entropies, a situation encountered when various phases of a substance exchange matter and reach equilibrium.

It is more convenient to describe chemical reactions by the change in the molar amounts of the reactants rather than the change in their masses, because chemical reaction rates and the laws of diffusion are most easily formulated in terms of molar amounts. Therefore, we shall rewrite Equation (4.1.1) in terms of the molar amounts $N_k$ of the constituent substances:

$$dU = TdS - pdV + \sum_{i} \mu_i dN_i + \ldots + \mu_n dN_n$$

i.e.

$$dU = TdS - pdV + \sum_{k} \mu_k dN_k$$

(4.1.2)

The above equation implies that $U$ is a function of $S$, $V$ and $N_k$, and that coefficients of $dS$, $dV$ and $dN_k$ are the corresponding derivatives:

$$\left( \frac{\partial U}{\partial S} \right)_{V,N_k} = T \quad \left( \frac{\partial U}{\partial V} \right)_{S,N_k} = -p \quad \left( \frac{\partial U}{\partial N_k} \right)_{S,V,N_{j\neq k}} = \mu_k$$

(4.1.3)

Chemical Reactions

Though Gibbs did not consider irreversible chemical reactions, Equation (4.1.1) he introduced contained all that was needed, which included all that was needed for a theory of irreversibility and entropy production in chemical processes. By making the important distinction between the entropy change $dS$ due to reversible exchange of matter and energy with the exterior, and irreversible increase of entropy $dS$ due to chemical reactions, De Donder formulated the thermodynamics of irreversible chemical transformations [2, 3]. Using the concept of chemical potential, De Donder took the 'uncompensated heat' of Clausius in the context of chemical reactions and gave it a clear expression.

Let us look at Equation (4.1.2) from the point of view of reversible entropy flow $dS$ and irreversible entropy production $dS$ that was introduced in the previous chapter. To make a distinction between irreversible chemical reactions and reversible exchange with the exterior, we express the change in the molar amounts $dN_k$ as a sum of two parts:

$$dN_k = d_r N_k + d_c N_k$$

(4.1.4)

in which $d_r N_k$ is the change due to irreversible chemical reactions and $d_c N_k$ is the change due to exchange of matter with the exterior. In Equation (4.1.2), Gibbs
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\[ \text{d}S = \text{d}_x S + \text{d}_y S \]  
(4.1.7)

in which

\[ \text{d}_x S = \frac{\text{d}U + p \text{d}V}{T} - \frac{1}{T} \sum_1^a \mu_k \text{d}_x N_k \]  
(4.1.8)

and

\[ \text{d}_y S = -\frac{1}{T} \sum_1^a \mu_k \text{d}_y N_k > 0 \]  
(4.1.9)

For a closed system, which by definition does not exchange matter, \( \text{d}_x N_k = 0 \). Since
the rates of chemical reaction specify \( \text{d}N_k/\text{dt} \), the rate of entropy production can be
written as

\[ \frac{\text{d}_x S}{\text{dt}} = -\frac{1}{T} \sum_1^a \mu_k \frac{\text{d}N_k}{\text{dt}} > 0 \]  
(4.1.10)

If we sum (4.1.8) and (4.1.9) we recover (4.1.2):

\[ \text{d}U = T \text{d}S - p \text{d}V + \sum_1^a \mu_k \text{d}N_k \]  
(4.1.11)

Further development of this theory relates chemical potential to measurable system
variables such as \( p \), \( T \) and \( N_k \). The pioneering work of De Donder established a clear
connection between entropy production and irreversible chemical reactions: the rate
of entropy production \( \text{d}_x S/\text{dt} \) is related directly to the rates of chemical reactions
that specify \( \text{d}N_k/\text{dt} \). In a closed system, if initially the system is not in chemical
equilibrium, then chemical reactions will take place that will irreversibly drive the
system towards equilibrium. And, according to the Second Law of thermodynamics,
this will happen in such a way that (4.1.10) is satisfied.

AFFINITY

De Donder also defined the affinity of a chemical reaction, which enables us to write
expression (4.1.10) in an elegant form, as the product of a thermodynamic force and
a thermodynamic flow. The concept of affinity can be understood through the fol-
lowing simple example.

