

BIO134: Chemical Kinetics

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Prerequisites

- Basic knowledge of A-level Kinetics. (e.g., S-Cool AS&A2 Level Chemistry Revision Guide, http://www.s-cool.co.uk/topic_index.asp?subject_id=7)

Readings

- Housecroft and Constable, Chemistry, 2nd ed., Prentice Hall, Chapter 14.
- Atkins, The Elements of Physical Chemistry, 3rd ed., Oxford, Chapter 10-11.

Acknowledgments

Many of the diagrams in this lecture note have been downloaded from the web pages of these textbooks.

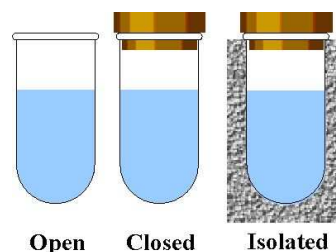
1 Thermodynamics

Let us first fix some terminologies.

Open systems can exchange both energy (heat) and matter with its surroundings.

Closed systems can exchange energy (heat) but not matter with its surroundings.

Isolated systems can exchange neither energy (heat) nor matter with its surroundings.



1.1 The 1st and 2nd Laws

The 1st and 2nd laws of thermodynamics can be stated as follows. It is important to note that these apply for energy and entropy within an isolated system.

The 1st law :

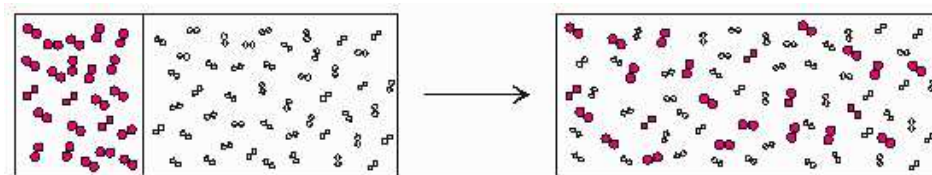
The total energy E_{tot} of an isolated system conserves: $\Delta E_{\text{tot}} = 0$.

The 2nd law :

The total entropy S_{tot} of an isolated system tends to increase: $\Delta S_{\text{tot}} \geq 0$.

in which ΔE_{tot} and ΔS_{tot} are changes of E_{tot} and S_{tot} associated with processes occurring in the system.

A typical example of the 2nd law is seen in the diagram below as spontaneous mixing of the two kinds of gases.



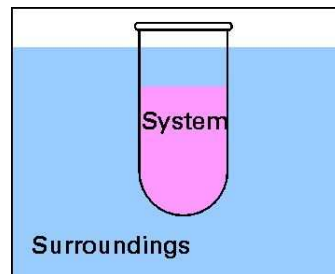
The entropy of the system is closely related to the randomness of the system. In this example of gas mixing, the randomness increases spontaneously, which means that the entropy also increases. In order to define the entropy more precisely in terms of the randomness, we need to learn Statistical Mechanics. However, this is beyond the scope of this lecture course, and we will content with the qualitative connection between the entropy and the randomness.

An important thing to note here is that the spontaneous mixing occurs even when the gases are ideal, i.e., no interaction between the molecules. In this case, there is no energy change (gain or loss) upon mixing of the gases. This means that, the mixing

is not driven by the energy gain but by the entropy gain in terms of the 2nd law of thermodynamics.

1.2 Gibbs Free Energy

Let us now consider a System in contact with Surroundings (i.e., heat bath). We assume that the System is closed and the total system of ‘System and Surroundings’ is isolated. The System can thus exchange heat with the Surroundings. The Surroundings is, on the other hand, supposed to be large enough such that its temperature T is kept constant.



From the 1st law of thermodynamics,* the enthalpy change of the total system is zero: $\Delta H_{\text{tot}} = 0$. Because the total enthalpy change is the sum of the enthalpy change of the System and the Surroundings, $\Delta H_{\text{tot}} = \Delta H_{\text{sys}} + \Delta H_{\text{surr}}$, it follows that

$$\Delta H_{\text{sys}} = -\Delta H_{\text{surr}} \quad (1)$$

In other words, the heat is exchanged solely between the System and the Surroundings and goes nowhere else (because the total system is isolated). The enthalpy gain of the System is precisely equal to the loss of the Surroundings.

