Affinity for Spontaneous Chemical Reaction: Law of Mass Action

The differential change in Gibbs energy of a closed system $dG$ is related to the change in chemical composition – organisation using equation (a) where $A$ is the affinity for spontaneous chemical reaction such that $A \cdot d\xi \geq 0$.

$$dG = -S \cdot dT + V \cdot dp - A \cdot d\xi$$  \hspace{1cm} (a)

Spontaneous chemical reaction is driven by the affinity for spontaneous change, $A$. Eventually the system reaches a minimum in Gibbs energy $G$ where the affinity for spontaneous change is zero.

In general terms, $A^{eq} = -\sum v_j \cdot \mu_j^{eq} = 0$  \hspace{1cm} (b)

We identify chemical equilibrium as the state where the chemical potentials driving the chemical flow from reactants to products are balanced by the chemical potentials driving chemical flow from products to reactants [1]. The condition given in equation (b) is based on the first and second laws of thermodynamics [1]. These two laws do not lead to quantitative statements concerning the rate of change of chemical composition; i.e. the dependence of the concentration of reactants and products on time.

At a given time $t$, the rate of change of composition $v$ is defined by equation (c).

$$v = d\xi / dt$$  \hspace{1cm} (c)

Hence, with $A \cdot d\xi > 0$, $A \cdot v > 0$  \hspace{1cm} (d)

Therefore for chemical reaction in a closed system, the signs of $A$ and $v$ are identical. [1] Moreover if the system is at thermodynamic equilibrium such that $A$ is zero, then $v$ is zero. The latter sentence establishes a crucial link between chemical kinetics and chemical thermodynamics. However away from equilibrium we have no information concerning the rate of change of composition. The required property is the ratio $d\xi / dt$ at time $t$ characterising the rate of change of the extent of chemical reaction. Intuitively one might argue that the rate depends on the affinity for spontaneous reaction—the greater the affinity for reaction the faster the reaction. The key equation might take the following form.

$$d\xi / dt = L \cdot A$$  \hspace{1cm} (e)
Here $L$ is a phenomenological parameter, describing the phenomenon of chemical reaction. Unfortunately no further progress can be made because we have no way of measuring the affinity $A$ for chemical reaction; no affinity meter is available which we can plunge into the reacting system and ‘read off’ the affinity.[2] In these terms the analysis comes to a halt.

In the context of chemical kinetics, the rate of chemical reaction is defined by equation (f) where $n_j$ refers to the amount of chemical substance $j$ as either product or reactant; positive for product

$$v = \pm V^{-1} \cdot \frac{dn_j}{dt} \quad (f)$$

For chemical reaction involving solutes in dilute solution the volume $V$ of the system (at fixed $T$ and $p$) is effectively independent of time.

Then, $v = \pm dc_j / dt \quad (g)$

The kinetics of chemical reactions in solution are simpler than those for reactions in the gas phase [3] and we confine comment to the former.

The relationship between velocity $v$ and the chemical composition of a solution is described by the Law of Mass Action as proposed by Guldberg and Waage in 1867 [4]. The developments reported by Harcourt and Essen (1867), Bredig and Stern and by Lapworth in 1904 and by Goldschmidt in 1930 were important. Hammett [3] comments that by the 1930s the subject had emerged from the ‘dark ages’. Hammett draws attention to the contributions made by Bartlett, Ingold and Pedersen in the decades of 1920 and 1930. Effectively these authors showed that the rate of chemical reaction at time $t$ is a function of the concentrations of substances in the systems at that time, $t$. In the textbook case the spontaneous chemical reaction [5,6] between two chemical substances $X$ and $Y$ at fixed $T$ and $p$ in aqueous solution, has the following form.

$$x \cdot X(aq) + y \cdot Y(aq) \rightarrow \text{products} \quad (h)$$

$$\text{Rate of reaction} = k \cdot [X]^\alpha \cdot [Y]^\beta \quad (i)$$

Here $\alpha$ and $\beta$ are orders of reaction with respect to substances $X$ and $Y$. These orders have to be determined from the experimental kinetic data because they do not necessarily correspond to the stoichiometric coefficients in the chemical equation [7].

