Chapter 4
Thermochemistry

Abstract Thermochemistry deals with the heat transferred or released by a system during a change of its state or a chemical reaction. Calorimetry is an experimental method for measuring such heat transfers. The reaction enthalpy, the reaction entropy, and the Gibbs free energy of reaction are defined and related to the molar standard enthalpies of formation and molar standard entropies of reactants and products. The selection of problems in this chapter deals with key aspects of thermochemistry, such as the determination of molar heat of formation. Problem 4.3 exemplifies the use of the Gibbs free energy of reaction as a criterion for the occurrence of chemical processes.

4.1 Basic Concepts

It is assumed that the reader is familiar with stoichiometry and thermodynamics, especially the use of caloric state variables, which were introduced in Chap. 3.

4.1.1 Enthalpies of Formation

To predict the enthalpy change of a system in the course of a chemical reaction, textbooks introduce the molar enthalpy of formation h_f of a substance in a suitable standard state.[1]

> The molar standard enthalpy of formation $\Delta h_f^{\ominus}$ of a substance is the reaction enthalpy by which it is formed from its elements under standard state conditions.

Note that this definition implies that the standard enthalpy of the formation of elements in their standard state is zero. In the same way, the standard molar Gibbs free energy of formation of substances are defined and tabulated at a reference

[1] For the definition of the standard state see Sect. 3.4.1.

J. Vogt, *Exam Survival Guide: Physical Chemistry*,
DOI 10.1007/978-3-319-49810-2_4

temperature of 298.15 K. Tabulated standard molar entropies, however, are absolute values.[2]

4.1.2 The Molar Reaction Enthalpy and the Molar Reaction Entropy

Consider a chemical system before and after a reaction $\sum_J \nu_J X_J = 0$. The enthalpy change in the system H_r is the difference in its enthalpy before and after the reaction took place. Using the familiar concept of the extent of reaction ξ introduced in Chap. 2, the enthalpy change $H_r(\xi)$ is

$$H_r(\xi) = \sum_J \left(n_J^0 + \nu_J \xi\right)\, \Delta h_f(J) - \sum_J n_J^0\, \Delta h_f(J) = \sum_J \nu_J \xi\, \Delta h_f(J) \tag{4.1}$$

The **molar reaction enthalpy** is the change of H_r with ξ:

$$\Delta h_r = \frac{\partial}{\partial \xi} H_r(\xi) = \sum_J \nu_J\, \Delta h_f(J) \tag{4.2}$$

Note that unlike H_r, the molar reaction enthalpy Δh_r is an intensive property (see Sect. 3.1). Tabulated heats of formation refer to the standard state at the reference temperature 298.15 K. The standard molar reaction enthalpy is thus

$$\Delta h_r^\ominus = \sum_J \nu_J\, \Delta h_f^\ominus(J) \tag{4.3}$$

A process or chemical reaction characterized by $\Delta h_r > 0$ is called **endothermic**. In contrast, a process or reaction characterized by $\Delta h_r < 0$ is called **exothermic**. Similarly, the **molar standard reaction entropy** of this reaction is calculated from the molar standard entropies of the reactants:

$$\Delta s_r^\ominus = \sum_J \nu_J\, \Delta s^\ominus(J) \tag{4.4}$$

The **molar standard Gibbs free energy of reaction** is calculated from the standard free enthalpies of formation of the reactants or the values of $\Delta h_r^\ominus$ and $\Delta s_r^\ominus$ at the reference temperature T_r:

[2] For the calculation of the absolute entropy of monatomic gases based on statistical thermodynamics, see Problem 8.6.

$$\Delta g_r^{\ominus}(T) = \sum_J \nu_J \, \Delta g_f^{\ominus}(J) = \Delta h_r^{\ominus} - T\Delta s_r^{\ominus} \tag{4.5}$$

A process or chemical reaction characterized by $\Delta g_r > 0$ is called **endergonic**. In contrast, a process or reaction characterized by $\Delta g_r < 0$ is called **exergonic**.

