We test this in Figure 2 (Relationship of Pressure of Product to Initial Amount of Reactant) by plotting $P_{NO_2}$ at equilibrium versus the square root of the initial number of moles of $N_2O_4$. Figure 2 (Relationship of Pressure of Product to Initial Amount of Reactant) makes it clear that this is not a simple proportional relationship, but it is closer. Note in Figure 1 (Equilibrium Partial Pressures in Decomposition Reaction) that the equilibrium pressure $P_{N_2O_4}$ increases close to proportionally with the initial amount of $N_2O_4$. This suggests plotting $P_{NO_2}$ versus the square root of $P_{N_2O_4}$. This is done in Figure 3 (Equilibrium Partial Pressures), where we discover that there is a very simple proportional relationship between the variables plotted in this way. We have thus observed that

$$P_{NO_2} = c\sqrt{2P_{N_2O_4}} \tag{6}$$

where $c$ is the slope of the graph. (6) can be rewritten in a standard form

$$K_p = \frac{{P_{NO_2}}^2}{P_{N_2O_4}} \tag{7}$$

To test the accuracy of this equation and to find the value of $K_p$, we return to Table 1: Equilibrium Partial Pressures in Decomposition Reaction and add another column in which we calculate the value of $K_p$ for each of the data points. Table 2: Equilibrium Partial Pressures in Decomposition Reaction makes it clear that the "constant" in (7) truly is independent of both the initial conditions and the equilibrium partial pressure of either one of the reactant or product. We thus refer to the constant $K_p$ in (7) as the **reaction equilibrium constant**.

