22. CHEMICAL REACTIONS AS IRREVERSIBLE PROCESSES

Chapters 20 and 21 dealt with the equilibrium thermodynamics of chemical reactions. A chemical reaction is an irreversible process and is therefore invariably accompanied by the production of entropy. It is the task of Chapter 22 to examine chemical reactions as irreversible processes. This undertaking necessarily leads to the introduction of a number of concepts that are required in the treatment of the thermodynamics of the steady state, such as, in particular, the entropy production, energy dissipation, and energy retention functions. A consideration of chemical reactions as irreversible processes thus constitutes a natural transition from equilibrium to steady-state thermodynamics.

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22.1 De Donder's Inequality

Consider a chemical reaction taking place in a vessel that is closed but not isolated. It can thus exchange heat but not matter with its surroundings. By Eq.(5.6)\textsubscript{1} the infinitesimal change in entropy becomes

\[ dS = \delta Q/T + \delta Q'/T = d_eS + d_iS, \]  

(22.1)\textsubscript{1}

and substituting this equation into Eq.(20.6)\textsubscript{8} leads to

\[ d_eS + d_iS = \frac{dU + PdV}{T} + \frac{Ad\xi}{T}. \]  

(22.1)\textsubscript{2}

In the absence of any entropy produced within the reaction vessel, we would simply have

\[ Td_eS = \delta Q = dU + PdV. \]  

(22.1)\textsubscript{3}
If, however, entropy is generated within the vessel [cf. Eq. (5.6)] we additionally have the heat term

$$TdS = \delta Q' = Ad\xi \geq 0.$$  

The last relation is de Donder's inequality. It identifies the internally generated heat, $\delta Q'$, in a chemical reaction with the mass action term, $Ad\xi$, and states that this is positive semidefinite. It is zero when the internal changes are reversible, and positive when they are irreversible.

### 22.2 The General Criterion of Irreversibility

Since $d_i S$ represents production of entropy, de Donder's inequality in the form

$$d_i S > 0$$  

is a criterion of irreversibility. It is also the only general criterion of irreversibility.

### 22.3 Particular Criteria of Irreversibility

Criteria applicable under particular conditions are readily obtained from the Gibbs equation for the internal energy, $U$, and its first-order Legendre transforms. The changes in the thermodynamic potentials are given by Eqs. (20.6) to (20.6). We have, therefore,

$$\frac{\partial U}{\partial \xi} \bigg|_{S,V} = \frac{\partial H}{\partial \xi} \bigg|_{S,P} = \frac{\partial F}{\partial \xi} \bigg|_{T,V} = \frac{\partial G}{\partial \xi} \bigg|_{T,P} = -A$$  

and

$$dU = dH = dF = dG < 0$$

as the criteria of irreversibility in terms of the thermodynamic potentials $U$, $H$, $F$, and $G$, i.e., at constant $S$ and $V$, constant $S$ and $P$, constant $T$ and $V$, and constant $T$ and $P$, respectively. By these criteria all four potentials necessarily decrease as a chemical reaction takes place.

### 22.4 The Rate of Reaction

During the course of a reaction the extent of reaction, introduced in § 20.4, evolves with time until equilibrium is reached. The time derivative of the evolving extent of reaction is called the rate of reaction, $v$. The rate of reaction depends not only on the time but also on the temperature, $T$, and on the pressure, $P$. These latter may be arbitrary functions of time, i.e., we may have $T = T(t)$, and $P = P(t)$. However, if these functions are specified, the rate of reaction is completely determined and we may write simply
Now, by de Donder's inequality, $A\xi \geq 0$, we have

$$A \frac{d\xi}{dt} = Av \geq 0$$

whence,

<table>
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<th>if</th>
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<tr>
<td>$A &gt; 0$</td>
<td>$v \geq 0$</td>
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<tr>
<td>$A = 0$</td>
<td>$v = 0$</td>
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<tr>
<td>$A &lt; 0$</td>
<td>$v \leq 0$</td>
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Thus, the affinity has the same sign as the rate of reaction. If the affinity is zero, the rate of reaction is also zero, i.e., the system is at equilibrium. The latter follows because, if $v \neq 0$ when $A = 0$, the reaction would proceed with a finite rate at equilibrium, which is contradictory. Note, however, that we may have $v = 0$, $A \neq 0$. The system is then in false equilibrium (e.g., a mixture of gaseous hydrogen, $H_2$, and oxygen, $O_2$).

