THE BASES
OF
CHEMICAL
THERMODYNAMICS

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Swiss Federal Institute of Technology
Lausanne, Switzerland

Volume 2

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THE BASES OF CHEMICAL THERMODYNAMICS
Volume 2

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Preface

Our aim, in writing this two volume textbook, is to provide a simple yet logical treatment of the bases of Chemical Thermodynamics. It is our experience that the level of understanding improves when appropriate justifications are generously provided. In the many years that this course has been taught, we have endeavored to find the most easily grasped explanations or justifications.

Volume 1 presents the fundamental aspects of thermodynamics. It is designed to be appropriate for a first contact with the topic of thermodynamics. We illustrate the first and second laws of thermodynamics, the need to define the thermodynamic temperature scale, and the nature of entropy. We show how spontaneous processes always correspond to an increase of the global entropy. We explore the meaning of auxiliary thermodynamics functions, the origin and usefulness of partial molar quantities. We look into the description of gaseous systems and phase equilibria in systems where chemical reactions do not take place.

Volume 2 contains the tools that are necessary to deal with systems where chemical reactions take place. The variables of reaction are a key to this understanding. Criteria for chemical equilibrium and spontaneity of reactions are established. We illustrate how chemical reactions can provide work as, for example, in batteries. We analyze the effect of external factors on chemical equilibria.

We finally present the more complex situation of solutions, going from ideal to real solutions. The statistical aspect of thermodynamics and its importance are stretched and examined in the last chapter with many illustrative problems.

Most of the specific mathematical tools are presented either directly in the text if they are used mostly in one chapter, while material needed in several chapters is included in an appendix.

We have purposely kept intermediate steps in the derivations to enhance the clarity of the presentation.

To keep the topic easily accessible to beginners, we selected a primarily phenomenological approach.

Teachers may wish to include some of the problems provided as part of their lectures to illustrate points that they consider particularly important.

Students will definitely appreciate the problem sections where full solutions to the problems are provided to enhance the pedagogical value of this book.

Finally, it is a pleasure to thank here our colleagues who have contributed to improve this work by their varied comments and suggestions, Dr. G. Rothenberger and Dr. D. B. Matthews. Professor A. Wohlhauser provided invaluable help in the treatment of independent reactions. In the course of time, students and assistants have contributed to improve this book by their comments, suggestions and constructive criticisms. Finally, we thank the many individuals who read the final version of the manuscript helping to remove so many unaesthetic details.

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9 Energetics of Chemical Reactions

9.1 Introduction

We now focus our attention on a *closed system* in which a chemical reaction can take place. The reaction is written as :

$$|\nu_A|\, A + |\nu_B|\, B \longrightarrow |\nu_C|\, C + |\nu_D|\, D \tag{9.1}$$

Conventionally, species on the left hand side of equation 9.1 are designated as the reactants, while species on the right hand side are known as products, indicating our potential interest in the reaction when it takes place from left to right. The $|\nu|$ are the stoichiometric coefficients of the reaction. They are *positive integers* or *simple fractional numbers*. The stoichiometric coefficients originate in the conservation of atoms in the reactants (A, B) and products (C, D). We will frequently use this reaction as our typical reaction. We also use another formal representation of chemical reactions which lends itself better to mathematical use. We write reaction 9.1 as :

$$\nu_C\, C + \nu_D\, D + \nu_A\, A + \nu_B\, B = 0 \tag{9.2}$$

In equation 9.2, the stoichiometric coefficients are algebraic. The coefficients of the products C and D are conventionally taken as positive, while those of the reactants A and B, are negative. This convention has the same implication as equation 9.1, since it indicates that, when