**Relationship of Pressure of Product to Initial Amount of Reactant**

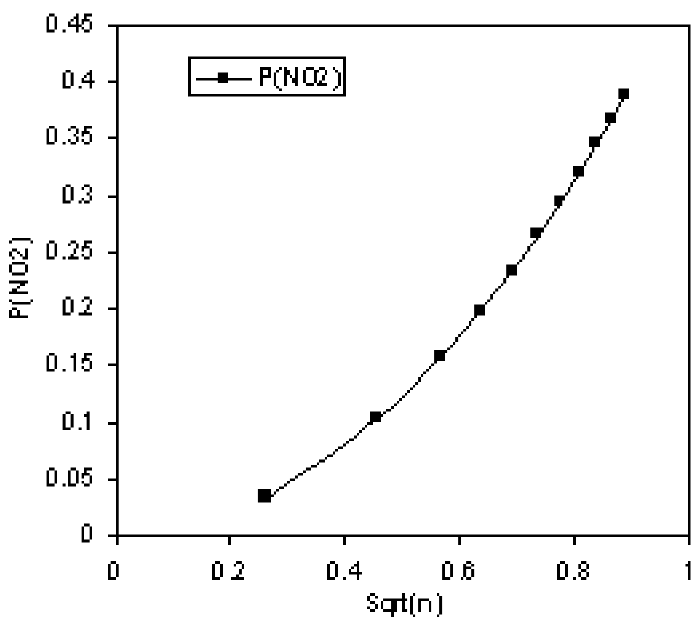


**Figure 2**

**Equilibrium Partial Pressures**

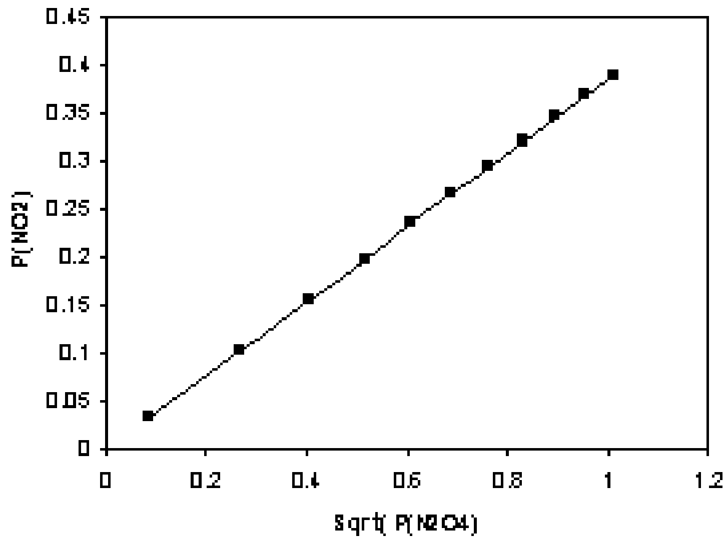


**Figure 3**

**Equilibrium Partial Pressures in Decomposition Reaction**

| **Initial** $n_{N_2O_4}$ | $P_{N_2O_4}$ **(atm)** | $P_{NO_2}$ **(atm)** | $K_p$ |
|---|---|---|---|
| 0.1 | 0.00764 | 0.0336 | 0.148 |
| 0.5 | 0.0710 | 0.102 | 0.148 |
| 1 | 0.166 | 0.156 | 0.148 |
| 1.5 | 0.267 | 0.198 | 0.148 |
| 2 | 0.371 | 0.234 | 0.148 |
| 2.5 | 0.478 | 0.266 | 0.148 |
| 3 | 0.586 | 0.294 | 0.148 |
| 3.5 | 0.695 | 0.320 | 0.148 |
| 4 | 0.805 | 0.345 | 0.148 |
| 4.5 | 0.916 | 0.368 | 0.148 |
| 5 | 1.027 | 0.389 | 0.148 |

**Table 2**

It is very interesting to note the functional form of the equilibrium constant. The product $NO_2$ pressure appears in the numerator, and the exponent 2 on the pressure is the stoichiometric coefficient on $NO_2$ in the balanced chemical equation. The reactant $N_2O_4$ pressure appears in the denominator, and the exponent 1 on the pressure is the stoichiometric coefficient on $N_2O_4$ in the chemical equation.

We now investigate whether other reactions have equilibrium constants and whether the form of this equilibrium constant is a happy coincidence or a general observation. We return to the reaction for the synthesis of ammonia (2).

In a previous section (Section 2: Goals), we considered only the equilibrium produced when 1 mole of $N_2$ is reacted with 3 moles of $H_2$. We now consider a range of possible initial values of these amounts, with the resultant equilibrium partial pressures given in Table 3: Equilibrium Partial Pressures of the Synthesis of Ammonia. In addition, anticipating the possibility of an equilibrium constant, we have calculated the ratio of partial pressures given by:

$$K_p = \frac{{P_{NH_3}}^2}{P_{N_2}{P_{H_2}}^3} \tag{8}$$

In Table 3: Equilibrium Partial Pressures of the Synthesis of Ammonia, the equilibrium partial pressures of the gases are in a very wide variety, including whether the final pressures are greater for reactants or products. However, from the data in Table 3: Equilibrium Partial Pressures of the Synthesis of Ammonia, it is clear that, despite these variations, $K_p$ in (8) is essentially a constant for all of the initial conditions examined and is thus the **reaction equilibrium constant** for this reaction (2).

**Equilibrium Partial Pressures of the Synthesis of Ammonia**

| **V (L)** | $n_{N_2}$ | $n_{H_2}$ | $P_{N_2}$ | $P_{H_2}$ | $P_{NH_3}$ | $K_p$ |
|---|---|---|---|---|---|---|
| 10 | 1 | 3 | 0.0342 | 0.1027 | 4.82 | $6.2 \times 10^5$ |
| 10 | 0.1 | 0.3 | 0.0107 | 0.0322 | 0.467 | $6.0 \times 10^5$ |
| 100 | 0.1 | 0.3 | 0.00323 | 0.00968 | 0.0425 | $6.1 \times 10^5$ |
| 100 | 3 | 3 | 0.492 | 0.00880 | 0.483 | $6.1 \times 10^5$ |
| 100 | 1 | 3 | 0.0107 | 0.0322 | 0.467 | $6.0 \times 10^5$ |
| 1000 | 1.5 | 1.5 | 0.0255 | 0.00315 | 0.0223 | $6.2 \times 10^5$ |