### 22.5 The Rate of Entropy Production

We now introduce three important new concepts related to the rate of reaction. The rate of entropy production, $\Theta$, i.e., the entropy produced per unit time, is

$$\Theta = \frac{dS}{dt} = \frac{\delta Q'}{Tdt} = \frac{A}{T} \frac{d\xi}{dt} = \frac{A}{T} v > 0 .$$

It is positive definite because of the thermodynamic irreversibility of any chemical reaction.

### 22.6 The Entropy Production Function

The entropy produced per unit time and unit volume, i.e., the rate of entropy production per unit volume, is called the entropy production function, or the entropy source density, or the entropy source strength. It becomes

$$\Phi = \frac{\Theta}{V} = \frac{A}{VT} v > 0$$

and is again positive definite in any single chemical reaction.
22.7 The Energy Dissipation and Energy Retention Functions

The product of $\Psi$ with the temperature, $T$, is called the energy dissipation function,

$$\Psi = T \Phi = \frac{A}{v} v > 0, \quad (22.7)_1$$

because it represents energy dissipated per unit volume and unit time. In any single chemical reaction the energy dissipation function is positive definite.

The negative inverse of the energy dissipation function,

$$T = -\frac{1}{\Psi} < 0, \quad (22.7)_2$$

will be called the energy retention function. Since the energy dissipated is taken as positive, $T$ stands for a negative amount of energy. This is retained in that it is not dissipated and is negative definite in any single chemical reaction.

22.8 The Phenomenological Equation

Since the affinity, $A$, and the extent of reaction, $\xi$, are conjugate quantities, so are $A$ and $v$. The rate of reaction, $v$, is clearly a function of $A/T$ which is appropriately called the driving force of the reaction. If $v$ depends linearly on $A/T$ we have

$$v = L \frac{A}{T} \quad (22.8)$$

where $L$ is the kinetic or phenomenological coefficient. Equation (22.8) is termed the phenomenological equation of the reaction. To assign meaning to the phenomenological coefficient, $L$, we need to find a suitable linear relation between $v$ and $A/T$.

22.9 Relation between the Rate of Reaction and its Driving Force

We seek a general expression linking $v$ and $A/T$. The overall rate of reaction, $v$, is the difference between the forward rate, $\overrightarrow{v}$, and the backward rate, $\overleftarrow{v}$. It is shown in the theory of chemical kinetics that

$$\overrightarrow{v} = k \prod_{j=1}^{r} c_j^{[v_j]} \quad \text{and} \quad \overleftarrow{v} = k \prod_{j=r+1}^{n} c_j^{[v_j]} \quad (22.9)_1$$

where $r$ is the number of reactants, $n - r$ is the number of products, and $k$ and $\overrightarrow{k}$ are called the kinetic constants. It is further shown in the kinetic theory that the ratio of the kinetic constants is equal to the equilibrium constant so that

$$\overrightarrow{k} / \overleftarrow{k} = K_e(T). \quad (22.9)_2$$
We thus have

\[ v = \overrightarrow{v} - \overrightarrow{v} = \overrightarrow{v} \left[ 1 - \frac{\prod_{j=1}^{j=n} c_j^{\nu_j}}{K_\nu(T) \prod_{j=1}^{j=n} c_j^{\nu_j}} \right] = \overrightarrow{v} \left[ 1 - \frac{\prod_{j=1}^{j=n} c_j^{\nu_j}}{K_\nu(T) \prod_{j=1}^{j=n} c_j^{\nu_j}} \right]. \]  

(22.9)_3

But, since the \( \nu_j \)'s of the reactants carry the negative sign,

\[ \prod_{j=1}^{j=n} c_j^{\nu_j} = \prod_{j=r+1}^{j=n} c_j^{\nu_j} / \prod_{j=1}^{j=r} c_j^{\nu_j}, \]  

