Print Notes – Installment 5 – Chem 123 Winter 2003 – Rossi

Reaction Kinetics – Reactions can approach equilibrium very quickly, or very slowly. Diamond spontaneously turns into graphite, but it does so *very* slowly. Liquid nitrogen evaporates spontaneously in open air at 25ºC, and it does so very quickly (if it is actually at room temperature, it boils like a banshee!). **Kinetics** is the study of how quickly chemical reactions take place, and by what route.

The Collision Model – Chemical reactions take place when bonds are formed or broken. If more than one reactant species is involved in (the mechanism of) a reaction, these must collide with the right kinetic energy and with the proper orientation if a collision is to lead to the formation of products. Higher temperatures increase the likelihood of forming high-energy intermediates.

Reaction Mechanism – A sequence of bond breaking / forming events that results in reactants turning into products is called a **mechanism** of a given reaction. Often one mechanism operates more rapidly than all the others, and this is generally referred to as *the* mechanism of the reaction. A reaction mechanism consists of a sequence of **elementary steps**. Here's an example, for the reaction $H_{2(g)} + Br_{2(\ell)} \rightleftarrows 2\ HBr_{(g)}$:

(1) $Br_{2(\ell)} \rightleftarrows Br_{2(g)}$ (This step is very fast and reaches equilibrium)
(2) $Br_{2(g)} \rightleftarrows 2\ Br_{(g)}$ (Again, this step is relatively fast and reaches equilibrium)
(3) $Br_{(g)} + H_{2(g)} \rightarrow HBr_{(g)} + H_{(g)}$ (This step is slow and controls the forward rate.)
(4) $H_{(g)} + Br_{2(g)} \rightarrow HBr_{(g)} + Br_{(g)}$ (This step is relatively fast, it doesn't control the rate.)

Reaction Rate – If the reaction $A + 2\ B \rightarrow 3\ C$ is being studied, the reaction rate is the number of *moles of reaction* that take place per unit volume, per unit time. This means that if the reaction rate is a steady 2.1 moles per hour per liter, 2.1 moles of A and 4.2 moles of B would be consumed per liter over the course of an hour. 6.3 moles per liter of C would be formed over the course of an hour. The reaction rate of a (homogenous reaction) always measures how many moles *per liter* of the *forward* reaction take place per unit time. The reaction rate can be negative (if the reaction is actually going in reverse: here that would be if C is turning into A and B). **Reaction rates in a closed system change as a function of time, as temperatures and concentrations change.**

Rate Laws – Since every reaction eventually reaches equilibrium, the (net) reaction rate eventually becomes equal to zero. For the reaction $A + 2\ B \rightarrow 3\ C$ the net reaction rate is the rate at which A + 2B combine, *minus* the rate at which 3C breaks up to form A + 2B. When the reaction reaches equilibrium, these two rates become equal. The absolute (not net) rate at which a reaction takes place in a specific direction is given by the **rate law** for that reaction. The forward rate law for our sample reaction would be of the form

$$\text{Forward rate} = k_f\,[A]^{\alpha}\,[B]^{\beta}$$

where k_f is called the **forward rate constant**, α is the **order** of the forward reaction in A, and β is the **order** of the forward reaction in B. The sum (α + β) is called the **overall forward reaction order**. α and β can be just about anything, including zero, but most often it will be a natural number (1, 2, 3, etc.). There is also a rate law for the reverse reaction: $\text{Reverse rate} = k_r\,[C]^{\gamma}$

Here k_r is called the **reverse rate constant** and γ is the **order** of the reverse reaction in C. Again, γ can be almost anything, but it is usually a natural number. The *net* rate of the reaction is

$$\textit{Net}\text{ rate} = \text{Forward rate} - \text{Reverse rate} = k_f\,[A]^{\alpha}\,[B]^{\beta}\ -\ k_r\,[C]^{\gamma}\ = \frac{-\Delta[A]}{\Delta t} = \frac{-\tfrac{1}{2}\Delta[B]}{\Delta t} = \frac{+\tfrac{1}{3}\Delta[C]}{\Delta t}$$

The rate constants k can be changed by changing the temperature – this changes both k_f and k_r, but by differing amounts. Increasing the temperature causes both k's to increase. The relationship between the temperature and the amount by which a given k increases is given by the Arrhenius equation:

$k = Ae^{\frac{-\Delta G^{\ddagger}}{RT}}$ where A is a value with a negligible dependence on temperature that takes into account how frequently reactants collide or vibrate, R is the gas constant, T is the absolute temperature, and $\Delta G^{\ddagger}$ is called the transition state free energy and is related to how much energy it takes to break the reactant bonds and how likely a collision will lead to the right geometry for reaction.

