Chapter 53 EQUILIBRIUM DYNAMICS

Having completed various types of calculations dealing with equilibrium, we now turn to additional qualitative aspects. The aspects here are based on the dynamics of balance. Again, although the equilibrium condition represents the point of being done, the system is not dead. The forward and reverse can still happen, as long as they happen to the same extent. But that balance can also be disrupted, and the dynamics allow the system to respond to that disruption and to establish a new point of balance.

Our coverage here is contained within three Principles of Equilibrium Dynamics. These Principles follow directly from our Q and K coverage so far. Recall the thermodynamic and kinetic conditions of equilibrium.

Thermodynamic: $\Delta G = 0$

$Q = K$

Kinetic: forward speed = reverse speed

If the system balance is disrupted then, at that moment in time, ΔG equals something other than zero, Q equals something other than K, and the forward speed does not equal the reverse speed. There will be some drive to shift the system in the exergonic (allowed) direction, whichever that might be. This shift will change the amounts in Q until it again equals K, at which time $\Delta G = 0$. Kinetically, the system will go in the faster direction, which corresponds to the exergonic direction, until the forward and reverse speeds are again equal.

The Principles here are not new and they are encompassed within our coverage so far, but they are a tidy way of packaging the qualitative effects which are possible based on Q and K. Although presented at first as to how a system responds to a disruption of balance, the Principles also provide guidance when we want to set up a system. For some particular reaction which we wish to do, we can design a set of starting conditions in such a way as to favor one side of the balanced equation. This is a very common practice in the laboratory or in industry. We will discuss such applications at the end of the Chapter.

53.1 Three Principles of Equilibrium Dynamics

For the First Principle, consider adding more of a reagent to, or removing some of a reagent from, a system which was at equilibrium balance. The reagent must be a Q component, meaning a gas or solute, so the increase or decrease changes an activity. For a gas, this means increasing or decreasing its pressure. For a solute, this means increasing or decreasing its concentration.

For a specific example, let's bring back weak acid dissociation, again using acetic acid (Example 4, Chapter 52).

$$CH_3CO_2H(aq) \rightleftharpoons CH_3CO_2^-(aq) + H^+(aq)$$

The Q (or K) expression is

$$Q = \frac{[CH_3CO_2^-]\,[H^+]}{[CH_3CO_2H]}$$

Consider dissolving 0.0500 mol CH_3CO_2H to make 1.00 L solution. Upon reaching equilibrium, $Q = K = 1.8 \times 10^{-5}$ and the conditions are the following.

	$[CH_3CO_2H]$	$[H^+]$	$[CH_3CO_2^-]$
Original equilibrium:	0.0491	0.00094	0.00094

Now add 1.00 mL of 1.00 M (0.00100 mol) hydrochloric acid. What happens?

First off, recall that HCl(aq) is a strong acid, which means it is $H^+(aq) + Cl^-(aq)$. The chloride ion has no effect here; it is simply a spectator ion. We need to focus on the $H^+(aq)$ part because that is part of the equilibrium itself. At the moment of the addition, $[H^+]$ would be suddenly larger.

	$[CH_3CO_2H]$	$[H^+]$	$[CH_3CO_2^-]$
Original equilibrium:	0.0491	0.00094	0.00094
At moment of HCl addition:	0.0491	0.00194	0.00094

The immediate effect is that $Q = 3.7 \times 10^{-5}$ which does not equal K: in fact, $Q > K$. Thus, Q is too large and the R/L ratio is too large. The exergonic direction is L ← R; the drive is to shift the system to the left in order to restore balance. By shifting left, $[CH_3CO_2H]$ increases, while $[CH_3CO_2^-]$ and $[H^+]$ decrease.

	$[CH_3CO_2H]$	$[H^+]$	$[CH_3CO_2^-]$
Original equilibrium:	0.0491	0.00094	0.00094
At moment of HCl addition:	0.0491	0.00194	0.00094
Restore equilibrium:	0.0495	0.00157	0.00057

Upon restoring equilibrium, Q again equals K, but the numbers for the individual reagents are different than the numbers before the addition of HCl(*aq*).

This example shows the effect of increasing a reagent on the right side of the equation. The immediate effect is to change Q and disrupt the balance. There is then a drive to shift in the allowed direction until once again $Q = K$. We will now generalize this approach into four scenarios, depending on whether a Q component is increased or decreased and whether it occurs on the left or on the right side of the equation.

- Scenario A. Increase a Q component on the right side. This is the scenario just done for acetic acid. Now we treat it as a general case.