ν_C moles of C and ν_D moles of D are formed, $|\nu_A|$ moles of A have reacted with $|\nu_B|$ moles of B. A general reaction can be written :

$$\sum_{\mathrm{i}} \nu_{\mathrm{i}} M_{\mathrm{i}} = 0 \qquad \mathrm{i} = 1, 2, \ldots, n \tag{9.3}$$

where the M_{i} refer to chemical species *i,* and *n* is the number of species present in the system. If a species present in the system does not take part in the reaction, its stoichiometric coefficient is simply zero. When several reactions may take place simultaneously, they will be represented by :

$$\sum_{\mathrm{i}} \nu_{\mathrm{i,k}} M_{\mathrm{i}} = 0 \qquad \begin{cases} \mathrm{i} = 1, 2, \ldots, n \\ \mathrm{k} = 1, 2, \ldots, r \end{cases} \tag{9.4}$$

Each of the *r* reactions written in this way implies that atoms are conserved during a chemical reaction.

9.2 The Extent of Reaction

We now consider a *closed system* where only one reaction can take place. We write the equations for both the typical reaction 9.1 and the general formalism (equation 9.3). Let n_{i}^{0} be the number of moles of species *i* in the initial state of the system. When the reaction occurs, the variations of the number of moles of each species, n_{i}, are not independent, as indicated by the stoichiometric coefficients. This fact can be written :

$$\left.\begin{array}{l} \dfrac{\mathrm{d}n_1}{\nu_1} = \ldots = \dfrac{\mathrm{d}n_{\mathrm{i}}}{\nu_{\mathrm{i}}} = \ldots = \mathrm{d}\xi \\[2ex] \dfrac{\mathrm{d}n_A}{\nu_A} = \dfrac{\mathrm{d}n_B}{\nu_B} = \dfrac{\mathrm{d}n_C}{\nu_C} = \dfrac{\mathrm{d}n_D}{\nu_D} = \mathrm{d}\xi \quad \text{for the typical reaction 9.1} \end{array}\right\} \tag{9.5}$$

where the variable ξ (units of mol) relates the changes in the amount of the chemical species present. By integrating the system of differential equations 9.5 and taking $\xi = 0$ as the initial state of the system, we get :

$$\left.\begin{array}{ll} n_1 = n_1^0 + \nu_1\,\xi, \ldots, & n_{\mathrm{i}} = n_{\mathrm{i}}^0 + \nu_{\mathrm{i}}\,\xi, \ldots \\[1ex] n_A = n_A^0 + \nu_A\,\xi & n_B = n_B^0 + \nu_B\,\xi \\ n_C = n_C^0 + \nu_C\,\xi & n_D = n_D^0 + \nu_D\,\xi \end{array}\right\} \tag{9.6}$$

where we should recall that ν_A and ν_B are negative numbers. Since all the numbers of moles are always positive (or zero), the range of valid ξ values is limited. When the variable ξ spans the entire range of valid values, we cover all of the possible states of the system linked to the chemical reaction, ξ is called the ***extent of the reaction***. This variable is an extensive variable like the number of moles. If the n_i^0 for the reactants are sufficiently large such that $\xi = 1$ mol is an allowed value, then this value of ξ corresponds to the conversion of a number of moles equal to the stoichiometric coefficients.

> *An increase of ξ by 1 mol corresponds to the conversion of numbers of moles of reactants to numbers of moles of products corresponding to the stoichiometric coefficients of the reaction.*

9.3 Variables of Reaction

9.3.1 Gibbs Energy of Reaction (Free Enthalpy of Reaction)

We consider a *closed system*, in which only a single chemical reaction can take place. Let us write the expression of the differential of its Gibbs energy for *an isothermal and isobaric process*. Using 5.26 and 9.5, we have :

$$\left.\begin{aligned} \mathrm{d}G &= \sum_i \mu_i \,\mathrm{d}n_i \\ &= \sum_i \mu_i \nu_i \,\mathrm{d}\xi = \Delta_r G \,\mathrm{d}\xi \\ \text{with} \qquad \Delta_r G &= \sum_i \nu_i \mu_i \end{aligned}\right\} \tag{9.7}$$

The quantity $\Delta_r G$ is referred to as the ***Gibbs energy of reaction*** or the ***free enthalpy of reaction***. It is an *intensive variable*. Like chemical potentials, it *depends on the composition of the system*. It corresponds to what the change of the Gibbs energy of the system would be, if, *at constant composition*, the extent of reaction ξ increased by 1 mol. A number of moles of reactants equal to the stoichiometric coefficients is then transformed into the number of moles equal to the stoichiometric coefficients of products of the reaction.