We develop the argument by considering a chemical reaction in solution. An aqueous solution is prepared containing $n_\ell$ moles of water ($\ell$) and $n_X^0$ moles of
chemical substance X at time, t = 0 where \( n_X^0 >> n_1 \). Spontaneous chemical reaction leads to the formation of product Y, where at ‘t = 0’, \( n_Y^0 \) is zero.

Chemical reaction is described using equation (j).

\[
\begin{align*}
X(aq) & \rightarrow \quad Y(aq) \\
\text{At } t = 0 & \quad n_X^0 \rightarrow n_Y^0 = 0 \quad \text{mol}
\end{align*}
\]

The convention is for the chemical reaction to be written in the form ‘reactants → products’, such that the affinity for reaction A is positive and hence \( d\xi \) and \( d\xi/dt \) are positive.

Many chemical reactions of the form shown in equation (j) go to completion.

Thus \( \lim (t \rightarrow \infty) n_X = 0; n_Y = n_X^0 \) (k)

The minimum in Gibbs energy (where \( A = 0 \)) is attained when all reactant has been consumed.

**First Order Reactions**

A given closed system contains \( n_X^0 \) moles of chemical substance X which decomposes to form chemical substance Z. At time t, \( \xi \) moles of reactant X have formed product Z.

**Chemical Reaction**

\[
X \rightarrow Z
\]

**Amounts at t = 0**

\[
\begin{align*}
X \quad & n_X^0 = 0 \quad \text{mol} \\
\text{Concentrations (t = 0)} & n_X^0 / V = 0 \quad \text{mol m}^{-3}
\end{align*}
\]

At time t

**Amounts**

\[
\begin{align*}
X \quad & n_X^0 - \xi \quad \xi \quad \text{mol} \\
\text{Concentrations} & (n_X^0 - \xi)/V = \xi/V \quad \text{mol m}^{-3}
\end{align*}
\]

The law of mass action is the extra-thermodynamic assumption which relates the rate of change of concentration to the composition of the system.

Then,

\[
- \frac{d[(n_X^0 - \xi)/V]}{dt} = \frac{d[\xi/V]}{dt} = k \cdot \frac{[n_X^0 - \xi]}{V}
\]

The constant of proportionality, rate constant \( k \), in this case has units of s\(^{-1}\).

Then in terms of reactant X, \( \frac{d\xi}{dt} = k \cdot [n_X^0 - \xi] \) (m)

Chemical reaction proceeds leading to a decrease in the Gibbs energy of the system until \( n_X^0 = \xi \) such that all reactant has been consumed. At this point
(dξ/dt) is zero, the system is at chemical equilibrium and the Gibbs energy is a minimum. Further from equation (m),
\[ \int_{\xi=0}^{\xi} \frac{d\xi}{n_X^0 - \xi} = \int_{t=0}^{t} k \cdot dt \quad (n) \]

The Law of Mass Action is the most important extra-thermodynamic equation in chemistry.

**Second Order Reactions**

A given closed system contains \( n_X^0 \) and \( n_Y^0 \) moles of chemical substances X and Y respectively at fixed T and p. Spontaneous chemical reaction produces chemical substance Z. At time t, \( \xi \) moles of product Z are formed from chemical substances X and Y.

- **Chemical Reaction**
  \[ X + Y \rightarrow Z \]
- **Amounts at t = 0;**
  \( n_X^0 \) \( n_Y^0 \) 0 mol
- **Concentrations (t = 0)**
  \( n_X^0 /V \) \( n_Y^0 /V \) 0 mol m\(^{-3}\)

At time t

- **Amounts**
  \( n_X^0 - \xi \) \( n_Y^0 - \xi \) \( \xi \) mol
- **Concentrations**
  \( (n_X^0 - \xi)/V \) \( (n_Y^0 - \xi)/V \) \( \xi /V \) mol m\(^{-3}\)

The Law of Mass Action is the extra-thermodynamic assumption, relating the rate of change of concentration to the composition of the system. Then,

\[ -\frac{d[(n_X^0 - \xi)/V]}{dt} = -\frac{d[(n_Y^0 - \xi)/V]}{dt} = \frac{d[\xi/V]}{dt} = k \cdot \frac{[n_X^0 - \xi]}{V} \cdot \frac{[n_Y^0 - \xi]}{V} \quad (o) \]

The unit of rate constant k is ‘m\(^3\) mol\(^{-1}\) s\(^{-1}\)’.

