

Reaction Kinetics in Chemistry

LAW OF MASS ACTION IN STATISTICAL THERMODYNAMICS

The Gibbs free energy G of a physical system is defined by:

$$G = U - T\sigma + pV$$

where

U	=	total potential energy
T	=	temperature
σ	=	entropy
p	=	pressure
V	=	volume

For a chemical system, the potential energy U is the sum of the potential energies U_j of chemical species j . The chemical potential μ of a chemical is defined by

$$\mu \equiv \frac{\partial G}{\partial N}_{(T,p)}$$

where N is the total number of molecules. Here the subscript in T and p indicates the definition holds only under constant temperature and pressure conditions.

For an *ideal gas* it can be shown [1] that

$$\mu = T(\log n - \log c) \tag{1}$$

where

n	=	concentration
c	=	$n_Q Z_{int}$
n_Q	=	$\left(\frac{MT}{2\pi\hbar^2}\right)^{3/2}$ is the quantal concentration
M	=	mass of molecule/atom
\hbar	=	Planck's constant = $6.62618 \times 10^{-34} Js$
Z_{int}	=	internal partition function

The internal partition function Z_{int} is the sum of Boltzmann factors $e^{-E_k/T}$ associated with the vibrational and rotational energies E_k of the chemical gas. In statistical thermodynamics, an ideal gas is a collection of noninteracting particles for which $n/n_Q \ll 1$ (in the *classical regime*). Given these definitions and facts, a “Law of Mass Action” can be derived relating equilibrium concentrations of reacting chemicals.

Let μ_j be the chemical potential of chemical j . Further let N_j denote the number of molecules of chemical j . Then (for an ideal gas) one has:

$$dG = \sum_j \mu_j dN_j - \sigma dT + V dp = 0$$

at equilibrium. If temperature and pressure are constant, $dT = dp = 0$ so that

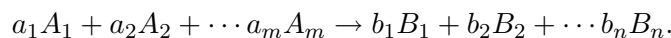
$$\sum_j \mu_j dN_j = 0$$

It can be shown [1] that this expression implies the product of the concentrations must be constant or that

$$\prod_j n_j = K(T) \tag{2}$$

where the *equilibrium constant* K depends only on the temperature. Here, \prod is the product notation.

Consider a chemical reaction



Here A_j denote the *reactants* and a_j denote the *stoichiometric constants* (usually positive integers). Similar definitions hold for the *products* B_j . Then, if each chemical “acts” like an ideal gas, equation (2) can be written

$$K(T) = \frac{\prod_j [A_j]}{\prod_k [B_k]} \tag{3}$$

where $[A]$ denotes the concentration of chemical A . In some settings, (3) is called the Law of Mass Action.

LAW OF MASS ACTION IN CHEMICAL KINETICS

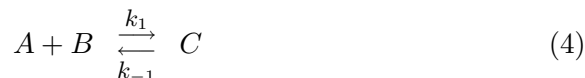
Simply stated, the Law of Mass Action in chemical kinetics states that the rate at which a chemical is produced is proportional to the product of the reactants. For example, if



then

$$\frac{d[C]}{dt} = k[A][B]$$

where t is time and k is some (constant) reaction rate. Many reactions are reversible. In the above example this would mean that C could spontaneously dissociate into its two components A and B . Then, one writes



In the reverse reaction $C \rightarrow A + B$, C is the reactant. Applying the law of mass action to (4), the resulting differential equations describing the rate of change of concentrations is:

$$\frac{d[A]}{dt} = k_{-1}[C] - k_1[A][B] \quad (5)$$

$$\frac{d[B]}{dt} = k_{-1}[C] - k_1[A][B] \quad (6)$$

$$\frac{d[C]}{dt} = -k_{-1}[C] + k_1[A][B] \quad (7)$$

One thing to note about the rate coefficients in this example is that they do not have the same units. Let T , L and M denote generic units of time, length and mass, respectively. furthermore we use the notation $[X]$ to denote the units of X . Then, $[k_{-1}] = T^{-1}$ whereas $[k_1] = L^3(MT)^{-1}$.

Rate coefficients can also have largely different magnitudes. For the reaction $A + B \rightarrow C$, one has

$$\frac{d[C]}{dt} = k[A][B].$$

Arrhenius theory dictates that

$$k = \alpha e^{-E_a/RT} \quad (8)$$

where α is some constant, $R = 8.31441 J(mol)^{-1}K^{-1}$ is the gas constant, T is temperature (in degrees kelvin) and E_a is the *activation energy* of the reaction. The activation energy is the energy required (per mole) for the reaction to take place. This energy required for molecules of different shapes and energies to combine may vary substantially. And, because of the exponential dependence of k on E_a , this may result in rate coefficients of hugely different magnitudes.

Lastly, note that for the example in (5)-(6),

$$\frac{d}{dt} ([A] + [C]) = 0$$

indicating that the sum of the concentrations $[A] + [C]$ is constant. This fact reflects the stoichiometry of the problem, or that for every A molecule lost, exactly one C molecule is created.

The Law of Mass Action for the more general reaction



is described by the differential relations

$$kAB^m = -\frac{dA}{dt} = \frac{1}{n-m} \frac{dB}{dt} = \frac{1}{p} \frac{dC}{dt} \quad (10)$$

where m, n and p are stoichiometric constants, and the $[\cdot]$ notation for concentration has been dropped. The associated differential equations describing the chemical kinetics are then given by:

$$\frac{dA}{dt} = -kAB^m \quad (11)$$

$$\frac{dB}{dt} = (n-m)kAB^m \quad (12)$$

$$\frac{dC}{dt} = pkAB^m \quad (13)$$

$$(14)$$

The extra factors $(n-m)$ and p in the equations for B and C are needed to account for the stoichiometry of the reaction. The reaction equation (9) states that for every reaction involving 1 molecule of A , p molecules of C are created and there is a net gain of $(n-m)$ molecules of B . This is reflected in the relations

$$\frac{d}{dt}(pA + C) = 0 \quad (15)$$

$$\frac{d}{dt}(pB + (m-n)C) = 0 \quad (16)$$

However, this interpretation works **only if** concentration is measured in molarity. Recall that if $[A]=1$ molar (or $[A]=1M$) then each liter of solution contains $N_a = 6.02 \times 10^{23}$ molecules of A . Since molecules have different *gram molecular weights*, one molar solutions of A and B may correspond to different “mass per unit volume” concentrations. Of course, by rescaling the molarity concentrations using the gram molecular weights, one can arrive at differential equations describing the chemical kinetics in terms of mass concentrations.

To illustrate another point, let us consider the reaction



This reaction could also be written



By the Law of Mass Action, C is produced at a rate which is proportional to the “three” reactants A , B and B , or

$$\frac{dC}{dt} = kABB = kAB^2$$

One would obtain the same result using $m = 2, n = 0, p = 1$ in the example (9)-(10).

Lastly, the reason the Law of Mass Action works is because (if concentrations are measured in molarity) at any given instant the number of possible reactions is proportional to the concentrations of the reactants. The probability of a collision, therefore, should also be proportional to the product of the concentrations of the reactants. If all collisions are equally probable and there are large numbers of molecules, the rate of change of concentration should then obey the Law of Mass Action

References

- [1] Kittel, C., H. Kroemer, Thermal Physics, 2nd ed. W.H. Freeman and Company, San Fransisco, 1980.