For a general process, where p, T as well as the extent of reaction can vary, the differential of the Gibbs energy is :

$$\left.\begin{aligned} \mathrm{d}G &= V\,\mathrm{d}p - S\,\mathrm{d}T + \left(\frac{\partial G}{\partial \xi}\right)_{p,\,T} \mathrm{d}\xi \\ \left(\frac{\partial G}{\partial \xi}\right)_{p,\,T} &= \sum_{\mathrm{i}} \nu_{\mathrm{i}}\,\mu_{\mathrm{i}} = \Delta_{\mathrm{r}} G \end{aligned}\right\} \tag{9.8}$$

The extensive variable ξ is associated to the intensive variable $\Delta_r G$. For a closed system, the changes in the numbers of moles of the various species present are all linked to the change in the reaction extent ξ.

9.3.2 Spontaneous Reaction. Equilibrium

We consider again a *closed system* in which a single chemical reaction can take place. Moreover, we assume that the system can only exchange work due to volume change with its surroundings. An infinitesimal *isothermal and isobaric* change can take place spontaneously if the corresponding change in the Gibbs energy is such that $\mathrm{d}G < 0$ (relation 5.82). Equation 9.7 shows that :

- *If $\Delta_r G > 0$, then the reaction takes place spontaneously from right to left since $dG < 0$ implies that $d\xi < 0$.*
- *If $\Delta_r G < 0$, then the reaction takes place spontaneously from left to right since $dG < 0$ implies that $d\xi > 0$.*
- *If $\Delta_r G = 0$, then the system is at equilibrium.*

The equilibrium condition is that the enthalpy of reaction be zero and it can also be written :

$$\Delta_{\mathrm{r}} G = \sum_{\mathrm{i}} \nu_{\mathrm{i}}\,\mu_{\mathrm{i}} = 0 \iff \begin{cases} \text{Chemical equilibrium is reached} \\ G \text{ has reached a minimum} \end{cases} \tag{9.9}$$

9.3.3 Systems where Several Reactions can Take Place Simultaneously

In the case of a system with n chemical species where *r independent reactions*[†] can occur, we can write, for each reaction, an equation corresponding to equation 9.5.

[†] We will see in detail in chapter 10 what independent reactions are, and how to determine their number for a given chemical system.

$$\left.\begin{aligned} &\frac{\mathrm{d}n_{1,\,\mathrm{k}}}{\nu_{1,\,\mathrm{k}}} = \ldots = \frac{\mathrm{d}n_{\mathrm{i},\,\mathrm{k}}}{\nu_{\mathrm{i},\,\mathrm{k}}} = \ldots = \mathrm{d}\xi_{\mathrm{k}} \\ &\qquad \Downarrow \\ &\mathrm{d}n_{\mathrm{i}} = \sum_{\mathrm{k}} \mathrm{d}n_{\mathrm{i},\,\mathrm{k}} = \sum_{\mathrm{k}} \nu_{\mathrm{i},\,\mathrm{k}}\, \mathrm{d}\xi_{\mathrm{k}} \end{aligned}\right\} \qquad \left\{\begin{aligned} &\mathrm{i} = 1, 2, \ldots, n \\ &\mathrm{k} = 1, 2, \ldots, r \end{aligned}\right. \tag{9.10}$$

where ξ_{k} is the extent of the k^{th} reaction. The differential of the Gibbs energy can be expressed in terms of the extents of reaction of the r independent reactions and of their Gibbs energy of reaction. Using 5.26, we obtain :