**Table 3**

Studies of many chemical reactions of gases result in the same observations. Each reaction equilibrium can be described by an equilibrium constant in which the partial pressures of the products, each raised to their corresponding stoichiometric coefficient, are multiplied together in the numerator, and the partial pressures of the reactants, each raised to their corresponding stoichiometric coefficient, are multiplied together in the denominator. For historical reasons, this general observation is sometimes referred to as the **Law of Mass Action**.

## 5 Observation 3: Temperature Dependence of the Reaction Equilibrium

We have previously observed that phase equilibrium, and in particular vapor pressure, depend on the temperature, but we have not yet studied the variation of reaction equilibrium with temperature. We focus our initial study on this reaction (3) and we measure the equilibrium partial pressures at a variety of temperatures. From these measurements, we can compile the data showing the temperature dependence of the equilibrium constant $K_p$ for this reaction in Table 4: Equilibrium Constant for the Synthesis of HI.

**Equilibrium Constant for the Synthesis of HI**

| T (K) | $K_p$ |
|---|---|
| 500 | $6.25 \times 10^{-3}$ |
| 550 | $8.81 \times 10^{-3}$ |
| 650 | $1.49 \times 10^{-2}$ |
| 700 | $1.84 \times 10^{-2}$ |
| 720 | $1.98 \times 10^{-2}$ |

**Table 4**

Note that the equilibrium constant increases dramatically with temperature. As a result, at equilibrium, the pressure of $HI$ must also increase dramatically as the temperature is increased.

These data do not seem to have a simple relationship between $K_p$ and temperature. We must appeal to arguments based on Thermodynamics, from which it is possible to show that the equilibrium constant should vary with temperature according to the following equation:

$$\ln\left(K_p\right) = -\frac{\Delta\left(H^\circ\right)}{RT} + \frac{\Delta\left(S^\circ\right)}{R} \tag{9}$$

If $\Delta\left(H^\circ\right)$ and $\Delta\left(S^\circ\right)$ do not depend strongly on the temperature, then this equation would predict a simple straight line relationship between $\ln\left(K_p\right)$ and $\frac{1}{T}$. In addition, the slope of this line should be $-\frac{\Delta\left(H^\circ\right)}{R}$. We test this possibility with the graph in Figure 4 (Inverse of Temperature vs. Natural Log of Equilibrium Constant).