  A system is at equilibrium and $Q = K$. If we then increase a Q component on the right side of the balanced equation, the immediate effect is that the R/L ratio is too large, and $Q > K$. The system can shift reverse, L ← R, to return to equilibrium.

- Scenario B. Increase a Q component on the left side.

  A system is at equilibrium and $Q = K$. If we then increase a Q component on the left side of the balanced equation, the immediate effect is that the R/L ratio is too small, and $Q < K$. The system can shift forward, L → R, to return to equilibrium.

- Scenario C. Decrease a Q component on the right side.

  A system is at equilibrium and $Q = K$. If we then decrease a Q component on the right side, the immediate effect is that the R/L ratio is too small, and $Q < K$. The system can shift forward, L → R, to return to equilibrium.

- Scenario D. Decrease a Q component on the left side.

  A system is at equilibrium and $Q = K$. If we then decrease a Q component on the left side, the immediate effect is that the R/L ratio is too large, and $Q > K$. The system can shift reverse, L ← R, to return to equilibrium.

The grand total of effects bring us to the First Principle.

> **First Principle.** For a system initially at equilibrium, increasing the amount of a Q component on one side of the equation will shift the system to the other side. Conversely, upon decreasing the amount of a Q component on one side, the shift is to that same side.

Let's apply this to another reaction, also used previously (Example 5, Chapter 52).

$$C(graph) + 2\,H_2(g) \rightleftharpoons CH_4(g)$$

What is the effect of adding more H_2 and increasing its pressure?

> H_2 is a Q component on the left side of the equation. The increase causes Q to be too low. The system can shift to the right.

What is the effect of adding more C(*graph*)?

> C is a solid and it is unity activity regardless of adding more. There is no effect on Q and there is no effect on the equilibrium within the system.

Notice that this First Principle is for increasing or decreasing a single Q component while keeping the volume the same. Next, for the Second Principle, we change the volume.

Consider a system at equilibrium balance, and then change the volume of the system. For gases, increasing the volume decreases all pressures; this can be done by opening the gas phase to additional tank space. For solutes, increasing the volume decreases all concentrations; this can be done by adding more solvent. These are examples of dilution. Conversely, decreasing the gas volume will increase the pressures of gases, and decreasing the solvent volume will increase the concentrations of solutes. Like the First Principle, activities are increasing or decreasing but, unlike the First Principle, <u>all</u> gases and <u>all</u> solutes are affected all at once. Now, let's see what that does.

We start with a solution example given by

$$A(aq) \rightleftharpoons Y(aq) + Z(aq)$$

which is exemplified by the acetic acid dissociation

$$CH_3CO_2H(aq) \rightleftharpoons CH_3CO_2^-(aq) + H^+(aq)$$

although for simplicity we will stick with just A, Y and Z. We need the Q expression

$$Q = \frac{[Y]\,[Z]}{[A]}$$

and we will now break down the concentrations into moles n and volume V.

$$[A] = \frac{n_A}{V} \qquad [Y] = \frac{n_Y}{V} \qquad [Z] = \frac{n_Z}{V}$$

This gives overall

$$Q = \frac{\frac{n_Y}{V} \times \frac{n_Z}{V}}{\frac{n_A}{V}} = \frac{n_Y \times n_Z}{n_A \times V}$$

and this is equal to K at equilibrium. Now, add more water to the system. What happens?

The added water increases V and dilutes all concentrations. Does that affect the equilibrium balance? Overall, there is a V term in the denominator of Q, so the immediate effect on the system is to decrease Q. That means $Q < K$ and the drive is to shift forward, L → R, to return to a new point of equilibrium. Apply this to the acetic acid equilibrium.

$$CH_3CO_2H(aq) \rightleftharpoons CH_3CO_2^-(aq) + H^+(aq)$$

If we add water, the immediate effect is to decrease all concentrations and decrease Q. In order to return to equilibrium, $[CH_3CO_2^-]$ and $[H^+]$ will increase while $[CH_3CO_2H]$ will decrease. In the end, more moles of CH_3CO_2H are actually dissociated at the new point of balance. The net result is that the percent dissociation increases upon dilution. This is an extremely important notion in many solution equilibria, as will be seen later in Chapter 55.

Watch the wording! <u>All</u> concentrations end up lower after the extra water is added, because <u>everything</u> got diluted. In addition to the dilution, however, a forward shift occurs which increases the moles of $CH_3CO_2^-$ and of H^+ while decreasing the moles of CH_3CO_2H. Although all concentrations are lower, the <u>relative</u> amounts of $[CH_3CO_2^-]$ and $[H^+]$ versus $[CH_3CO_2H]$ are greater.