$$\left.\begin{aligned} \mathrm{d}G &= V\,\mathrm{d}p - S\,\mathrm{d}T + \sum_{\mathrm{i}} \mu_{\mathrm{i}} \sum_{\mathrm{k}} \nu_{\mathrm{i},\,\mathrm{k}}\, \mathrm{d}\xi_{\mathrm{k}} \\ &= V\,\mathrm{d}p - S\,\mathrm{d}T + \sum_{\mathrm{k}} \Delta_{\mathrm{r}} G_{\mathrm{k}}\, \mathrm{d}\xi_{\mathrm{k}} \\ \text{where} \quad \Delta_{\mathrm{r}} G_{\mathrm{k}} &= \left(\frac{\partial G}{\partial \xi_{\mathrm{k}}}\right)_{p,\,T,\,\xi_{\mathrm{l} \neq \mathrm{k}}} = \sum_{\mathrm{i}} \nu_{\mathrm{i},\,\mathrm{k}}\, \mu_{\mathrm{i}} \end{aligned}\right\} \tag{9.11}$$

where $\Delta_{\mathrm{r}} G_{\mathrm{k}}$ is the Gibbs energy of reaction k. A spontaneous change can take place until G has reached its minimum value. The equilibrium of the system is obtained when $\mathrm{d}G = 0$. Since the process is isothermal, isobaric and the ξ_{K} are independent, this is achieved when :

$$\Delta_{\mathrm{r}} G_{\mathrm{k}} = \sum_{\mathrm{k}} \nu_{\mathrm{i},\,\mathrm{k}}\, \mu_{\mathrm{i}} = 0 \qquad \text{for} \qquad (\mathrm{k} = 1, 2, \ldots, r) \tag{9.12}$$

> *At equilibrium, a system where r independent reactions can take place implies the existence of r independent relations between the chemical potentials of the species it contains.*

The simultaneous evolution of the reactions affects the chemical potentials of the species. The *essential difference* here with the case of a single reaction is that the change in Gibbs energy of the system due to one particular reaction can be positive while the system evolution still corresponds to a decrease of its Gibbs energy. Some reactions, that would not take place if carried out alone, can occur if other reactions can take place simultaneously to make the whole process spontaneous. The reactions are said to be coupled.

9.3.4 Other Variables of Reaction

While the Gibbs energy of reaction plays a special role in chemistry since isothermal and isobaric conditions are frequently encountered, other variables of reaction must be considered and are useful to obtain many properties of the Gibbs energy of reaction. Let us consider any extensive variable, X, such as U, H, S, A, V, C_p, or C_V, as functions of p, T and the n_i, the numbers of moles of each species of the system. In a system where a single reaction can take place, under *isothermal and isobaric condition*, the expression for the differential of the variable is (equation 6.25) :

$$\left.\begin{aligned} \mathrm{d}X &= \left(\frac{\partial X}{\partial p}\right)_{T,\,n_\mathrm{i}} \mathrm{d}p + \left(\frac{\partial X}{\partial T}\right)_{p,\,n_\mathrm{i}} \mathrm{d}T + \sum_\mathrm{i} \overline{X_\mathrm{i}}\ \mathrm{d}n_\mathrm{i} \\ &= \sum_\mathrm{i} \overline{X_\mathrm{i}}\ \nu_\mathrm{i}\, \mathrm{d}\xi = \Delta_\mathrm{r} X\, \mathrm{d}\xi \\ \text{with } \Delta_\mathrm{r} X &= \sum_\mathrm{i} \nu_\mathrm{i}\ \overline{X_\mathrm{i}} = \left(\frac{\partial X}{\partial \xi}\right)_{p,\,T} \end{aligned}\right\} \quad (9.13)$$

where $\Delta_\mathrm{r}X$ is the variable of reaction corresponding to X. The variables of reaction have therefore simple expressions in terms of the partial molar quantities. We have :