On the other hand, the 2nd law predicts that the entropy of the total system tends to increase;

$$\Delta S_{\text{total}} = \Delta S_{\text{sys}} + \Delta S_{\text{surr}} \geq 0 \quad (2)$$

However, this does not appear very useful as it only deals with the total system and not the System in which the processes of our interest are taking place. We are more interested in predicting what will happen in the System rather than in the total system that include the Surroundings. We therefore wish to separate our discussion on the System from the Surroundings. To this end, it is useful to define the **Gibbs Free Energy** of the System by

$$\Delta G_{\text{sys}} = \Delta H_{\text{sys}} - T\Delta S_{\text{sys}} \quad (3)$$

This is useful because we can show that the 2nd law $\Delta S_{\text{tot}} \geq 0$ is essentially equivalent to $\Delta G_{\text{sys}} \leq 0$. Thanks to this, we only need to look at the quantities (enthalpy and entropy) of the System and do not have to be bothered by the Surroundings.

The equivalence of $\Delta S_{\text{tot}} \geq 0$ and $\Delta G_{\text{sys}} \leq 0$ can be demonstrated as follows. The essential point is that the heat bath (= the Surroundings) is large enough such that the

* Here we assume to be dealing with solution phase systems, as is usually the case in biochemistry, such that the volume change of the system may be neglected. In this case, it would be justified to consider that the enthalpy and the internal energy are identical. In other words, we neglect pV in $H = U + pV$.

equilibrium is maintained in the Surroundings in the course of the processes occurring in the System. Therefore, we may put

$$\Delta G_{\text{surr}} \cong 0 \quad \Rightarrow \quad \Delta H_{\text{surr}} \cong T \Delta S_{\text{surr}} \quad (4)$$

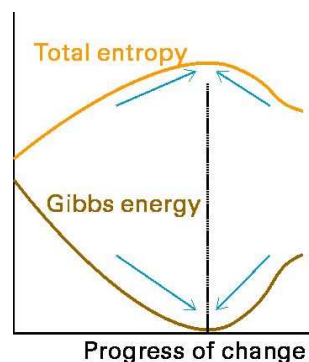
Putting this and Eq (1) into Eq (3), it follows

$$\Delta G_{\text{sys}} = -T(\Delta S_{\text{surr}} + \Delta S_{\text{sys}}) = -T \Delta S_{\text{tot}} \quad (5)$$

Because the absolute temperature T (in Kelvin) is always positive, Eq (3) means that the 2nd law $\Delta S_{\text{total}} \geq 0$ is equivalent to $\Delta G_{\text{sys}} \leq 0$. In other words, we can consider that ΔG_{sys} effectively contains the influences from the Surroundings, as can be understood from the derivation above.

In summary, the direction of the chemical processes is related to the Gibbs free energy change such that

- The reaction in the System occurs spontaneously only if $\Delta G_{\text{sys}} < 0$
- The System is in equilibrium when $\Delta G_{\text{sys}} = 0$



1.3 Standard Gibbs Free Energy and Equilibrium Constant

Let us consider a reaction between x moles of X and y moles of Y producing z moles of Z.



The Gibbs free energy change of the reaction is given by

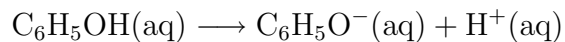
$$\Delta G = \Delta G^\circ + RT \ln Q = \Delta G^\circ + RT \ln \left[\frac{(a_Z)^z}{(a_X)^x (a_Y)^y} \right] \quad (7)$$

where $a_{X,Y,Z}$ are the activities of X, Y and Z, Q is the reaction **quotient**, R ($= 8.314 \times 10^{-3} \text{kJ mol}^{-1} \text{K}^{-1}$) is the gas constant, and ΔG° is the **standard free energy of the reaction**. At equilibrium, the free energy change of the reaction vanishes, $\Delta G = 0$, and the reaction quotient Q is equal to the **equilibrium constant** K . Then, Eq (7) becomes

$$0 = \Delta G^\circ + RT \ln K \quad \Rightarrow \quad \Delta G^\circ = -RT \ln K \quad (8)$$

Out of equilibrium, the reaction quotient Q is not equal to the equilibrium constant K ; in other words, the activities $a_{X,Y,X}$ are different from their equilibrium values. ΔG is then not equal to zero, and its sign determines the spontaneous direction of the reaction: forward or backward reaction when $\Delta G < 0$ or > 0 , respectively.

Question: The equilibrium constant of a reaction,



is $K = 1.3 \times 10^{-10}$ at 298 K.

Q1. Calculate ΔG° .

Q2. A mixture of $[\text{C}_6\text{H}_5\text{OH}] = 0.1 \text{ mol dm}^{-3}$ and $[\text{C}_6\text{H}_5\text{O}^-] = [\text{H}^+] = 10^{-5} \text{ mol dm}^{-3}$ was prepared. Will the reaction occur spontaneously?

In this way, ΔG determines the **direction** of the reaction. However, it is important to note that the **rate** of the reaction is not determined by ΔG .