Rate constants can also be changed by adding a **catalyst – a substance that causes both the forward and reverse rate constants to increase by the same proportion. Catalysts are not consumed in reactions.** The amount of catalyst can often be very small. **Inhibitors** are the opposite of catalysts, they slow the approach of a reaction to equilibrium without being consumed.

Note that if a container is filled with just A and B, at first there is no C and the reverse rate is zero. The forward rate is really big. As the forward reaction proceeds, some C is formed and the reverse rate picks up. At the same time [A] and [B] drop, so the forward rate slows down. The system reaches equilibrium when the forward and reverse rates become equal and the net rate drops to zero.

If you are lucky, you can somehow observe and monitor [A], [B], and/or [C] as a function of time. That allows you to determine the net rate of the reaction. If you are able to do this before the reverse rate becomes appreciable, it is pretty easy to determine k_f. But once the forward and reverse rates are both contributing to the net rate, forget about it. Trying to figure out how fast the forward reaction is happening, all by itself, is pretty hard, and so extraction of k_f becomes really difficult. Once you know k_f, however, and you wait for the system to come to equilibrium, you can readily determine k_r from the equilibrium concentrations and k_f:

This all assumes you know the reaction orders α, β, and γ. How do you determine those? Again, you look at rates for reactions that are just starting out. You do things like double [A] and see what effect that has on the net reaction rate, which during the initial stages is equal to the forward rate. If the forward rate doubles, that means α = 1. If it quadruples, α = 2. Similarly, you change [B] and see what that does. To get γ, you could (maybe) start with just C (no A or B) and watch what happened to the rate C turned into A and B when you doubled its initial concentration. Note that if A, B, or C is a pure solid or liquid, it does not appear in the rate equation, viz., its order is zero. Then changing the amount of that substance does not change the rate.

Equilibrium – In chemistry, this is the condition achieved by all chemical reactions, after the passage of a sufficient amount of time, where the rate of the forward reaction becomes equal to the rate of the reverse reaction. For the reaction A º B, the forward reaction is A turning into B. The reverse reaction is B turning into A. *At equilibrium, the concentration of A and B in a flask stop changing, but this is because A is turning into B just as fast as B is turning into A.* **Chemical reactions don't stop happening at equilibrium!**

At room temperature $H_{(g)} + H_{(g)}$ º $H_{2(g)}$ has $\Delta G^o = -406$ kJ/mol; it is (very) spontaneous in the forward direction. At plasma temperatures (above about 4400 K), the same reaction becomes spontaneous in the reverse direction, that is, ΔG becomes positive. However, some H atoms are present in any sample of H_2, even at room temperature, and some H_2 molecules are present in an H plasma, even at extremely high temperatures. Even if a reaction is spontaneous, it will never go to 100% completion. Similarly, even if a reaction has a very positive ΔG^o, it will occur to *some* extent. The actual equilibrium position between no reaction and complete reaction is numerically related to the value of ΔG, and is calculated using a **reaction quotient (Q)** of the form

$$Q_\alpha = \frac{\prod_m \alpha_{A_m}^{a_m}}{\prod_n \alpha_{A_m}^{a_m}} = \frac{\alpha_{B_1}^{b_1}\alpha_{B_2}^{b_2}\cdots\alpha_{B_M}^{b_M}}{\alpha_{A_1}^{a_1}\alpha_{A_2}^{a_2}\cdots\alpha_{A_N}^{a_N}} \quad \text{for the reaction} \quad a_1A_1 + a_2A_2 + \cdots + a_NA_N \rightleftharpoons b_1B_1 + b_2B_2 + \cdots + b_MB_M$$

where the A's are chemical reactants, the B's are chemical products, and the a's and b's are the coefficients needed to balance the chemical reaction. α_{B_1} is the *activity* of product B_1, a *dimensionless quantity* which is defined as follows for *ideal systems*:

1) If B_1 is a (nearly) pure condensed phase (a solid or liquid), its activity is defined to be 1
2) If B_1 is in solution, the activity of B_1 is the numerical value of its concentration, measured in moles per liter of solution
3) If B_1 is in the gas phase, its activity is the numerical value of its partial pressure, measured in atmospheres (actually, in bar)

(We will treat all our systems to be *ideal* in Chem 123; ideal gases and dilute solutions approximate this idyllic situation, with no ion pairing, no intermolecular forces acting between gas phase molecules, and the moles per liter of pure solids and liquids being fixed.)