4.1.3 Kirchhoff's Law

In practice, chemical reactions take place under different conditions concerning pressure and temperature. Based on Eq. (3.32) **Kirchhoff's law** can be derived, which allows the calculation of a reaction enthalpy at arbitrary temperature T from the respective value at a reference temperature T_r:

$$\Delta h_r(T) = \Delta h_r(T_r) + \int_{T_r}^{T} \sum_J \nu_J \, c_{p,J}(T') \, dT'. \tag{4.6}$$

Similarly, using the relation $dS = \frac{c_p \, dT}{T}$, the reaction entropy at T is

$$\Delta s_r(T) = \Delta s_r(T_r) + \int_{T_r}^{T} \sum_J \nu_J \, \frac{c_{p,J}(T')}{T'} \, dT'. \tag{4.7}$$

Note that these equations assume that no phase transition occurs in the temperature range under consideration between the reference temperatures T_r and T. In Problem 3.14 we dealt with the entropy change in a case in which a phase transition occurs.

4.1.4 Hess's Law

As enthalpy is a state function, the change in enthalpy between an initial state and a final state does not depend on the reaction pathway. This is the origin of **Hess's law**:

> The total reaction enthalpy of a given chemical reaction does not depend on the route taken. If a chemical reaction can be separated into several reaction steps, the total reaction enthalpy is the *sum* of the reaction enthalpies of the reaction steps.

Hess's law is useful to indirectly determine reaction enthalpies of reactions that are otherwise not accessible by an experiment.

4.2 Problems

Additional problems related to thermochemistry can be found in Chap. 5 (chemical equilibrium).

Problem 4.1 (Combustion Enthalpies) Isopropanol is produced by the hydration of propene,

$$\mathrm{CH_2CHCH_3(g) + H_2O(g) \rightarrow CH_3CHOHCH_3(g)} \qquad |\Delta h_x^{\ominus}. \qquad (4.8)$$

The following data are given: at 298.15 K, the molar standard heats of combustion of propene and isopropanol are 2,040 and 2,006 kJ mol^{-1} respectively. The constant pressure molar heat capacities of propene, isopropanol, and water are 64, 86, and 34 J K^{-1} mol^{-1} respectively.

a. Calculate the molar standard heat of reaction Eq. (4.8) at the reference temperature 298.15 K.
b. Calculate $\Delta h_x^{\ominus}$ at 550 K.

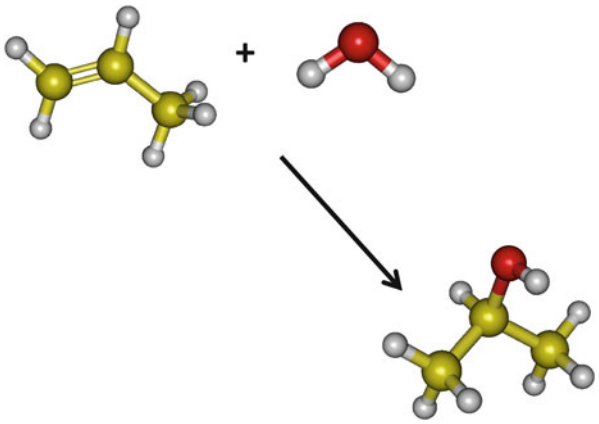

Fig. 4.1 Hydration of propene to isopropanol (2-propanol)

Solution 4.1 Combustion calorimetry offers the possibility of determining reaction enthalpies indirectly using Hess's law. In **subproblem (a)** we determine the molar standard reaction enthalpy $\Delta h_x^\ominus$ for the hydration of propene (Eq. (4.8), Fig. 4.1) from the given molar heats of combustion of the hydrocarbons propene and isopropanol. Technically, this reaction is conducted in a reactor containing a suitable catalyst. A direct determination of $\Delta h_x^\ominus$ is hampered by the fact that parallel reactions occur, e.g., the reaction to 1-propanol. Using Eq. (4.3) we write down an expression for $\Delta h_x^\ominus$,

$$\Delta h_x^\ominus = \Delta h_f^\ominus(\mathrm{C_3H_8O}) - \Delta h_f^\ominus(\mathrm{C_3H_6}) - \Delta h_f^\ominus(\mathrm{H_2O}) \tag{4.9}$$