Then,
\[ \frac{d\xi}{dt} = k \cdot V^{-1} \cdot [n_X^0 - \xi] \cdot [n_Y^0 - \xi] \quad (p) \]

Or,
\[ \int_{\xi=0}^{\xi} \frac{d\xi}{n_X^0 - \xi} \cdot [n_Y^0 - \xi] = \int_{t=0}^{t} k \cdot V^{-1} \cdot dt \quad (q) \]

In applications of equation (q), rate constant k and volume V are usually treated as independent of time.[8]

The foregoing analysis of kinetics of chemical reactions illustrates the application of the variable \( \xi \) in describing the composition of a closed system.

Most accounts of chemical kinetics start out with a consideration of concentrations of chemical substances in a given system. [9,10]
Nevertheless for each and every chemical reaction, the form of the relevant ‘Law of Mass Action’ has to be determined from the observed dependence of composition on time. The latter sentence does not do justice to the skills of chemists in this context.

**Reaction to Chemical Equilibrium**

In the previous section we considered those cases where chemical reaction goes to completion in that one or more of the reactants are consumed. For many cases this is not the case. Here we imagine that a dilute solution has been prepared using \( n_X^0 \) and \( n_Y^0 \) moles of solute reactants X and Y. Chemical reaction at fixed T and p proceeds spontaneously. The Gibbs energy of the system decreases reaching a minimum where the affinity for spontaneous reaction is zero. Chemical analysis shows that the resulting system contains product Z together with reactants X and Y, and that the chemical composition is independent of time; i.e. chemical kinetic equilibrium. Thus,

\[
\begin{align*}
X(aq) + Y(aq) & \rightleftharpoons Z(aq) \\
\text{At } t = 0 & \quad n_X^0 + n_Y^0 = 0 \text{ mol} \\
\text{At } t = \infty & \quad n_X^\text{eq} = n_X^0 - \xi^\text{eq} \quad n_Y^\text{eq} = n_Y^0 - \xi^\text{eq} \quad n_Z^\text{eq} = \xi^\text{eq} \quad \text{mol}
\end{align*}
\]

or,

\[
\begin{align*}
\frac{c_X^\text{eq}}{V} & = \left( \frac{n_X^0 - \xi^\text{eq}}{V} \right) \quad \frac{c_Y^\text{eq}}{V} = \left( \frac{n_Y^0 - \xi^\text{eq}}{V} \right) \quad \frac{c_Z^\text{eq}}{V} = \left( \frac{\xi^\text{eq}}{V} \right)
\end{align*}
\]

A number of assumptions are based on the Law of Mass Action.

At time \( t \), rate of forward reaction = \( k_f \cdot c_X(t) \cdot c_Y(t) \)

and rate of the reverse reaction = \( k_r \cdot c_Z(t) \)

Rate constants \( k_f \) and \( k_r \) are initially assumed to be independent of the extent of reaction. A key conclusion is now drawn. Because at ‘\( t \rightarrow \infty \)’, the properties of the system are independent of time, the system is ‘at chemical equilibrium where the rates of forward and reverse reactions are balanced.

Then, \( k_f^\text{eq} \cdot c_X^\text{eq} \cdot c_Y^\text{eq} = k_r^\text{eq} \cdot c_Z^\text{eq} \) \hspace{1cm} (r)

Hence, \( \frac{d\xi^\text{eq}}{dt} = 0 \) \hspace{1cm} (s)

and \( k_f^\text{eq} \cdot \left( \frac{n_X^0 - \xi^\text{eq}}{V} \right) \cdot \left( \frac{n_Y^0 - \xi^\text{eq}}{V} \right) = k_r^\text{eq} \cdot \frac{\xi^\text{eq}}{V} \) \hspace{1cm} (t)

At this point we encounter a key problem -- we cannot determine \( k_f^\text{eq} \) and \( k_r^\text{eq} \) because at equilibrium the composition of the system is independent of time.
Nevertheless we can express the ratio of rate constants as a function of the composition at equilibrium.

\[ \frac{k_{i}^{eq}}{k_{r}^{eq}} \cdot \left( \frac{n_{X}^{0} - \zeta_{eq}}{V} \right) \cdot \left( \frac{n_{Y}^{0} - \zeta_{eq}}{V} \right) = \frac{\zeta_{eq}}{V} \]  

The ratio \( \frac{k_{i}^{eq}}{k_{r}^{eq}} \) is characteristic of the system (at defined \( T \) and \( p \)), defining what we might call a 'Law of Mass Action equilibrium constant', \( K(lma) \).