**Inverse of Temperature vs. Natural Log of Equilibrium Constant**

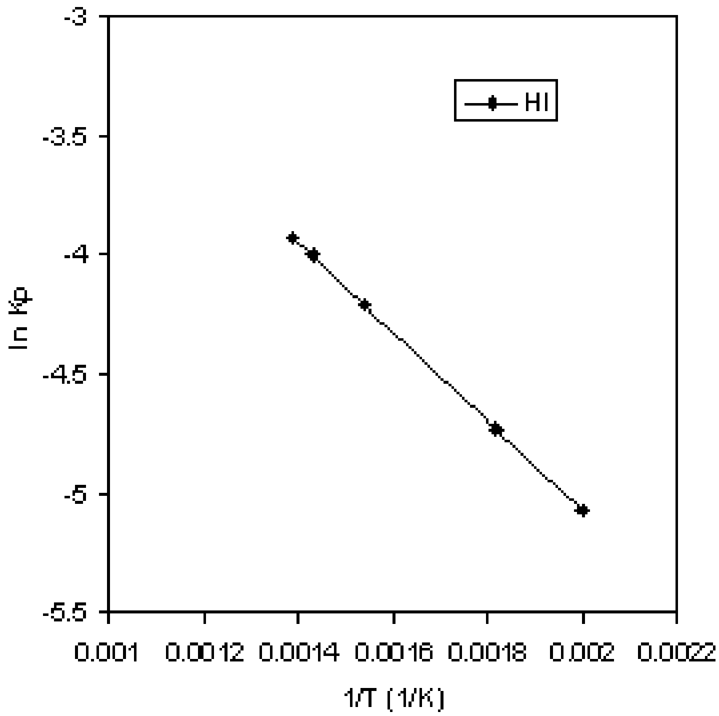


**Figure 4**

In fact, we do observe a straight line through the data. In this case, the line has a negative slope. Note carefully that this means that $K_p$ is **increasing** with temperature. The negative slope via (9) means that $-\frac{\Delta\left(H^{\circ}\right)}{R}$ must be negative, and indeed for this reaction (3) in this temperature range, $\Delta\left(H^{\circ}\right) = 15.6\frac{\mathrm{kJ}}{\mathrm{mol}}$. This value matches well with the slope of the line in Figure 4 (Inverse of Temperature vs. Natural Log of Equilibrium Constant).

Given the validity of (9) in describing the temperature dependence of the equilibrium constant, we can also predict that an exothermic reaction with $\Delta\left(H^{\circ}\right) < 0$ should have a positive slope in the graph of $\ln\left(K_p\right)$ versus $\frac{1}{T}$, and thus the equilibrium constant should **decrease** with increasing temperature. A good example of an exothermic reaction is the synthesis of ammonia (2) for which $\Delta\left(H^{\circ}\right) = -99.2\frac{\mathrm{kJ}}{\mathrm{mol}}$. Equilibrium constant data are given in Table 5: Equilibrium Constant for the Synthesis of Ammonia. Note that, as predicted, the equilibrium constant for this exothermic reaction decreases rapidly with increasing temperature. The data from Table 5: Equilibrium Constant for the Synthesis of Ammonia is shown in Figure 5 (Inverse of Temperature vs. Natural Log of Equilibrium Constant), clearly showing the contrast between the endothermic reaction and the exothermic reaction. The slope of the graph is positive for the exothermic reaction and negative for the endothermic reaction. From (9), this is a general result for all reactions.

**Equilibrium Constant for the Synthesis of Ammonia**

| T (K) | $K_p$ |
|---|---|
| 250 | $7 \times 10^8$ |
| 298 | $6 \times 10^5$ |
| 350 | $2 \times 10^3$ |
| 400 | 36 |