$$\left.\begin{aligned} \Delta_\mathrm{r}U &= \sum_\mathrm{i} \nu_\mathrm{i}\, \overline{U}_\mathrm{i} \quad & \Delta_\mathrm{r}S &= \sum_\mathrm{i} \nu_\mathrm{i}\, \overline{S}_\mathrm{i} \quad & \Delta_\mathrm{r}V &= \sum_\mathrm{i} \nu_\mathrm{i}\, \overline{V}_\mathrm{i} \\ \Delta_\mathrm{r}H &= \sum_\mathrm{i} \nu_\mathrm{i}\, \overline{H}_\mathrm{i} \quad & \Delta_\mathrm{r}A &= \sum_\mathrm{i} \nu_\mathrm{i}\, \overline{A}_\mathrm{i} \quad & \Delta_\mathrm{r}C_p &= \sum_\mathrm{i} \nu_\mathrm{i}\, \overline{C}_{p\,\mathrm{i}} \end{aligned}\right\} \quad (9.14)$$

9.3.5 Standard Variables of Reaction

The chemical potentials or the partial molar quantities that are part of the expressions for variables of reaction depend on the composition of the system. Thermodynamic tables contain numerical values of molar quantities for numerous systems for a state of the system known as the *standard state*. From the values found in the tables, it is subsequently possible to evaluate the variables of interest to various degrees of approximation. The standard state can be selected in various ways as we already saw in chapter 7. In the tables, the standard states as well as the units used can vary. In general, the tables contain, as well as the physical state of the species, solid (with the crystalline form for solids if several exist), liquid or gas, the pertinent information needed to fully characterize the standard state that has been selected for the tabulation.

- The standard state pressure $p^\ominus$ selected has always a value 1. It can be 1 atm (old convention) or 1 bar (most recent convention).

- The selected temperature is often 298.15 K, which corresponds to 25°C.

- The standard state for a species that is gaseous under standard conditions, corresponds to the pure substance behaving as an ideal gas under the standard pressure (Equation 7.60).

- The standard state for a solvent or a pure solid or a liquid, corresponds to the pure substance under the standard pressure $p^\ominus$.

- For solutes, several different standard states can be used. The various possible choices as well as the reasons that motivate their selection will be presented in chapter 12.

To evaluate a standard variable of reaction, we consider a system which in its initial state contains the number of moles of reactants corresponding to their stoichiometric coefficients, taken (pure) in their standard state (for gases, the standard state is a hypothetical state where the gas behaves as an ideal gas). The final state corresponds to the number of moles of products present in the stoichiometric equation again in their standard state. In the stoichiometric equation, the physical state of the species, reactants or products, are mentioned. This is illustrated in Table 9.1 for the reaction 9.1 when all the species participating in the reaction are gaseous.

The variables of reaction thus evaluated are referred to as : $\Delta_r G_T^\ominus$, $\Delta_r H_T^\ominus$, $\Delta_r S_T^\ominus$, etc…

Initial state		Final state
$p = 1$ atm or 1 bar, T $\lvert \nu_A \rvert$ moles of pure A ideal gas behavior	Chemical process $\longrightarrow$	$p = 1$ atm or 1 bar, T $\lvert \nu_C \rvert$ moles of pure C ideal gas behavior
$p = 1$ atm or 1 bar, T $\lvert \nu_B \rvert$ moles of pure B ideal gas behavior		$p = 1$ atm or 1 bar, T $\lvert \nu_D \rvert$ moles of pure D ideal gas behavior

Table 9.1 Chemical process from an initial standard state of the reactants to a final standard state of the products, for reaction 9.1. The gases behave as ideal gases.

The ***standard variables of reaction*** can be expressed using the result of equation 9.14. Since all of the species are in their standard state, the partial molar quantities are simply the standard molar quantities. We obtain :

$$\left.\begin{array}{ll} \Delta_r U^\ominus = \sum_i \nu_i U_i^\ominus & \Delta_r A^\ominus = \sum_i \nu_i A_i^\ominus \\ \Delta_r H^\ominus = \sum_i \nu_i H_i^\ominus & \Delta_r G^\ominus = \sum_i \nu_i \mu_i^\ominus \\ \Delta_r S^\ominus = \sum_i \nu_i S_i^\ominus & \Delta_r C_p^\ominus = \sum_i \nu_i C_{p\,i}^\ominus \\ \multicolumn{2}{c}{\Delta_r V^\ominus = \sum_i \nu_i V_i^\ominus} \end{array}\right\} \qquad (9.15)$$

We should note here that standard molar entropy, standard molar heat capacity and standard molar volume are the only standard extensive variables that are known in an absolute way. The other standard molar quantities in equation 9.15 are not known absolutely and their values depend on the selection of a reference for the energy scale.