Let's do a gas example.

$$B(g) + C(g) \rightleftharpoons X(g)$$

An example of this was another reaction from Chapter 52 (Example 3)

$$SO_2(g) + Cl_2(g) \rightleftharpoons SO_2Cl_2(g)$$

but we'll do the derivation with just B, C and X for simplicity.

$$Q = \frac{P_X}{P_B\,P_C}$$

Each pressure term can be broken down

$$P_B = \frac{n_B\,RT}{V} \qquad P_C = \frac{n_C\,RT}{V} \qquad P_X = \frac{n_X\,RT}{V}$$

which gives overall

$$Q = \frac{\dfrac{n_X RT}{V}}{\dfrac{n_B RT}{V} \times \dfrac{n_C RT}{V}} = \frac{n_X \times V}{n_B \times n_C \times RT}$$

and this is equal to K at equilibrium. Now, open the system to more volume. What happens?

The added volume decreases all pressures. Does that affect the equilibrium balance? Overall, there is a V term in the numerator, so the immediate effect is also to increase Q. Now, $Q > K$ and the drive is to shift the system in reverse, L ← R, to return to equilibrium. Applying this to the SO_2/Cl_2 reaction,

$$SO_2(g) + Cl_2(g) \rightleftharpoons SO_2Cl_2(g)$$

increasing the volume decreases all pressures but then there will also be a shift which will increase the amounts of $P(SO_2)$ and $P(Cl_2)$ relative to the amount of $P(SO_2Cl_2)$. The moles of SO_2 and of Cl_2 will increase while the moles of SO_2Cl_2 will decrease.

OK, here is the important observation for both of these cases. Increasing the volume in both systems decreased the concentrations and pressures overall, but it also shifted the system to the side of the equation with more Q components. In other words, dilution favors the formation of more particles in the system, and the system shifts to that side of the equation which has more. In the acid dissociation, the right side has two moles of Q components while the left side has only one mole; dilution shifts to the right.

$$CH_3CO_2H(aq) \rightleftharpoons CH_3CO_2^-(aq) + H^+(aq)$$

Q components:	one mole	two moles

dilution shifts to the right → → →

In the SO_2/Cl_2 reaction, the left side has two moles of Q components while the right side has only one; the shift is to the left.

$$SO_2(g) + Cl_2(g) \rightleftharpoons SO_2Cl_2(g)$$

Q components:	two moles	one mole

← ← ← dilution shifts to the left

Let's do one more, using the equilibrium from Example 6 in Chapter 52.

$$CHF_3(g) + 3\ HCl(g) \rightleftharpoons CHCl_3(g) + 3\ HF(g)$$

This equation has four moles of Q components on both sides of the equation. Now what happens upon increasing volume? Go ahead and take a crack at it. Set up Q and then set up the nRT/V terms.

You will find that all V terms drop out. Thus, when you have the same number of gases on both sides of the equation, then the volume effect cancels. This will also be true when there are the same number of solutes on both sides. Increasing the volume decreases all pressures and concentrations, but Q stays equal to K and no relative shift happens.

This brings us to the Second Principle.

Second Principle. For a system initially at equilibrium, increasing the volume (dilution) favors the side of the equation with more Q components. Conversely, decreasing the volume favors the side with fewer Q components. If the same number of Q components are on both sides of the equation, then a change in volume will not shift the system either way.

We'll bring back the equilibrium from Case A in Chapter 51.

$$H_2(g) + I_2(s) \rightleftharpoons 2\ HI(g)$$

What is the effect of decreasing the volume of the system?

> Decreasing the volume increases all pressures and shifts the balance to the side with fewer Q components. The left side has only one Q component while the right side has two. The shift is to the left.

Now let's try it with I_2 as gas phase.

$$H_2(g) + I_2(g) \rightleftharpoons 2\,HI(g)$$

What is the effect of decreasing the volume of the system?

> All pressures increase but there is no shift to the left or right because both sides have two moles of Q components.

This ends the Second Principle. Now for the Third, which is a bit different.

Consider a system at equilibrium balance, and then upsetting the balance by changing the temperature of the system. Now what?

Since K itself depends on T, then changing T changes the value of K. This effect is different from the prior two. In the prior two, we changed Q but K stayed the same; now we are changing K. The immediate effect is still the same: Q does not equal K.