Thus \( K(lma) = k_{i}^{eq} / k_{r}^{eq} \)  

In other words, the property \( K(lma) \) is based on a balance of reaction rates whereas the thermodynamic equilibrium constant is based on a balance of chemical potentials. With reference to equation (v), at fixed \( T \) and \( p \), the thermodynamic condition is given in equation (w).

\[ \mu_{X}^{eq}(aq) + \mu_{Y}^{eq}(aq) = \mu_{Z}^{eq}(aq) \]  

For \( p \approx p^{0} \), \( K^{0}(T) = \frac{(m_{Z} \cdot \gamma_{Z} / m^{0})^{eq} \cdot (m_{Y} \cdot \gamma_{Y} / m^{0})^{eq}}{(m_{X} \cdot \gamma_{X} / m^{0})^{eq}} \)  

Therefore the question is raised--- how is \( K(lma) \) related to \( K^{0}(T) \)? In the absence of further information, a leap of faith by chemists sets \( K(lma) \) equal to \( K^{0}(T) \). We avoid debating the meaning of the phrase ‘rate constants at equilibrium’ [7].

**Energy of Activation**

Spontaneous chemical reaction involving a single solute \( X(aq) \) can be described using a rate constant \( k \) for a solution at fixed \( T \) and \( p \) where the concentration of solute \( X \) at time \( t \) is \( c_{X}(aq) \).

If we can assume that in solution there are no solute-solute interactions, rate constant \( k \) is not dependent on the composition of the solution. In thermodynamic terms, the thermodynamic properties of solute \( X \) are ideal; for such a system rate constant \( k \) is independent of time and initial concentration of solute \( X \). In other words experiment yields the property \( k(T,p) \) for a given solution indicating that the rate constant is a function of temperature and pressure. For nearly all chemical reactions in solution rate constants increase with increase in temperature, a dependence described by the Arrhenius equation. [11]

\[ k = A \cdot \exp(-E_{A} / R \cdot T) \]  

Then rate constant, \( k \) increases with increase in temperature. The idea emerges that spontaneous conversion of reactant to products is inhibited by an ‘energy’ barrier.
Further in the limit $T \to \infty$, $\ln(k) = A$, the pre-exponential factor which has the same units as rate constant $k$.

The assumption in the foregoing comments is that $E_A$ is independent of temperature such that for example a first order rate constant $\ln(k/s^{-1})$ is a linear function of $T^{-1}$.

Thus, $\ln(k/s^{-1}) = \ln(A/s^{-1}) - (E_A / R \cdot T)$  \( (z) \)

The latter pattern is generally observed but there are many well-documented cases where the plot is not linear. In other words it is incorrect to conclude that equation (y) somehow predicts how rate constants depend on temperature. There is no substitute for actually measuring this dependence.

**Transition State Theory**

The law of mass action and the concept of an activation energy for a given chemical reaction are extrathermodynamic. This conclusion is unfortunate, implying that the treatment of kinetic data for reactions in solution is completely divorced from the thermodynamic treatment of the properties of solution. One can understand therefore why Transition Sate Theory (TST) attracts so much interest.\[12,13\] At the very least, this theory offers analysis of kinetic data a patina of thermodynamic respectability.

We describe TST with respect to a chemical reaction where the dependence of composition on time is described using a first order rate constant.

For chemical reactions in the gas phase, statistical thermodynamics offers a reasonably straightforward approach to the description of both reactants and a transition state in which one vibrational mode for the transition state is transposed into translation along the reaction co-ordinate. The theory was re-expressed in terms of equations which could be directly related to the thermodynamics of the process of reaction in solutions.

Chemical reaction proceeds from reactant $X(aq)$ to products through a transition state $X^\neq(aq)$. As the reaction proceeds the amount of solute $X$, $n_X(aq)$ decreases but at all times reactant $X(aq)$ and transition state $X^\neq(aq)$ are in chemical equilibrium.

Thus $X(aq) \leftrightarrow X^\neq \rightarrow \text{products} \quad (za)$

The condition ‘chemical equilibrium’ is quantitatively expressed in terms of chemical potentials.