9.3.6 Standard Variables of Formation

In order to be able to prepare consistent tables of thermodynamic data, it is convenient to introduce the ***standard variables of formation*** of chemical species which are just a special case of the standard variables of reaction. These are usually found in chemical thermodynamic data tables.

The standard variable of formation of a species corresponds to the change in the corresponding extensive variable when ***one mole* of substance is formed** in its *standard state* from the appropriate number of moles of the most stable state of each element it contains taken in its standard state.

- The initial state corresponds to the elements present in the substance, taken in their standard state at the same temperature in the physical state of interest mentioned in the reaction (usually their most stable state at the chosen temperature and standard pressure), the number of moles being equal to the stoichiometric coefficients.

- The final state is *one mole of the species* of interest in its standard state, at the temperature of interest and in the appropriate physical state as mentioned in the reaction.
- The standard variables of formation of an element in its most stable state at temperature T and standard state pressure $p^\ominus$ are zero, by definition. The reaction of formation of the elements from themselves corresponds to no change.

The standard variables of formation of a species at a temperature T are represented by : $\Delta_\mathrm{f}G^\ominus_T$, $\Delta_\mathrm{f}H^\ominus_T$, $\Delta_\mathrm{f}S^\ominus_T$, $\Delta_\mathrm{f}U^\ominus_T$, $\Delta_\mathrm{f}C_p{}^\ominus{}_T$, $\Delta_\mathrm{f}A^\ominus_T$, …

Using equation 9.15, the standard variables of formation can be related to standard molar quantities. Let us consider, as an example, the formation of ammonia at 25°C.

$$\frac{1}{2}\mathrm{N_2\,(g)} + \frac{3}{2}\mathrm{H_2\,(g)} \longrightarrow \mathrm{NH_3\,(g)} \tag{9.16}$$

Under 1 bar at 298.15 K, the elements that constitute ammonia, nitrogen and hydrogen, are stable as molecules. The standard enthalpy of formation of ammonia that is found in the tables, corresponds to (equation 9.15) :

$$\Delta_\mathrm{f}H^\ominus_{298.15}\,(\mathrm{NH_3}) = H^\ominus_{298.15}\,(\mathrm{NH_3}) - \frac{1}{2}H^\ominus_{298.15}\,(\mathrm{N_2}) - \frac{3}{2}H^\ominus_{298.15}\,(\mathrm{H_2}) \tag{9.17}$$

In thermodynamic tables, data can be found on a number of chemicals. The data found most frequently are :

$\Delta_\mathrm{f}G^\ominus_{298.15}$	Standard Gibbs energy of formation
$\Delta_\mathrm{f}H^\ominus_{298.15}$	Standard enthalpy of formation
$S^\ominus_{298.15}$	Standard entropy
$C^\ominus_{p\ 298.15}$	Standard molar heat capacity at constant pressure

Only the first two are *standard variables of formation*. They always refer to one mole of the species that is been formed. The other two are *standard molar quantities*. The last three can be used to obtain the first one and to calculate other standard formation or reaction variables (for example at different temperatures). The standard Gibbs energies of formation allow the calculations of standard Gibbs energy of a reaction, $\Delta_\mathrm{r}G^\ominus_{298.15}$, which leads to the knowledge of the equilibrium constant of a reaction (as we will see in chapter 10).

9.4 Hess's Law

9.4.1 Content

Hess's Law is a direct consequence of the fact that the change of a state function during a thermodynamic change is independent of the path selected to effect the change. It applies to reaction enthalpies and can be stated in the following way :

> *The enthalpy of a reaction is equal to the sum of the enthalpies of other reactions into which it can be formally decomposed.*

Since variables of reactions are evaluated from the change of some extensive variable between two well defined states, this law can be generalized to any variable of reaction.