In a closed system, consider a chemical reaction of the form

\[ X + Y \rightleftharpoons 2Z \]  
(4.1.12)
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\[
\begin{align*}
\text{Fig. 4.2} & \quad \text{The changes in entropy } \, dS \, \text{due to irreversible chemical reactions is formulated using the concept of affinity. For the above reaction, the affinity } A = \mu_X + \mu_Y - 2\mu_Z, \text{ in which } \mu \text{ is the chemical potential.}
\end{align*}
\]

\[
A = \mu_X + \mu_Y - 2\mu_Z = 0 \quad (4.1.18)
\]

In Chapter 9, which is devoted to the thermodynamics of chemical processes, we will see how chemical potentials can be expressed in terms of experimentally measurable quantities such as concentrations and temperature. Equations such as (4.1.18) are specific predictions regarding the states of chemical equilibrium. These predictions have been amply verified by experiment, and today they are routinely used in chemistry.

For a general chemical reaction of the form

\[
a_1 A_1 + a_2 A_2 + a_3 A_3 + \ldots + a_n A_n \rightleftharpoons b_1 B_1 + b_2 B_2 + b_3 B_3 + \ldots + b_m B_m \quad (4.1.19)
\]

the changes in the molar amounts of the reactants \( A_k \) and the products \( B_k \) are related in such a way that a change \( dX \) in one of the species (reactants or products) completely determines the corresponding changes in all the other species. Consequently, there is only one independent variable, which can be defined as

\[
\frac{dN_{A_1}}{-a_1} = \frac{dN_{A_2}}{-a_2} = \ldots = \frac{dN_{A_n}}{-a_n} = \frac{dN_{B_1}}{b_1} = \frac{dN_{B_2}}{b_2} = \ldots = \frac{dN_{B_m}}{b_m} = d\xi \quad (4.1.20)
\]

The affinity \( A \) of the reaction (4.1.19) is defined as

\[
A \equiv \sum_{k=1}^{n} a_k \mu_{A_k} - \sum_{k=1}^{m} b_k \mu_{B_k} \quad (4.1.21)
\]

in which \( \mu_{A_k} \) is the chemical potential of the reacting species \( A_k \), etc. If several simultaneous reactions occur in a closed system, then an affinity \( A_k \) and a degree of advancement \( \xi_k \) can be defined for each reaction and the change of entropy is written as
4.2 General Properties of Affinity

The affinity of a reaction is a state function, completely defined by the chemical potentials. In the following chapters we will see how the chemical potential of a substance can be expressed in terms of state variables such as pressure, temperature and concentration. Thus, affinity can be expressed as a function of \( p, T \) and \( N_i \) or it can also be expressed as a function of \( V, T \) and \( N_i \). For a closed system, since all the changes in \( N_i \) can only be due to chemical reactions, it can be expressed in terms of \( V, T, \xi_k \) and the initial values of the molar amounts \( N_{i0} \). There are some general properties of affinities that follow from the fact that chemical reactions can be interdependent when a substance is a reactant in more than one reaction.

Affinity and Direction of Reaction

The sign of affinity can be used to predict the direction of reaction. Consider the reaction \( X + Y \rightleftharpoons 2Z \). The affinity is given by \( A = \mu_x + \mu_y - 2\mu_z \). The sign of the velocity of reaction \( \frac{d\xi}{dt} \) indicates the direction of reaction, i.e. whether the net conversion is from \( X + Y \) to \( 2Z \) or from \( 2Z \) to \( X + Y \). From the definition of \( \xi \) it follows that if \( \frac{d\xi}{dt} > 0 \) then the reaction 'proceeds to the right': \( X + Y \rightarrow 2Z \); if \( \frac{d\xi}{dt} < 0 \) then the reaction 'proceeds to the left': \( X + Y \leftarrow 2Z \). The Second Law requires that \( A(\frac{d\xi}{dt}) \geq 0 \). Thus, we arrive at the following relation between the sign of \( A \) and the direction of the reaction:

- if \( A > 0 \), the reaction proceeds to the right;
- if \( A < 0 \), the reaction proceeds to the left.