As temperature changes, K can increase or it can decrease and it depends on whether the reaction is exothermic or endothermic. That connection is not necessarily obvious since it only involves the sign of $\Delta H°$. Let's take a gander.

We first consider heat as a part of a reaction, beginning with heat on the left side of the equation.

$$\text{A} + \text{heat} \rightleftharpoons \text{Z}$$

Forward is endothermic and heat is needed in the L → R direction. At higher temperature, the system will have more heat (more thermal energy) and this will enable more A to form more Z in the forward direction; there is a greater drive to the right, and the balance will lie more to the right at equilibrium. Therefore, K increases in the endothermic direction at higher T.

Now consider heat on the right side of the equation.

$$\text{A} \rightleftharpoons \text{Z} + \text{heat}$$

Forward is exothermic and heat is released in the L → R direction. At higher temperature, the system will have more heat (more thermal energy) and this will enable more Z to form more A in the reverse direction; there is a greater drive to the left, and the balance will lie more to the left at equilibrium. Thus, K decreases in the exothermic direction at higher T.

We actually discussed this a bit in Sections 41.2 and 41.3 with respect to the effects of T on solubility equilibria. We hadn't done a ΔG or K at that time, but we did cover the qualitative endothermic/exothermic approach as done here. Go back and look.

This qualitative approach has a more mathematical basis. The actual connection between K, T and $\Delta H°$ derives from the usual $\Delta G°$ relationships.

$$\Delta G° = -RT\ln K = \Delta H° - T\Delta S°$$

Dividing by $-T$ gives

$$R\ln K = \Delta S° - \Delta H°/T$$

and this places the temperature effect on K with the $\Delta H°$ term. Thus, whether K increases or decreases as the temperature changes will depend only on the sign of $\Delta H°$. If you stare at this equation long enough, you will be able to justify the conclusions from the endothermic/exothermic approaches above, and it's usually easier to just go with those approaches anyway. The bottom line is the Third Principle.

> **Third Principle.** Increasing temperature increases the value of K for an endothermic process and decreases the value of K for an exothermic process.

Another way of saying this is that increasing the temperature shifts the balance in the endothermic direction, whether that be forward or reverse.

This concludes our Principles of Equilibrium Dynamics.

53.2 Applications

While the three Principles were presented as how a system at equilibrium responds to an upset, they also give us clues for how to set up reactions in order to improve the outcome. We first touched on this way back in Section 8.1 when we first got into limiting and excess reagents, and we raised the question of why anyone would even want an excess of anything.

> ❝ Why would you want to put too much of one reactant into the pot? Isn't that wasteful? Well, maybe, but not necessarily. There are many reasons for doing this and it's a very common practice in the laboratory and in industry. Having extras of one reactant often helps to make the whole process go better and faster. How? Well, I can't go into that right now because we haven't covered enough other turf. Much of this ties into "equilibrium" which will get a bit of mention in Chapter 12 and much more extensive coverage in much later chapters. Some of the reasons tie into the speed of reactions which will be discussed beginning in Chapter 48. Some of this ties into still other aspects. We're not really in a spot where I can go into details. ❞

We answered some of these questions in the prior kinetics coverage. Section 50.4:

> ❝ Time is a very practical matter. A timeframe of ten minutes for a reaction in the laboratory is very convenient; a timeframe of ten days is much less so, and a timeframe of ten weeks is worse. Heating can speed up a process, but it depends on how much faster it goes for how much hotter. In industry, time and temperature are money, often on a huge scale, and rates become an important consideration. ❞

> ❝ The time for the reaction to take is inversely connected to the speed of the reaction: a faster reaction takes less time. The rate law provides an arithmetic relationship for the speed based on the rate constant, *k*, and the concentrations of one or more components. Concentrations can be changed, and increasing the concentration of one or more of the components in the rate law will speed up the reaction. ❞

We will now elaborate on these various aspects.

If you want to make some compound in the laboratory or in industry, then you want to design a reaction or a series of reactions which will (hopefully) produce this compound easily, cheaply, in a reasonable period of time and in high yield. The "easily" part refers to many factors such as how many steps are involved, what kind of setup is required (flasks, beakers, tanks, high or low pressure, high or low temperature, etc.), the safety and environmental concerns of reagents (and solvents) along with their cleanup or disposal afterwards, etc. The "cheaply" part depends on what you are making and on what reactants you need. Some things are inherently expensive and there is a range of expense. For a simple illustration, if you are a gold chemist, then you make gold compounds and you need expensive gold reactants for these; the other reactants will be cheap in comparison. The "reasonable period of time" will depend on the kinetics. The "high yield" will depend partly on equilibrium aspects although other factors can also come into play.