**Table 5**

**Inverse of Temperature vs. Natural Log of Equilibrium Constant**

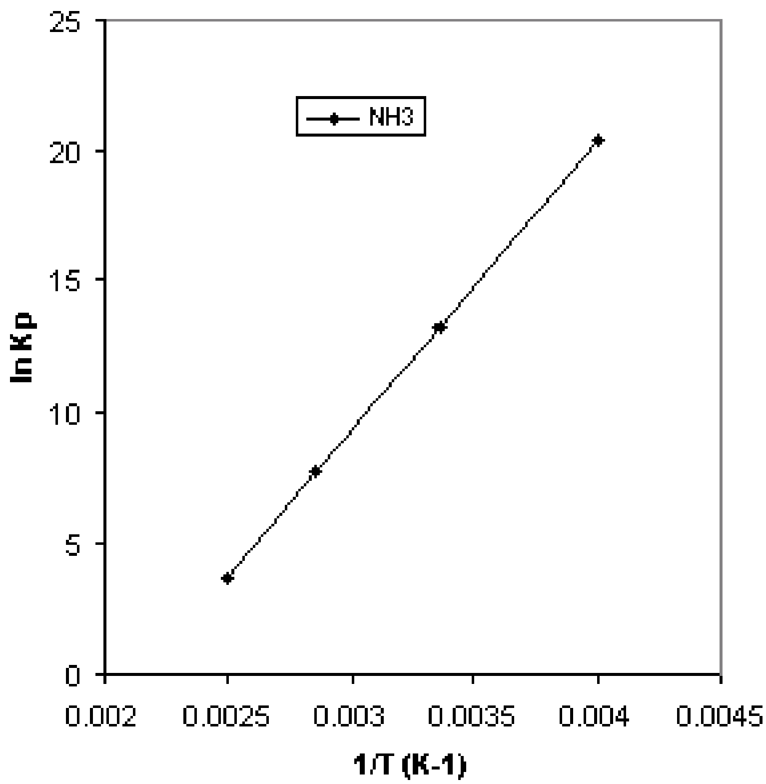


**Figure 5**

## 6 Observation 4: Changes in Equilibrium and Le Châtelier's Principle

One of our goals at the outset was to determine whether it is possible to control the equilibrium which occurs during a gas reaction. We might want to force a reaction to produce as much of the products as possible. In the alternative, if there are unwanted by-products of a reaction, we might want conditions which minimize the product. We have observed that the amount of product varies with the quantities of initial materials and with changes in the temperature. Our goal is a systematic understanding of these variations.

A look back at Table 1: Equilibrium Partial Pressures in Decomposition Reaction and Table 2: Equilibrium Partial Pressures in Decomposition Reaction shows that the equilibrium pressure of the product of the reaction increases with increasing the initial quantity of reaction. This seems quite intuitive. Less intuitive is the variation of the equilibrium pressure of the product of this reaction (2) with variation in the volume of the container, as shown in Table 3: Equilibrium Partial Pressures of the Synthesis of Ammonia. Note that the pressure of $NH_3$ decreases by more than a factor of ten when the volume is increased by a factor of ten. This means that, at equilibrium, there are fewer moles of $NH_3$ produced when the reaction occurs in a larger volume.

To understand this effect, we rewrite the equilibrium constant in (8) to explicit show the volume of the container. This is done by applying **Dalton's Law of Partial Pressures**, so that each partial pressure is given by the Ideal Gas Law:

$$\begin{aligned} K_p &= \frac{{n_{NH_3}}^2\left(\frac{RT}{V}\right)^2}{n_{N_2}\frac{RT}{V}{n_{H_2}}^3\left(\frac{RT}{V}\right)^3} \\ &= \frac{{n_{NH_3}}^2}{n_{N_2}{n_{H_2}}^3\left(\frac{RT}{V}\right)^2} \end{aligned} \tag{10}$$

Therefore,

$$K_p\left(\frac{RT}{V}\right)^2 = \frac{{n_{NH_3}}^2}{n_{N_2}{n_{H_2}}^3} \tag{11}$$

This form of the equation makes it clear that, when the volume increases, the left side of the equation decreases. This means that the right side of the equation must decrease also, and in turn, $n_{NH_3}$ must decrease while $n_{N_2}$ and $n_{H_2}$must increase. The equilibrium is thus shifted from products to reactants when the volume increases for this reaction (2).

The effect of changing the volume must be considered for each specific reaction, because the effect depends on the stoichiometry of the reaction. One way to determine the consequence of a change in volume is to rewrite the equilibrium constant as we have done in (11).

Finally, we consider changes in temperature. We note that $K_p$ increases with $T$ for endothermic reactions and decreases with $T$ for exothermic reactions. As such, the products are increasingly favored with increasing temperature when the reaction is endothermic, and the reactants are increasingly favored with increasing temperature when the reaction is exothermic. On reflection, we note that when the reaction is exothermic, the reverse reaction is endothermic. Putting these statements together, we can say that the reaction equilibrium always shifts in the direction of the endothermic reaction when the temperature is increased.

All of these observations can be collected into a single unifying concept known as **Le Châtelier's Principle**.

**Rule 1:** Le Châtelier's Principle

When a reaction at equilibrium is stressed by a change in conditions, the equilibrium will be reestablished in such a way as to counter the stress.