Next, we express the unknown molar enthalpies of formation occurring on the right side using the given heats of combustion. Combustion means the complete reaction of a substance with oxygen (see Problem 2.2 in Chap. 2). If the reactant is a hydrocarbon, the combustion products are CO_2 and H_2O. To exploit the heats of combustion provided for propene and isopropanol (2-propanol), we must formulate the equation for their combustion. In the case of propene, we have

$$\mathrm{C_3H_6} + \frac{9}{2}\mathrm{O_2} \rightarrow 3\mathrm{CO_2} + 3\mathrm{H_2O} \quad |\Delta h_c^\ominus(P) = -2040\,\mathrm{kJ\,mol^{-1}}. \tag{4.10}$$

For isopropanol, we have

$$\mathrm{C_3H_8O} + \frac{9}{2}\mathrm{O_2} \rightarrow 3\mathrm{CO_2} + 4\mathrm{H_2O} \quad |\Delta h_c^\ominus(I) = -2006\,\mathrm{kJ\,mol^{-1}}. \tag{4.11}$$

Be aware that combustion reactions are exothermic ($\Delta h_c^\ominus$ negative), and the heat *released* to the surroundings is thus positive. Using Eq. (4.3), we can set up two equations that relate the molar combustion enthalpies of these substances to their formation enthalpies. Note that gaseous O_2 is an element in its standard state. Its enthalpy of formation is thus zero.

$$\Delta h_c^\ominus(P) = 3\Delta h_f^\ominus(\mathrm{H_2O}) + 3\Delta h_f^\ominus(\mathrm{CO_2}) - \Delta h_f^\ominus(\mathrm{C_3H_6}) \tag{4.12}$$

$$\Delta h_c^\ominus(I) = 4\Delta h_f^\ominus(\mathrm{H_2O}) + 3\Delta h_f^\ominus(\mathrm{CO_2}) - \Delta h_f^\ominus(\mathrm{C_3H_8O}) \tag{4.13}$$

If we now subtract Eq. (4.13) from Eq. (4.12), we obtain

$$\Delta h_c^\ominus(P) - \Delta h_c^\ominus(I) = \Delta h_f^\ominus(\mathrm{C_3H_8O}) - \Delta h_f^\ominus(\mathrm{C_3H_6}) - \Delta h_f^\ominus(\mathrm{H_2O}) \tag{4.14}$$

By comparing this expression with Eq. (4.9), we see that the reaction enthalpy sought is simply the difference in the combustion enthalpies:

$$\Delta h_x^\ominus = \Delta h_c^\ominus(P) - \Delta h_c^\ominus(I) = (-2040 + 2006)\,\mathrm{kJ\,mol^{-1}} = -34\,\mathrm{kJ\,mol^{-1}} \tag{4.15}$$

An alternative solution is based on the graphical representation of the reactions Eqs. (4.8), (4.10), and (4.11) in a Born Haber cycle diagram, as illustrated in Fig. 4.2. It is obvious that the reaction of propene and water can be realized by the exothermic combustion of propene followed by the endothermic synthesis of three CO_2 and four H_2O molecules to form isopropanol. According to Hess's law (see Sect. 4.1.4) the total molar reaction enthalpy Δh_x is the sum of the molar reaction enthalpies in the sequence of reaction steps, i.e., $\Delta h_c(P)$ and $-\Delta h_c(I)$, as indicated in the figure.

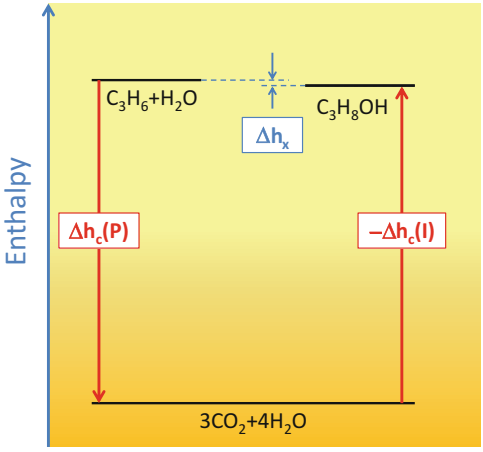

Fig. 4.2 Born Haber cycle diagram for the hydration of propene (schematic). The reaction of propene (C_3H_6) and water to isopropanol (C_3H_8O) is realized by the combustion of propene followed by the synthesis of the combustion products to form isopropanol