As noted in the quote from Section 50.4, we can usually speed things up by heating or by increasing one or more concentrations of reactants. Thus, you can increase the concentration of one reactant without increasing all of them (as long as that reactant is in the rate law). In addition, a catalyst will also increase rates, if one is available. Let's also consider the equilibrium aspects, especially the magnitude of *K*. If *K* is very large, then the reaction will be done when the system lies far to the right side of the balanced equation. Under this condition, we can keep reactants in stoichiometric amounts and still form a high yield of products. On the other hand, if *K* is moderate or even small, then we need to maximize the shift to the right side of the equation in order to make more product. This is typically done by using excess amounts of some reactants while one reactant stays limiting. The limiting reactant is usually the expensive one, or the one hardest to work with, or the most toxic one, or etc. This approach using excess reagents follows from the First Principle: by putting in excess amounts of some reactants, the final equilibrium outcome will lie more to the right side of the equation and we can get a higher yield of product for a given amount of limiting reagent. In some systems, it is also possible to remove product as it is formed; again by the First Principle, this serves to shift the point of equilibrium balance to the right. Precipitation reactions are a good example of this: the product leaves the solution as a solid and that keeps *Q* low, which gives an even greater shift to the right. We can also utilize the Second Principle as a guide to whether we want high or low pressures and concentrations in order to optimize our yield.

Then there's *T*.

Although speeds increase as temperature increases, increasing T can work for or against equilibrium and yield, as given by the Third Principle. The outcome depends on whether the reaction is exothermic or endothermic. For an endothermic process, a higher T will increase K and favor the right side of the equation, which gives a higher yield with more product. On the other hand, for an exothermic process, a higher T will decrease K and decrease product formation. We could cool down an exothermic reaction to favor the right side more, but then that slows down everything kinetically. Thus, the selection of temperature for a process can lead to trade-offs.

Let's illustrate some of the points using the industrial synthesis of ammonia. This was briefly noted at the end of Section 50.3 as one of the most important examples of catalysis. Its primary importance lies in fertilizer production and this is essential to addressing the needs of modern human populations. Despite this positive, it still has negatives as were also noted back then.

For this discussion, consider the formation equation for ammonia.

$$1/2\ N_2(g) + 3/2\ H_2(g) \rightleftharpoons NH_3(g)$$

$$K = \frac{P(NH_3)}{P(N_2)^{1/2}\ P(H_2)^{3/2}}$$

The N_2 comes from the air, once it is processed to deplete O_2 and other things. The H_2 comes from other industrial processes which convert hydrocarbons (from fossil fuels and natural gas) and water to CO_2 and H_2. Given the huge scale of H_2 production overall, the CO_2 production is a big negative since this is a substantial contribution to atmospheric $CO_2(g)$.

Here are the thermodynamic parameters at 298.15 K for the formation reaction.

$$\Delta H° = -45.90\ \text{kJ} \qquad \Delta S° = -99.06\ \text{J/K} \qquad \Delta G° = -16.37\ \text{kJ} \qquad K = 738.0$$

The process is exergonic at this temperature, albeit not overwhelmingly so. K is decent for ending up toward the right side of the equation. As an example, consider a reaction which starts with the pressures of N_2 and H_2 as given by their coefficients in the balanced equation. Thus, we start with 0.500 atm N_2 and 1.500 atm H_2. At equilibrium, there would be

$$0.0159\ \text{atm}\ N_2 \qquad 0.0477\ \text{atm}\ H_2 \qquad 0.968\ \text{atm}\ NH_3$$

and that would be a very good yield and a very good result. End of story? No.

Unfortunately, the reaction does not run at an appreciable rate at 298.15 K. Even the industrial catalysts will not speed up the reaction to run at a reasonable rate at that temperature. The N_2 triple bond is simply too strong. The H_2 bond must also be broken, but it is not nearly so difficult as the N≡N bond. There is no choice but to increase temperature, and drastically so.

Increasing T by hundreds and hundreds of degrees does accelerate the reaction tremendously, even though it still needs the catalyst. Unfortunately, the reaction is exothermic, so increasing T decreases K substantially. That means there has to be a trade-off between the kinetics and the thermodynamics in the setup.