9.4.2 Application

This law can be used to obtain the standard enthalpy of a reaction from standard enthalpies of formation. Let us consider as an example, the oxidation of ammonia by oxygen :

$$2\ NH_3\ (g) + \frac{5}{2} O_2\ (g) \longrightarrow 2\ NO\ (g) + 3\ H_2O\ (g) \qquad (9.18)$$

The standard enthalpy of reaction can be computed from the initial and final states of a system as presented in Table 9.2.

Initial state		Final state
p = 1 atm or 1 bar, T 2 moles of pure NH_3 ideal gas	reaction $\longrightarrow$	p = 1 atm or 1 bar, T 2 moles of pure NO ideal gas
p = 1 atm or 1 bar, T $\frac{5}{2}$ moles of pure O_2 ideal gas		p = 1 atm or 1 bar, T 3 moles of pure H_2O ideal gas

Table 9.2 Initial and final standard state of the oxidation of gaseous ammonia according to reaction 9.18. The gases behave as ideal gases.

Using Hess's law, we can consider an intermediate state of the system made of the elements of the reactants. We write :

$$2\,NH_3\,(g) + \frac{5}{2}O_2\,(g) \longrightarrow N_2\,(g) + 3\,H_2\,(g) + \frac{5}{2}O_2\,(g) \tag{9.19}$$

$$N_2\,(g) + 3\,H_2\,(g) + \frac{5}{2}O_2\,(g) \longrightarrow 2\,NO\,(g) + 3\,H_2O\,(g) \tag{9.20}$$

Let us write the standard enthalpies of reactions for the reactions 9.19 and 9.20 in terms of the standard variables of formation. Taking into account the fact that the standard enthalpy of formation of the elements are conventionally taken as zero, we have :

$$\left.\begin{aligned} \Delta_r H_T^\ominus(9.19) &= -2\,\Delta_f H_T^\ominus(NH_3\,(g)) \\ \Delta_r H_T^\ominus(9.20) &= 2\,\Delta_f H_T^\ominus(NO\,(g)) + 3\,\Delta_f H_T^\ominus(H_2O\,(g)) \end{aligned}\right\} \tag{9.21}$$

Enthalpies of formation of N_2, H_2 and O_2 are not in equation 9.21 since they are zero. For reaction 9.18, we obtain :

$$\left.\begin{aligned} \Delta_r H_T^\ominus(9.18) &= \Delta_r H_T^\ominus(9.19) + \Delta_r H_T^\ominus(9.20) \\ &= 2\,\Delta_f H_T^\ominus(NO\,(g)) + 3\,\Delta_f H_T^\ominus(H_2O\,(g)) \\ &\quad -2\,\Delta_f H_T^\ominus(NH_3\,(g)) \end{aligned}\right\} \tag{9.22}$$

Using directly equations 9.15 for reaction 9.18, we would have found :

$$\begin{aligned} \Delta_r H_T^\ominus(9.18) &= 2\,H_T^\ominus(NO\,(g)) + 3\,H_T^\ominus(H_2O\,(g)) \\ &\quad -2\,H_T^\ominus(NH_3\,(g)) - \frac{5}{2}H_T^\ominus(O_2\,(g)) \end{aligned} \tag{9.23}$$

which corresponds to what we would obtain using equation 9.15 in equation 9.22.