Moreover, the inspection of the Born Haber cycle in Fig. 4.2 reveals a typical difficulty of experimental calorimetry: accuracy. To obtain the standard molar heat of reaction $\Delta h_x^{\ominus}$ sought, we must subtract comparatively large combustion enthalpies and the result $\Delta h_x^{\ominus}$ is smaller orders of magnitude. A precise measurement of heats of combustion is thus the key to obtaining useful results. The goal is to achieve *chemical accuracy*, which means that a heat of formation is determined with a maximum uncertainty of 1 kcal mol^{-1}.

The value for $\Delta h_x^{\ominus}$ is valid for the reference temperature $T_r = 298.15\,K$. In practice, the hydration of propene is conducted at a higher temperature. In **subproblem (b)** we determine $\Delta h_x^{\ominus}$ at $T_2 = 550\,K$. This is an application of Kirchhoff's law (see Sect. 4.1.3). Moreover, this task is simplified by the fact that the constant pressure molar heat capacities given are assumed to be constant over the temperature range specified.[3] Using Eq. (4.6) under special consideration of reaction

[3] A problem with temperature-dependent heat capacities can be found in Chap. 5 (Problem 5.6).

Eq. (4.8), the reaction enthalpy sought is

$$\begin{aligned}\Delta h_x^{\ominus}(550\,\mathrm{K}) &= \Delta h_x^{\ominus}(298.15\,\mathrm{K}) + \int_{T_r}^{T_2} \left(c_p\,(\mathrm{C_3H_8O}) - c_p\,(\mathrm{C_3H_6}) - c_p\,(\mathrm{H_2O})\right)\,dT \\ &= -34{,}000\,\mathrm{J\,mol^{-1}} + (86 - 64 - 34)\,\mathrm{J\,K^{-1}\,mol^{-1}}\,(550 - 298.15)\,\mathrm{K} \\ &= -37\,\mathrm{kJ\,mol^{-1}} \end{aligned} \tag{4.16}$$

Problem 4.2 (Solvation Enthalpy)

a. Under standard conditions, 1 g of LiCl powder is dissolved in 50 ml of water (Fig. 4.3). As the solution is stirred, the temperature increases from 298 to 302.2 K. The constant pressure molar heat capacity of water is $75.3\,\mathrm{J\,K^{-1}\,mol^{-1}}$. Estimate the molar standard heat of solvation of LiCl. You may ignore the contribution of the dissolved LiCl to the heat capacity of the solution. The density of water is $1\,\mathrm{g\,ml^{-1}}$.

b. In another experiment, 1 g KCl(s) is dissolved in the same amount of water under the same conditions. A temperature reduction of 1.1 K was measured. Determine the molar standard heat of solvation of KCl and calculate the standard heat of formation of $K^+(aq)$ relative to the value of Li^+, if the standard heats of formation for KCl and LiCl are −436.7 and $-408.7\,\mathrm{kJ\,mol^{-1}}$ respectively.

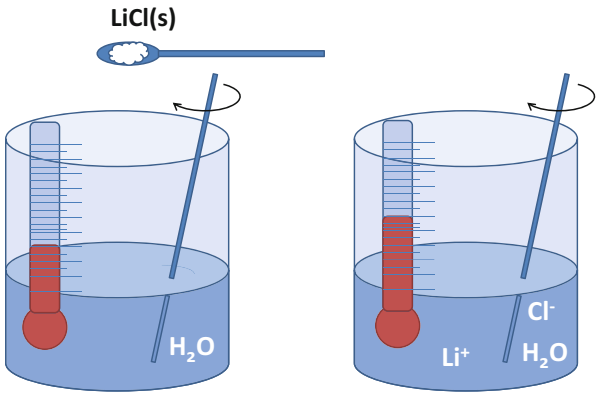

Fig. 4.3 A simple form of calorimetry to measure the heat of solvation of a salt

Solution 4.2 This problem deals with a very simple case of calorimetry. LiCl is an ionic crystal and completely dissolves in water according to

$$\mathrm{LiCl(s)} \rightarrow \mathrm{Li^+(aq) + Cl^-(aq)} \quad |\Delta h_{\mathrm{solv}}^{\ominus} \tag{4.17}$$

