Thermodynamics and Kinetics

A given system at temperature $T$ and pressure $p$ is prepared using $n_1$ moles of water ($l$), the solvent, together with $n_X^0$ and $n_Y^0$ moles of chemical substances $X$ and $Y$ respectively at time ‘$t = 0$’. The molalities of these solutes are $m_X^0$ ($= n_X^0 / n_1 \cdot M_1 = n_X^0 / w_1$) and $m_Y^0$ ($= n_Y^0 / n_1 \cdot M_1 = n_Y^0 / w_1$) respectively at time ‘$t = 0$’; the concentrations are $c_X^0$ ($= n_X^0 / V$) and $c_Y^0$ ($= n_Y^0 / V$) respectively.

Spontaneous chemical reaction leads to the formation of product $Z$. Here we consider this spontaneous change from the standpoints of chemical thermodynamics and chemical kinetics.

Thermodynamics

The spontaneous chemical reaction is driven by the affinity for chemical reaction, $A$ [1]. At each stage of the reaction the composition is described by the extent of reaction $\xi$. The affinity $A$ is defined by the thermodynamic independent variables, $T$, $p$ and $\xi$.

Thus \[ A = A(T, p, \xi) \] \hspace{1cm} (a)

Therefore \[ dA = \left( \frac{\partial A}{\partial T} \right)_{p, \xi} dT + \left( \frac{\partial A}{\partial p} \right)_{T, \xi} dp + \left( \frac{\partial A}{\partial \xi} \right)_{T, p} d\xi \] \hspace{1cm} (b)

At constant $T$ and $p$, \[ dA = \left( \frac{\partial A}{\partial \xi} \right)_{T, p} d\xi \] \hspace{1cm} (c)

In terms of thermodynamics, the reference point is thermodynamic equilibrium where the affinity for spontaneous change is zero and the composition is $\xi^{eq}$.

Chemical Kinetics

In the context of chemical reaction in solution, the system under study is, conventionally, a very dilute solution so that from a macroscopic standpoint the system at ‘$t = 0$’ is slightly displaced from equilibrium where $A$ is zero. Thus chemists exploit their skill in monitoring for a solution the change with time of the absorbance at fixed wavelength, electrical conductivity, $pH$… In a key assumption, the rate of change of composition $d\xi / dt$ is proportional to the affinity $A$ for spontaneous change[2]; \[ \frac{d\xi}{dt} = L \cdot A \] \hspace{1cm} (d)
Here \( L \) is a phenomenological constant describing, in the present context, the phenomenon of spontaneous chemical reaction.

In general terms for processes at fixed temperature and pressure, the phenomenological property \( L \) is related the isobaric – isothermal dependence of affinity \( A \) on extent of chemical reaction by a relaxation time \( \tau_{T,p} \).

Thus \[
L^{-1} = -\left( \frac{\partial A}{\partial \xi} \right)_{T,p} \cdot \tau_{T,p} \quad (e)
\]

Relaxation time \( \tau_{T,p} \) is a macroscopic property of a given system (at defined \( T \) and \( p \)) which chemists understand in terms of spontaneous chemical reaction (in a closed system). The task for chemists is to identify the actual chemical reaction in a given closed system.

**Thermodynamics and Chemical Kinetics**

In most treatments of chemical reactions the reference state is chemical equilibrium [3] where away from equilibrium the property \( dA \) equals the affinity \( A \) on the grounds that at equilibrium, \( A = A_{eq} = 0 \). Hence combination of equations (c), (d) and (e) yields the key kinetic-thermodynamic equation.

\[
\frac{d\xi}{dt} = -A \cdot (\tau_{T,p})^{-1} \cdot \left( \frac{\partial A}{\partial \xi} \right)_{T,p}^{-1} \quad (f)
\]

Equation (6) relates the rate of change of composition to the affinity for chemical reaction and relaxation time \( \tau_{T,p} \). Equation (f) is therefore the key equation describing spontaneous chemical reaction in a closed system. In this context we stress the importance of equation (f).

**Law of Mass Action**

Equation (f) is an interesting and important description of the kinetics of chemical reaction. In fact the link between the rate of chemical reaction \( (d\xi/dt) \) and the affinity for spontaneous change \( A \) is intuitively attractive. However while one may monitor the dependence of composition on time, \( d\xi/dt \), it is not immediately obvious how one might estimate the affinity \( A \) and the property \( \left( \frac{\partial A}{\partial \xi} \right)_{T,p} \) at time \( t \). The Law of Mass Action offers a way forward although this law does not emerge from either the First or Second Laws of Thermodynamics. As Hammett [4] notes the Law of Mass Action was ‘first derived from limited observations’ and became ‘established through
accumulation of observations with the principle and in the absence of contradictory evidence’. After the ‘Dark Ages’, came the renaissance and ‘Bartlett and Ingold and Peterson… accepting without question or comment the validity of the law of mass action’ [4].

The link back to thermodynamics was constructed using Transition State Theory developed by Eyring and described by Glasstone, Laidler and Eyring [5]. Therefore the phenomenological Law of Mass Action was brought into the fold of thermodynamics by offering a language which allowed activation parameters to be understood in terms of, for example, standard enthalpies and standard isobaric heat capacities of activation.

**Footnotes**