The formula up above is a real mathematical mouthful, so if it freaks you out just look at some examples and you will get it:
The reaction quotient for the formation of H_2 gas from H atoms is determined as follows:
1) Write the reaction: $H_{(g)}$ º $H_{2(g)}$
2) Balance it: $2H_{(g)}$ º $H_{2(g)}$ (It's really easy to forget to do this: don't! It's critical!)
3) Write the Q:

$$Q_\alpha = \frac{\alpha_{H_2}}{\alpha_H^2} = \frac{\frac{P_{H_2}}{1\text{ atm}}}{\left(\frac{P_H}{1\text{ atm}}\right)^2} = \frac{P_{H_2}}{(P_H)^2}\cdot\text{atm}$$

Often, Q_P, a pressure reaction quotient, is used: $Q_P = \frac{P_{H_2}}{(P_H)^2}$ (this has units of atm^{-1}!)

The reaction quotient (Q_α) for the combustion of methane is determined as follows:
1) Write the reaction: $CH_{4(g)} + O_{2(g)}$ º $CO_{2(g)} + H_2O_{(\ell)}$
2) Balance it: $CH_{4(g)} + 2\,O_{2(g)}$ º $CO_{2(g)} + 2\,H_2O_{(\ell)}$
3) Write the Q_α: $Q_\alpha = \frac{\alpha_{CO_2}\alpha_{H_2O}^2}{\alpha_{CH_4}\alpha_{O_2}^2} = \frac{\alpha_{CO_2}(1)^2}{\alpha_{CH_4}\alpha_{O_2}^2} = \frac{\alpha_{CO_2}}{\alpha_{CH_4}\alpha_{O_2}^2}$ Note that because it is a pure liquid, $H_2O_{(\ell)}$ has α=1 and can be left out.

Alternately, we can use a pressure reaction quotient, $Q_P = \frac{P_{CO_2}}{P_{CH_4}\left(P_{O_2}\right)^2}$, which has units of atm^{-2}, and thus changes with temperature.

Note that Q_α for the reaction $H_2O_{(\ell)}$ º $H_2O_{(g)}$ is simply $Q_\alpha = Q_\alpha = \frac{\alpha_{H_2O_{(g)}}}{\alpha_{H_2O_{(\ell)}}} = \frac{\alpha_{H_2O_{(g)}}}{1} = \alpha_{H_2O_{(g)}} = \frac{P_{H_2O}}{\text{atm}}$. If a drop of water is placed in a dry, sealed container, some of it will turn into gaseous water. This continues to happen until the drop evaporates completely, or the partial pressure of water in the container rises to the point where the rate at which gaseous water turns back into liquid water becomes equal to the rate at which liquid water is turning into gaseous water: equilibrium! How much water has to be present in the gas phase before this becomes the case depends on temperature, so the Q_α at which equilibrium is attained changes with temperature.

Equilibrium Constants – It turns out that there is a specific value of Q_α obtained when a reaction reaches equilibrium. It is called K_{eq}. It is temperature dependent. It is not dependent on other things. When $Q_\alpha = K_{eq}$, a reaction is at equilibrium.
K_{eq} is related to ΔG^o in the following way: $\Delta G^o = -R\,T\ln(K_{eq})$
The more negative ΔG^o is for a reaction, the more spontaneous the reaction is. The more the products are favored over the reactants. The more positive $R\,T\ln(K_{eq})$ is, and at a given temperature the larger K_{eq} is. This makes sense, because it means that the concentration of products required to make Q equal to K_{eq} is larger.

Le Châtelier's Principle – A system at equilibrium, when disturbed, reacts to counteract the disturbance.
* If the net effect of the disturbance is to decrease Q_α, the reaction tries to increase it by making the reaction go forward
* If the net effect of the disturbance is to increase Q_α, the reaction tries to decrease it by making the reaction go in reverse
* If heat transfers into the reaction vessel, this acts as an impetus for the reaction to occur in the direction that absorbs heat