In **subproblem (a)** we determine the standard molar heat of solvation $\Delta h^{\ominus}_{\text{solv}}$ of this reaction. We exploit the temperature change $\Delta T = +4.2\,\text{K}$ of the solution and the molar heat capacity of the solvent water given. We notice that the increase in temperature indicates that the dissolution of LiCl is an exothermic process. Apparently, we ignore any heat transfer to the environment, i.e., the amount of heat

$$Q = C_p \Delta T \tag{4.18}$$

involved with the temperature jump in the solution is directly related to the heat of reaction. The heat capacity C_p of the solution is approximately given by the heat capacity of water. The amount of water is determined using the density ρ and the molar mass $M_{\text{H}_2\text{O}}$ which is $18\,\text{g mol}^{-1}$:

$$C_p = n_{\text{H}_2\text{O}} c_{p,\text{H}_2\text{O}} = \frac{m_{\text{H}_2\text{O}}}{M_{\text{H}_2\text{O}}} c_{p,\text{H}_2\text{O}} = \frac{\rho V}{M_{\text{H}_2\text{O}}} c_{p,\text{H}_2\text{O}} = 209.17\,\text{J K}^{-1} \tag{4.19}$$

As a consequence, the heat released by the reaction was

$$Q = 209.17\,\text{J K}^{-1} \times 4.2\,\text{K} = 878.5\,\text{J}. \tag{4.20}$$

To determine the molar heat of solvation, we need to know the amount of 1 g LiCl. From the periodic system, we take the atomic weights of Li and Cl and obtain the molar mass $M_{\text{LiCl}} = 42.39\,\text{g mol}^{-1}$. Hence, the amount of 1 g LiCl is $n_{\text{LiCl}} = \frac{1\,\text{g}}{42.39\,\text{g mol}^{-1}} = 0.0236\,\text{mol}$. The molar standard heat of solvation is thus $\Delta h^{\ominus}_{\text{solv}} = \frac{-Q}{n_{\text{LiCl}}} = -37.2\,\text{kJ mol}^{-1}$.

In the same way, we can proceed in **subproblem (b)**, where the same experiment leads to a temperature reduction of 1.1 K for the salt KCl, indicating an endothermic reaction. The molar mass of KCl is $M_{\text{KCl}} = 74.55\,\text{g mol}^{-1}$ and 1 g of KCl thus corresponds to an amount of $n_{\text{KCl}} = 0.0134$ mol. A temperature reduction of 1.1 K is consistent with a heat loss of $Q = -230.0$ J. The molar heat of solvation for KCl is thus $\Delta h^{\ominus}_{\text{solv}} = \frac{-Q}{n_{\text{KCl}}} = +17.2\,\text{kJ mol}^{-1}$.

The second part of the subproblem deals with the determination of heats of formation from the calorimetric results obtained so far. Although it is principally not possible to determine the absolute heat of formation of an ion in aqueous solution by performing an experiment,[4] we can use Hess' law and eliminate the unknown heat of formation of chlorine, which is the anionic species occurring in both reactions:

$$\text{LiCl(s)} \rightarrow \text{Li}^+\text{(aq)} + \text{Cl}^-\text{(aq)} \quad |\Delta h^{\ominus}_{\text{solv}}(\text{LiCl})$$

$$\text{KCl(s)} \rightarrow \text{K}^+\text{(aq)} + \text{Cl}^-\text{(aq)} \quad |\Delta h^{\ominus}_{\text{solv}}(\text{KCl})$$

[4] Electrolyte solutions are electrically neutral, requiring at least two different kinds of charged species in a calorimetric experiment.