$\mu_X^{eq}(aq; T; p) = \mu_X^{eq}(aq; T; p) \quad (zb)$
Conventionally where kinetics of reactions in solution are addressed, the composition of solutions is expressed in terms of concentrations using the unit, mol dm$^{-3}$. Then equation (zc) is formed assuming that ambient pressure is close to the standard pressure, $p^0$; $c_r = 1$ mol dm$^{-3}$. Hence,

$$
\mu^0_X(\text{aq}; T) + R \cdot T \cdot \ln(\frac{c_X \cdot y_X}{c_r}) = \mu^0_y(\text{aq}; T) + R \cdot T \cdot \ln(\frac{c_y \cdot y_y}{c_r})
$$

The standard Gibbs energy of activation $\Delta^a G^0(\text{aq}; T)$ is given by equation (zd) leading to the definition of an equilibrium constant $K^0(\text{aq}; T)$ with $p = p^0$.

$$
\Delta^a G^0(\text{aq}; T) = \mu^0_y(\text{aq}; T) - \mu^0_X(\text{aq}; T)
$$

By definition, $\Delta^a G^0(\text{aq}; T) = -R \cdot T \cdot \ln(K^0(\text{aq}; T))$ (zf)

Therefore, $c_x = K^0(\text{aq}; T) \cdot c_X \cdot y_X / y_y$ (zg)

Through the course of chemical reaction, as the concentration of reactant $X(\text{aq})$ decreases, the condition given in equation (zb) holds. Chemical reaction is not instantaneous because $\mu^0_y(\text{aq}; T) > \mu^0_X(\text{aq}; T)$; a barrier exists to chemical reaction. Consequently the concentration $c_x$ is small. The analysis up to equation (zf) is based on a thermodynamic description of equilibrium between reactant and transition states. In the limit that the solution is very dilute, $y_X = y_y = 1$ at all time $t$, $T$ and $p$.

Thus at given $T$ and $p$, [14] $k = \frac{k_B \cdot T}{h} \cdot \exp\left(\frac{-\Delta^a G^0}{R \cdot T}\right)$ (zh)

Then, $k = \frac{k_B \cdot T}{h} \cdot \exp\left(\frac{-\Delta^a H^0}{R \cdot T} + \frac{\Delta^a S^0}{R}\right)$ (zi)

$\Delta^a G^0$ is the standard Gibbs energy of activation defined in terms of reference chemical potentials of transition state and reactants. Here $k_B$ is the Boltzmann constant and $h$ is Planck’s constant [15].

$$
\Delta^a G^0 = -R \cdot T \cdot \ln\left(\frac{h \cdot k(T)}{k_B \cdot T}\right)
$$

At temperature $T$, $\Delta^a G^0(\text{aq}; T)$ is re-expressed in terms of standard enthalpy and standard entropy of activation [16].

Then, $\Delta^a G^0(\text{aq}; T) = \Delta^a H^0(\text{aq}; T) - T \cdot \Delta^a S^0(\text{aq}; T)$ (zk)

The standard isobaric heat capacity of activation [17,18],

$$
\Delta^a C^p = \frac{\partial (\Delta^a G^0/T)}{\partial T}
$$
\[
\Delta^* C^0_p(aq) = \left( \frac{\partial \Delta^* H^0(aq)}{\partial T} \right)_p (z\ell)
\]

In summary transition state theory allows kinetic data to be analysed using the protocols and equations of thermodynamics.

Analysis of the dependence of rate constants at fixed temperature as a function of pressure yields standard volumes of activation \(\Delta^* V^0(aq;T)\). In further exercises this volumetric parameter is measured as functions of pressure at temperature \(T\) and of temperature at fixed pressure [20].

Nevertheless a word of caution is in order. Johnston [21] points out that diagrams describing the progress of chemical reaction through several intermediates are often misleading. Such diagrams should be based on reference chemical potentials otherwise misleading conclusions can be drawn; see also [22 - 28].

Footnotes


[2] In fact in the treatment of data obtained using fast reaction techniques (e.g. temperature jump and pressure-jump) where the displacement from equilibrium is small, it is assumed that the rate of response is linearly related to the affinity for chemical reaction.


‘Neither did they (i.e. Guldberg and Waage] make any contributions to kinetics since they worked in terms of forces and not of rates, although they did tentatively suggest that rates might be proportional to forces’.