Consider the reaction at 700.0 K, which is in the general range of industrial conditions for this process. The thermodynamic parameters at 700.0 K are now the following.

$$\Delta H° = -52.62\ \text{kJ} \qquad \Delta S° = -114.01\ \text{J/K} \qquad \Delta G° = 27.19\ \text{kJ} \qquad K = 0.009354$$

Note the low value of K. If we start with 0.500 atm N_2 and 1.500 atm H_2 then, at equilibrium, there would be

$$0.494\ \text{atm}\ N_2 \qquad 1.48\ \text{atm}\ H_2 \qquad 0.0119\ \text{atm}\ NH_3$$

which is now a terrible way for trying to make NH_3. End of story? No.

By the Second Principle, a change in volume will change the point of equilibrium balance. There are fewer Q components on the right side of the equation, so we want to decrease volume. For gases, this is the same as increasing pressure. For this reason, the industrial process uses high pressures. If the system were to start with 40.0 atm N_2 and 120.0 atm H_2, then there would be

$$24.9\ \text{atm}\ N_2 \qquad 74.8\ \text{atm}\ H_2 \qquad 30.2\ \text{atm}\ NH_3$$

at equilibrium at 700.0 K. This now becomes a workable amount. Unfortunately, the process is still not fast enough to produce that much NH_3 in the given time, but that's all part of the trade-offs. After passing the gases through the system with its heterogeneous catalyst, the mixture of gases is cooled and kept at high pressure. The NH_3 condenses due to its far greater intermolecular forces (hydrogen bonding!) and the leftover $N_2(g)$ and $H_2(g)$ are fed back through the reactor along with additional amounts of each in order to repeat the cycle.

This industrial production of ammonia is ranked as one of the most important scientific advancements in the 20th century, due to its overwhelming impact on global food supply. It took an extensive study of the thermodynamics and the kinetics (especially in catalyst development) which are involved in order to accomplish that. Even though the balanced equation looks fairly simple, there is much in the details. Despite its success, the quest remains for developing new catalysts which work faster and at lower temperature. Going even further, there is tremendous interest in developing new reactions which do not rely on H_2 in order to cut down on CO_2 emissions.

With that, we close on the Principles of Equilibrium Dynamics and some of their applications. We also close on equilibria systems in general and now narrow the focus to aqueous systems.

Problems

1. True or false.
   a. Dilution favors that side of an equation which has more gas or solute particles.
   b. For every equilibrium system, decreasing the volume will shift the equilibrium position to the right.
   c. For an exothermic process, the equilibrium constant will increase at higher temperatures.
   d. Adding more solid reactant to a system increases *Q*.

2. Consider the following system at equilibrium.

$$BaSO_4(s) + H^+(aq) \rightleftharpoons Ba^{2+}(aq) + HSO_4^-(aq) \qquad \Delta H^\circ = 48.2 \text{ kJ}$$

   Will the following actions favor a shift to the right side, to the left side, or have no such effect?
   a. Decrease temperature.
   b. Add a soluble barium salt.
   c. Increase the amount of water solvent.
   d. Add more $BaSO_4(s)$.

3. Consider the following system at equilibrium.

$$P_4(s) + 12\ HCl(g) \rightleftharpoons 4\ PCl_3(g) + 6\ H_2(g) \qquad \Delta H^\circ = -47.08 \text{ kJ}$$

   Will the following actions favor a shift to the right side, to the left side, or have no such effect?
   a. Add more P_4.
   b. Increase H_2 pressure.
   c. Add $Ne(g)$ to increase the total pressure in the system.
   d. Decrease the volume of the system.

4. Consider the following system at equilibrium.

$$Cl_2O(g) + 2\ HCl(g) \rightleftharpoons H_2O(g) + 2\ Cl_2(g) \qquad \Delta H^\circ = -138.21 \text{ kJ}$$

   Will the following actions favor a shift to the right side, to the left side, or have no such effect?
   a. Decrease Cl_2O pressure.
   b. Increase temperature.
   c. Increase the volume of the system.
   d. Add $He(g)$ to increase the total pressure of the system.

5. Consider the following process as a way of making methyl alcohol, CH_3OH.

$$CO_2(g) + 3\,H_2(g) \rightleftharpoons CH_3OH(g) + H_2O(g) \qquad \Delta H° = -48.97\text{ kJ}$$

You want to increase the yield of CH_3OH at equilibrium. Which of the following actions will do so?

a. Increase the pressure of CO_2.

b. Add some $H_2O(g)$ to the system initially.

c. Decrease the system volume.

d. Increase temperature.