Using Eq. (4.3), we write

$$\Delta h^{\ominus}_{\text{solv}}(\text{LiCl}) = \Delta h^{\ominus}_f(\text{Li}^+) + \Delta h^{\ominus}_f(\text{Cl}^-) - \Delta h^{\ominus}_f(\text{LiCl}) \tag{4.21}$$

$$\Delta h^{\ominus}_{\text{solv}}(\text{KCl}) = \Delta h^{\ominus}_f(\text{K}^+) + \Delta h^{\ominus}_f(\text{Cl}^-) - \Delta h^{\ominus}_f(\text{KCl}) \tag{4.22}$$

Subtraction of both equations yields

$$\begin{aligned}\Delta h^{\ominus}_f(\text{K}^+) - \Delta h^{\ominus}_f(\text{Li}^+) &= \Delta h^{\ominus}_{\text{solv}}(\text{KCl}) - \Delta h^{\ominus}_{\text{solv}}(\text{LiCl}) + \Delta h^{\ominus}_f(\text{KCl}) - \Delta h^{\ominus}_f(\text{LiCl}) \\ &= (17.2 + 37.2 - 436.7 + 408.7)\,\text{kJ mol}^{-1} = 26.4\,\text{kJ mol}^{-1}\end{aligned}$$

This is just the heat of formation sought *relative* to the value for Li^+ ions.

Problem 4.3 (Ellingham Diagram) Consider a sealed reaction vessel containing graphite (C(s)), nickel oxide (NiO(s)), and noble gas. The vessel may be heated to a high temperature.

a. Use the thermochemical data in Table 4.1 to determine the temperature above which nickel oxide is reduced to nickel according to the following reactions:

$$2\text{NiO(s)} + \text{C(s)} \rightarrow 2\text{Ni(s)} + \text{CO}_2\text{(g)} \quad |\Delta g^{\ominus}_1 \tag{4.23}$$

$$\text{NiO(s)} + \text{C(s)} \rightarrow \text{Ni(s)} + \text{CO(g)} \quad |\Delta g^{\ominus}_2 \tag{4.24}$$

You may assume that reaction enthalpies and entropies are constant over the whole temperature range.

b. Plot the Gibbs free energy of reaction as a function of temperature for each of the following reactions:

$$2\text{Ni(s)} + \text{O}_2\text{(g)} \rightarrow 2\text{NiO(s)} \quad |\Delta g^{\ominus}_3 \tag{4.25}$$

$$\text{C(s)} + \text{O}_2\text{(g)} \rightarrow \text{CO}_2\text{(g)} \quad |\Delta g^{\ominus}_4 \tag{4.26}$$

$$2\text{C(s)} + \text{O}_2\text{(g)} \rightarrow 2\text{CO(g)} \quad |\Delta g^{\ominus}_5 \tag{4.27}$$

Interpret this Ellingham diagram and use it to determine the temperature above which nickel oxide is reduced by carbon.

Solution 4.3 According to thermodynamics, the stability of a compound against reaction with other reactants is governed by the Gibbs free energy of reaction, which depends on temperature (Eq. (4.5)). If $\Delta g^{\ominus}_r$ is positive, the compound is stable. A negative sign, in contrast, favors its reaction. In metallurgy, a practical

Table 4.1 Thermochemical standard data for selected substances, valid for the reference temperature 298.15 K

Substance	$\Delta h_f^\ominus$ (kJ mol^{-1})	$s^\ominus$ (J K^{-1} mol^{-1})
Ni(s)	0	29.9
NiO(s)	−239.7	38.0
C(s)	0	5.74
CO(g)	−110.5	197.7
CO_2(g)	−393.5	216.8
O_2(g)	0	205.2

tool to estimate the stability of metals and their oxides against reaction with carbon is the **Ellingham diagram**. Here, we take the example of the reduction of nickel oxide to become acquainted with this method. The nickel oxide in the vessel may be reduced by carbon in two ways, with carbon monoxide or carbon dioxide as a gaseous reaction product.