(22.9)_4

and we find

\[ v = \overrightarrow{v} \left[ 1 - \frac{\prod_{j=1}^{j=r} c_j^{\nu_j}}{K_\nu(T)} \right] = \overrightarrow{v} \left[ 1 - \frac{\prod_{j=1}^{j=r} P_j^{\nu_j}}{K_p(T)} \right], \]  

(22.9)_5

where the second equation follows because

\[ K_\nu(T) / \prod_{j=1}^{j=n} c_j^{\nu_j} = 1 = K_p(T) / \prod_{j=1}^{j=r} P_j^{\nu_j}, \]  

(22.9)_6

by Eqs.(21.2)_7 and (21.3)_2. Using Eq.(21.2)_8 we obtain

\[ v = \overrightarrow{v} \left[ 1 - \exp \left( - \frac{A}{RT} \right) \right], \]  

(22.9)_7

as the sought-for general relation between \( v \) and \( A/T \).

22.10 Dynamic Equilibrium – The Steady State

Equation (22.9)_7 is not a linear relation between \( v \) and \( A/T \). However, as equilibrium is approached, \( A \) becomes quite small and the exponential may then be approximated by \( 1 - A/RT \). At the same time, both the forward and the backward reaction rates approach the same value, the equilibrium rate, \( v_{eq} \). Hence,

\[ \text{This is required by the principle of microscopic reversibility (cf. § 23.9).} \]
In this limit, therefore, a *dynamic equilibrium* or *steady state* will be reached in which the rate at which products are formed equals the rate at which reactants are reformed (microscopic reversibility, see § 23.9). We then regain Eq. (22.8) with $L$ now given by

$$L = \frac{v_{eq}}{R}.$$  \hspace{1cm} \text{(22.10)2}

Equation (22.10)2 identifies the phenomenological coefficient, $L$, as the equilibrium rate of reaction divided by $R$, the universal gas constant. It is in the nature of chemical reactions that a linear phenomenological equation applies only quite close to equilibrium and that, hence, a meaningful interpretation of the phenomenological coefficient is possible only in that limit.

### 22.11 Scalar Steady-State Theory

We may now rewrite the phenomenological equation, Eq.(22.8), in the terminology of the theory of the steady state to be discussed more fully in the next Chapter. The equation then takes the form

$$J = LF$$  \hspace{1cm} \text{(22.11)1}

where

$$J = \nu = \frac{d\xi}{dt}$$  \hspace{1cm} \text{(22.11)2}

(i.e., the rate of reaction) is termed the *thermodynamic scalar flux*, and

$$F = \frac{A}{T}$$  \hspace{1cm} \text{(22.11)3}

is called the *thermodynamic scalar driving force*.

Because the variables in Eq.(22.11) are all scalars, the thermodynamics of chemical reactions in dynamic equilibrium is called a scalar steady-state theory.

### 22.12 Simultaneous Reactions

In the preceding sections we were concerned with entropy production in a single reaction. If $k$ reactions occur simultaneously (cf. § 21.10), rewriting Eq.(20.5)2 for the case of multiple reactions yields

$$A_k = -\Sigma j \mu_j v_{jk}$$  \hspace{1cm} \text{(22.12)1}
22. CHEMICAL REACTIONS AS IRREVERSIBLE PROCESSES

for the affinity of the $k$th reaction. By de Donder's inequality and the additivity of the entropy, the entropy production in the interior of the system is then given by

$$d_iS = \frac{1}{T} \sum_k v_k A_k d\xi_k .$$  \hfill (22.12)_2$$

Hence, the rate of entropy production per unit volume, i.e., the entropy production function, results as

$$\Phi = \frac{1}{VT} \sum_k v_k A_k ,$$  \hfill (22.12)_3$$

and we obtain

$$T = -T\Phi = -\frac{1}{V} \sum_k v_k A_k .$$  \hfill (22.12)_4$$

for the energy retention function.

22.13 Coupled Reactions

When two reactions occur simultaneously, we have

$$\Phi = \frac{1}{VT} (A_1 v_1 + A_2 v_2)$$  \hfill (22.13)$$

for the entropy production function. It is perfectly possible to have two reactions occurring simultaneously for which $A_1 v_1 < 0$ and $A_2 v_2 > 0$, provided that $\Phi > 0$. Such reactions are called coupled reactions. They are of great importance in biological processes.