[5] The condition ‘spontaneous change’ signals a ‘natural’ direction but that does mean that the process is instantaneous. The properties of the system are dependent on time. We make this point to counter such statements as

[6] Thermodynamics in the form of the first and second laws offers no way forward. Intuitively one might argue that the rate of change of composition would be directly related to the affinity for spontaneous reaction, $A$ where $\pi$ is a proportionality factor characteristic of the system, temperature and pressure.

Thus, $\frac{d\xi}{dt} = \pi \cdot A$ where $\lim_{(A \to 0)} \frac{d\xi}{dt} = 0$

In fact we might draw an analogy with Ohm’s law whereby electric current $i$ (= rate of flow of charge) is proportional to the electric potential gradient, $\Delta \phi$, the constant of proportionality being the electrical conductivity, $L$; $i = L \cdot \Delta \phi$ where $L$ is characteristic of the system, temperature and pressure. Indeed such a kinetic force-flow link might be envisaged. Indeed an link emerges with the phenomenon of electric potential driving an electric current through an electrical circuit.

Electric current = rate of flow of charge, unit = Ampere.

Electric potential has the unit, volt.

The product, $I \cdot V = [A] \cdot [J A^{-1} s^{-1}] = [W]$ Here $W$ is the SI symbol for the unit of power, watt.

Rate of chemical reaction $\frac{d\xi}{dt}=[mol \ s^{-1}]$

Affinity $A= [J mol^{-1}]$

Then $A \cdot \frac{d\xi}{dt}=[J mol^{-1}] \cdot [mol s^{-1}] = [W]$ Interestingly chemists rarely refer to the 'wattage' of a chemical reaction.

[7] One cannot help be concerned with accounts which describe chemical equilibrium in terms of rates of chemical reaction. As we understand the argument runs along the following lines. For a chemical equilibrium having the following stochiometry, $X+Y<=>Z$ at equilibrium the rates of forward and reverse reactions are balanced.

$k_f \cdot [X] \cdot [Y] = k_r \cdot [Z]$

Here $k_f$ and $k_r$ are the forward and reverse rate constants.

Then $K= \frac{k_f}{k_r} = [Z]/[X].[Y]$
The argument loses some of its force if one turns to accounts dealing with chemical kinetics when questions of order and molecularity are raised. In any case one cannot measure rates of chemical reactions 'at equilibrium' because at equilibrium 'nothing is happening'. Even in those cases where the rates of chemical reactions 'at equilibrium' are apparently measured the techniques rely on following the return to equilibrium when the system is perturbed.

[8] In nearly all applications of the law of mass action to chemical reactions in solution a derived rate constant is based on a description of the composition on time at fixed $T$ and $p$. Therefore the calculated rate constant is an isobaric-isothermal property of the system. Nevertheless the volume is usually taken as independent of time. Certainly in most applications in solution chemistry the solutions are quite dilute and so throughout the course of the reaction the volume is effectively constant. An interesting point now emerges in that a given rate constant is an isothermal-isobaric-isochoric property.


[11] $E_A = [J \text{ mol}^{-1}]$ such that $E_A / R \cdot T = [J \text{ mol}^{-1}] / [J \text{ K}^{-1} \text{ mol}^{-1}] \cdot [K] = [l]$


[14] \[ \frac{k_B \cdot T}{h} = \frac{[J \text{ K}^{-1}] \cdot [K]}{[J \text{ s}]} = [s^{-1}] \]

[15] \[ \frac{k_B \cdot T}{h} \cdot c_x = [s^{-1}] \cdot [\text{mol dm}^{-3}] = [\text{mol dm}^{-3} \text{ s}^{-1}] \]

$k \cdot [X(aq)] = [s^{-1}] \cdot [\text{mol dm}^{-3}] = [\text{mol dm}^{-3} \text{ s}^{-1}]$

$^* K^0(aq; T) \cdot c_X \cdot y_X / y_x = [l] \cdot [\text{mol dm}^{-3}] \cdot [l] / [l] = [\text{mol dm}^{-3}]$

\[ \frac{h \cdot k(T)}{k_B \cdot T} = \frac{[J \text{ s}] \cdot [s^{-1}]}{[J \text{ K}^{-1}] \cdot [K]} = [l] \]

[16]