This statement is best understood by reflection on the types of "stresses" we have considered in this section. When a reactant is added to a system at equilibrium, the reaction responds by consuming some of that added reactant as it establishes a new equilibrium. This offsets some of the stress of the increase in reactant. When the temperature is raised for a reaction at equilibrium, this adds thermal energy. The system shifts the equilibrium in the endothermic direction, thus absorbing some of the added thermal energy, countering the stress.

The most challenging of the three types of stress considered in this section is the change in volume. By increasing the volume containing a gas phase reaction at equilibrium, we reduce the partial pressures of all gases present and thus reduce the total pressure. Recall that the response of this reaction (2) to the volume increase was to create more of the reactants at the expense of the products. One consequence of this shift is that more gas molecules are created, and this increases the total pressure in the reaction flask. Thus, the reaction responds to the stress of the volume increase by partially offsetting the pressure decrease with an increase in the number of moles of gas at equilibrium.

Le Châtelier's principle is a useful mnemonic for predicting how we might increase or decrease the amount of product at equilibrium by changing the conditions of the reaction. From this principle, we can predict whether the reaction should occur at high temperature or low temperature, and whether it should occur at high pressure or low pressure.

# 7 Review and Discussion Questions

**Exercise 1**

In the data given for equilibrium of this reaction (3), there is no volume given. Show that changing the volume for the reaction does not change the number of moles of reactants and products present at equilibrium, *i.e.* changing the volume does not shift the equilibrium.

**Exercise 2**

For this reaction (4) the number of moles of $NO_2$ at equilibrium increases if we increase the volume in which the reaction is contained. Explain why this must be true in terms of dynamic equilibrium, give a reason why the rates of the forward and reverse reactions might be affected differently by changes in the volume.

**Exercise 3**

We could balance (2) by writing

$$2N_2\,(g) + 6H_2\,(g) \rightarrow 4NH_3\,(g) \quad (12)$$

Write the form of the equilibrium constant for the reaction balanced as in (12). What is the value of the equilibrium constant? (Refer to Table 3: Equilibrium Partial Pressures of the Synthesis of Ammonia.) Of course, the pressures at equilibrium do not depend on whether the reaction is balanced as in (2) or as in (12). Explain why this is true, even though the equilibrium constant can be written differently and have a different value.

**Exercise 4**

Show that the equilibrium constant $K_p$ in (8) for this reaction (2) can be written in terms of the concentrations or particle densities, *e.g.*$[N_2] = \frac{n_{N_2}}{V}$, instead of the partial pressures. In this form, we call the equilibrium constant $K_c$. Find the relationship between $K_p$ and $K_c$, and calculate the value of $K_c$.

**Exercise 5**

For each of these reactions, predict whether increases in temperature will shift the reaction equilibrium more towards products or more towards reactants.

### 7.1

$2CO\,(g) + O_2\,(g) \rightarrow 2CO_2\,(g)$

### 7.2

$O_3\,(g) + NO\,(g) \rightarrow NO_2\,(g) + O_2\,(g)$

### 7.3

$2O_3\,(g) \rightarrow 3O_2\,(g)$

**Exercise 6**

Plot the data in Table 4: Equilibrium Constant for the Synthesis of HI on a graph showing $K_p$ on the y-axis and $T$ on the x-axis. The shape of this graph is reminiscent of the graph of another physical property as a function of increasing temperature. Identify that property, and suggest a reason why the shapes of the graphs might be similar.

**Exercise 7**

Using Le Châtelier's principle, predict whether the specified "stress" will produce an increase or a decrease in the amount of product observed at equilibrium for the reaction:

$$2H_2\left(g\right) + CO\left(g\right) \rightarrow CH_3OH\left(g\right) \tag{13}$$

$$\Delta\left(H^\circ\right) = -91\frac{\text{kJ}}{\text{mol}}$$

### 7.1

Volume of container is increased.

### 7.2

Helium is added to container.

### 7.3

Temperature of container is raised.

### 7.4

Hydrogen is added to container.

### 7.5

$CH_3OH$ is extracted from container as it is formed.