In **subproblem (a)**, we use the thermochemical data provided in Table 4.1 to calculate the molar standard reaction enthalpies (Eq. (4.3)) and the molar standard reaction entropies (Eq. (4.4)) for the reactions Eqs. (4.23) and (4.24). For reaction Eq. (4.23), we obtain

$$\Delta h_1^\ominus = \Delta h_f^\ominus(\mathrm{CO_2}) - 2\Delta h_f^\ominus(\mathrm{NiO}) = 85.9\,\mathrm{kJ\,mol^{-1}} \tag{4.28}$$

where we have already taken into account that the molar standard heat of formation of Ni(s) and C(s) is zero. Moreover, the molar standard reaction entropy for this reaction is

$$\Delta s_1^\ominus = s^\ominus(\mathrm{CO_2}) + 2s^\ominus(\mathrm{Ni}) - 2s^\ominus(\mathrm{NiO}) - s^\ominus(\mathrm{C}) = +194.9\,\mathrm{J\,K^{-1}\,mol^{-1}} \tag{4.29}$$

Thus, at the reference temperature 298.15 K, the molar Gibbs free energy of reaction is endergonic,

$$\Delta g_1^\ominus(298.15\,\mathrm{K}) = +27.8\,\mathrm{kJ\,mol^{-1}}$$

and thus, not favored by thermodynamics. If we now assume that these values for the reaction entropy and the reaction enthalpy are constant, in good approximation even for higher temperatures, we can look for the temperature where $\Delta g_1^\ominus$ changes its sign, i.e. the temperature above which the reaction is exergonic:

$$\Delta g_1^\ominus(T_1) = \Delta h_1^\ominus - T_1 \Delta s_1^\ominus \stackrel{!}{=} 0 \Leftrightarrow T_1 = \frac{\Delta h_1^\ominus}{\Delta s_1^\ominus} = \frac{85{,}900\,\mathrm{J\,mol^{-1}}}{194.9\,\mathrm{J\,K^{-1}\,mol^{-1}}} = 440.7\,\mathrm{K}. \tag{4.30}$$

In the same way in which we determine the molar reaction enthalpy and entropy for the reaction Eq. (4.24), where NiO is reduced and carbon monoxide is formed, we obtain:

$$\Delta h_2^\ominus = \Delta h_f^\ominus(\mathrm{CO}) - \Delta h_f^\ominus(\mathrm{NiO}) = 129.2\,\mathrm{kJ\,mol^{-1}} \tag{4.31}$$

and

$$\Delta s_2^{\ominus} = s^{\ominus}(\mathrm{CO}) + s^{\ominus}(\mathrm{Ni}) - s^{\ominus}(\mathrm{NiO}) - s^{\ominus}(\mathrm{C}) = +183.9\,\mathrm{J\,K^{-1}\,mol^{-1}} \qquad (4.32)$$

This reaction is also endergonic at the reference temperature 298.15 K ($\Delta g_2^{\ominus} = +74.4\,\mathrm{kJ\,mol^{-1}}$) and becomes exergonic above

$$T_2 = \frac{\Delta h_2^{\ominus}}{\Delta s_2^{\ominus}} = \frac{129{,}200\,\mathrm{J\,mol^{-1}}}{183.9\,\mathrm{J\,K^{-1}\,mol^{-1}}} = 702.6\,\mathrm{K}. \qquad (4.33)$$

To conclude, thermodynamics predicts that nickel oxide may be reduced by carbon above $T_1 = 441\,\mathrm{K}$ under the formation of CO_2, and above $T_2 = 703\,\mathrm{K}$ under the production of CO.

In **subproblem (b)**, we follow a second method to obtain the same result. We consider the three oxidation reactions, namely the oxidation of nickel (Eq. (4.25)), the oxidation of carbon to CO_2 (Eq. (4.26)), and to CO (Eq. (4.27)). For each of these reactions, we can again use the data in Table 4.1 to determine the molar Gibbs free energy of reaction as a function of temperature. These plots are straight lines, owing to the functional form $\Delta g_r^{\ominus}(T) = \Delta h_r^{\ominus} - T\Delta s_r^{\ominus}$. They are shown in Fig. 4.4.