9.4.3 Generalization

The result obtained for $\Delta_r H^\ominus_T$ can be generalized to any standard variable of reaction. We have :

$$\Delta_r X^\ominus_T = \sum_i \nu_i \, X^\ominus_{i,T} = \sum_i \nu_i \, \Delta_f X^\ominus_{i,T} \tag{9.24}$$

and a standard variable of reaction may be obtained from the standard variables of formation. In view of Hess's law and equations 9.15, we can write the following relations for some of the standard variables of reaction :

$$\left.\begin{aligned} \Delta_r G^\ominus_T &= \sum_i \nu_i \, \mu^\ominus_{i,T} = \sum_i \nu_i \, \Delta_f G^\ominus_{i,T} \\ \Delta_r H^\ominus_T &= \sum_i \nu_i \, H^\ominus_{i,T} = \sum_i \nu_i \, \Delta_f H^\ominus_{i,T} \\ \Delta_r U^\ominus_T &= \sum_i \nu_i \, U^\ominus_{i,T} = \sum_i \nu_i \, \Delta_f U^\ominus_{i,T} \\ \Delta_r S^\ominus_T &= \sum_i \nu_i \, S^\ominus_{i,T} = \sum_i \nu_i \, \Delta_f S^\ominus_{i,T} \end{aligned}\right\} \tag{9.25}$$

For a reaction taking place at temperature T, we can write, using 5.1, 5.2 and 5.3 :

$$\left.\begin{aligned} \Delta_r A &= \Delta_r U - T\,\Delta_r S \\ \Delta_r G &= \Delta_r H - T\,\Delta_r S \end{aligned}\right\} \tag{9.26}$$

While these relations are of course valid for the variables of reactions in general, they can be applied to standard variables of reaction to relate the various values found in the tables of thermodynamic data.

9.4.4 Example

To illustrate our findings, let us calculate the standard enthalpy and the standard Gibbs energy (standard free enthalpy) of reaction for the complete oxidation of ethanol by oxygen at 298.15 K. The reaction is :

$$C_2H_5OH\,(l) + 3\,O_2\,(g) \longrightarrow 2\,CO_2\,(g) + 3\,H_2O\,(l) \tag{9.27}$$

Substance	$\Delta_f H^\ominus_{298.15}$		$S^\ominus_{298.15}$		$C^\ominus_{p298.15}$	
Units	$\mathrm{kJ\,mol^{-1}}$	$\mathrm{kcal\,mol^{-1}}$	$\mathrm{J\,mol^{-1}K^{-1}}$	$\mathrm{cal\,mol^{-1}K^{-1}}$	$\mathrm{J\,mol^{-1}K^{-1}}$	$\mathrm{cal\,mol^{-1}K^{-1}}$
Standard pressure	1 bar	1 atm	1 bar	1 atm	1 bar	1 atm
C_2H_5OH (l)	– 277.69	– 66.37	160.67	38.4	111.46	26.64
O_2 (g)			205.146	49.00	29.36	7.017
CO_2 (g)	– 393.51	– 94.051	213.75	51.06	37.11	8.87
H_2O (l)	– 285.83	– 68.315	69.91	16.71	75.291	17.995

1 cal = 4.184 J

Table 9.3 Thermodynamic data for the oxidation of ethanol by oxygen.

In table 9.3, we have gathered the thermodynamic data concerning the species of this system. We have included two different standard pressures and different energy units. Selecting the standard pressure as 1 bar, let us write the expressions for the standard enthalpy of reaction for reaction 9.27 :

$$\left.\begin{aligned}
\Delta_r H^\ominus_{298.15} &= \sum_i \nu_i\, \Delta_f H^\ominus_{i\,298.15} \\
&= 2\, \Delta_f H^\ominus_{298.15}\,(CO_2\,(g)) + 3\, \Delta_f H^\ominus_{298.15}\,(H_2O\,(l)) \\
&\quad - \Delta_f H^\ominus_{298.15}\,(C_2H_5OH\,(l)) \\
&= 2\,(-\,393.51) + 3\,(-\,285.830) - (-\,277.69) \\
&= -\,1366.82\ \mathrm{kJ\,mol^{-1}}
\end{aligned}\right\}\quad (9.28)$$

The standard enthalpy of reaction obtained is negative. During this process, the system delivers heat to the surroundings. In such a case, the reaction is said to be ***exothermic***. If the standard enthalpy of a reaction is positive, then the reaction is said to be ***endothermic***.

In a similar way, we can calculate the standard reaction entropy, using 9.14 or 9.15.

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