Additivity of Affinities

A chemical reaction can be the net result of two or more successive chemical reactions. For instance:

\[
2C(s) + O_2(g) \rightleftharpoons 2CO(g) \quad A_1
\]

\[
2CO(g) + O_2(g) \rightleftharpoons 2CO_2(g) \quad A_2
\]

\[
2[C(s) + O_2(g) \rightleftharpoons CO_2(g)] \quad 2A_3
\]

which shows that reaction (4.2.3) is the net result or 'sum' of the other two. By definition the affinities of the above three reactions are:

\[
A_1 = 2\mu_C + \mu_{O_2} - 2\mu_{CO}
\]

\[
A_2 = 2\mu_{CO} + \mu_{O_2} - 2\mu_{CO_2}
\]

\[
A_3 = \mu_C + \mu_{O_2} - \mu_{CO_2}
\]
for which, as indicated, the corresponding affinity $A_i$ is assumed to be positive. We then expect the reaction to proceed to the right so that $\frac{d\xi_i}{dt} > 0$. It is possible to drive the reaction (4.2.10) effectively to the left, making $\frac{d\xi_i}{dt} < 0$, by ‘coupling’ it to another reaction:

$$T \iff D \quad A_t > 0, \quad A_t(\frac{d\xi_t}{dt}) > 0 \quad (4.2.11)$$

The two reactions (4.2.10) and (4.2.11) could be coupled so that their total entropy production $A_i(\frac{d\xi_i}{dt}) + A_t(\frac{d\xi_t}{dt}) > 0$ but $A_i(\frac{d\xi_i}{dt}) < 0$. An example of a mechanism that makes such reaction reversal possible is (Figure 4.3)

$$Z + T \iff Z^* + D \quad A_t > 0, \quad A_t(\frac{d\xi_t}{dt}) > 0 \quad (4.2.12)$$

$$Z^* + W \iff X + Y \quad A_t > 0, \quad A_t(\frac{d\xi_t}{dt}) > 0 \quad (4.2.13)$$

$$Z + W + T \iff X + Y + D \quad A > 0, \quad A(\frac{d\xi_i}{dt}) > 0 \quad (4.2.14)$$

Once again, as indicated, the affinities and velocities of reactions (4.2.11)-(4.2.13) are assumed positive. The net reaction $Z + W + T \iff X + Y + D$ is an effective

**Figure 4.3** Entropy production in coupled reactions. The left and right panels show different ways of representing the same net reaction $Z + W + T \rightarrow X + Y + D$ resulting from two reaction steps. The left panel shows a reaction scheme and the corresponding chemical potentials in which entropy production of both reaction steps are positive. The right panel shows a reinterpretation of the same net reaction when the intermediate $Z$ that couples the two reactions is in a steady state. In this case, the entropy production of one reaction is positive and the other is negative, but their sum, the total entropy production, remains positive.
When chemical potentials of a substance in adjacent parts of a system are unequal, diffusion of that substance takes place until the chemical potentials in the two parts equalize. The process is similar to flow of heat due to a difference in temperature. Diffusion is another irreversible process for which we can obtain the rate of increase in entropy in terms of chemical potentials.

DISCRETE SYSTEMS

For simplicity, let us consider a system consisting of two parts of equal temperature $T$, one with chemical potential $\mu_1$ and molar amount $N_1$ and the other with chemical potential $\mu_2$ and molar amount $N_2$ as shown in Figure 4.4. The flow of particles from one part to another can also be associated with an 'extent of reaction', though no real chemical reaction is taking place here:

$$-dN_1 = dN_2 = d\xi$$  \hfill (4.3.1)

Following Equation (4.1.14), the entropy change for this process can be written as

$$dS = \frac{dU + pdV}{T} + \frac{A}{T} d\xi$$  \hfill (4.3.2)

$$= \frac{dU + pdV}{T} + \frac{A}{T} d\xi$$  \hfill (4.3.3)

in which the corresponding affinity $A = \mu_1 - \mu_2$. If $dU = dV = 0$, then the transport of particles results in the change of entropy given by

$$dS = \frac{\mu_2 - \mu_1}{T} d\xi > 0$$  \hfill (4.3.4)