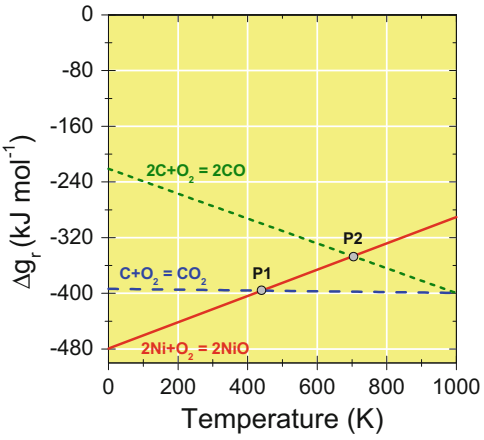

Fig. 4.4 Ellingham diagram for oxidation reactions Eqs. (4.25), (4.26), and (4.27). The intersection points $P1$ and $P2$ of the lines are at the temperatures T_1 and T_2 obtained in subproblem (a)

It is striking that the three lines have quite different slopes owing to the very different reaction entropies. Gaseous species have a much higher standard entropy than the solid elements and compounds, as can be seen in Table 4.1. Moreover, the entropies of the three gaseous species are similar. In a reaction that does not change the number of gaseous species, the reaction entropy is thus small. This is the case for the dashed line in Fig. 4.4, representing the oxidation of carbon to carbon dioxide. The oxidation of carbon to carbon monoxide increases the number of gaseous species; therefore, the reaction entropy is positive and the standard Gibbs free energy of reaction has a negative slope (short dashed line). The oxidation of nickel, on the

other hand, reduces the number of gaseous species; $\Delta g_r^{\ominus}(T)$ has a positive slope (solid line). The three lines have intersection points with each other. Two of them are indicated as $P1$ and $P2$. The temperatures of the intersection points, 441 and 703 K, match the temperatures T_1 and T_2 we have determined in subproblem (a). How can this be explained? The idea behind the Ellingham diagram is to compare the Gibbs free energies of reaction of oxidation reactions. If the oxidation of a substance has a higher $\Delta g_r^{\ominus}$ than the oxidation reaction of another species, the former is reduced rather than oxidized. In this sense, we can set up a sequence of reactions in which NiO is reduced and carbon is oxidized:

$$2\mathrm{NiO(s)}+\mathrm{C(s)} \rightarrow 2\mathrm{Ni(s)}+\mathrm{O_2(g)}+\mathrm{C(s)} \rightarrow 2\mathrm{Ni(s)}+\mathrm{CO_2(g)} \quad |\Delta g_1^{\ominus} = \Delta g_4^{\ominus} - \Delta g_3^{\ominus} \tag{4.34}$$

and

$$2\mathrm{NiO(s)} + 2\mathrm{C(s)} \rightarrow 2\mathrm{Ni(s)} + \mathrm{O_2(g)} + 2\mathrm{C(s)} \rightarrow 2\mathrm{Ni(s)} + 2\mathrm{CO(g)} \quad |2\Delta g_2^{\ominus} = \Delta g_5^{\ominus} - \Delta g_3^{\ominus} \tag{4.35}$$

The first reaction is reaction Eq. (4.23); the second is reaction Eq. (4.24) with the stoichiometric numbers multiplied by two. It is obvious that the conditions $\Delta g_1^{\ominus} = 0$ and $\Delta g_2^{\ominus} = 0$ are identical to the condition for the intersection points, i.e., $\Delta g_4^{\ominus} = \Delta g_3^{\ominus}$ for the reduction of nickel and production of CO_2, and $\Delta g_5^{\ominus} = \Delta g_3^{\ominus}$ for the reduction of nickel and production of CO. The sense of the Ellingham diagram becomes apparent if the Gibbs free energies of reaction of a larger number of oxidation reactions are plotted on the same diagram. A look at such a diagram then provides quick information if oxidation or reduction is favored in the presence of another element or its oxides. The weak temperature dependence of the reaction enthalpy and the reaction entropy can be included in the diagram, in addition to phase transitions that lead to a characteristic bending of the lines. However, such diagrams only reflect the thermodynamics of these reactions, not the kinetics.