
7 Introduction to thermodynamics

7.1 INTRODUCTION

Thermodynamics, the study of energy, is one of the most important subjects in all of science. Historically, it evolved from the desire to understand the efficiency of machines, in particular of steam engines. Much of its terminology, therefore, centers around heat and work, especially work associated with expanding gas. Thermodynamics, however, deals with the transfer of other forms of energy, such as that associated with chemical reactions. Although heat and mechanical work done by expanding gas are important in geology, for example in the cooling of a magma or the explosion of a volcano, it is in the study of chemical energies that thermodynamics is of greatest value to petrology. It is particularly useful in the study of processes that take place within the Earth, where they cannot be observed directly. The increased availability in recent years of thermodynamic data for the common minerals and magmas has resulted in a rapid growth in the application of thermodynamics to petrologic problems, and computer programs now use these data to calculate the compositions of minerals crystallizing from magmas and the mineral assemblages that can form in metamorphic rocks under any given temperature and pressure.

The general applicability of thermodynamics stems from the fundamental nature of the principles on which it is based, namely simple observations on the behavior of energy. For example, although energy can be converted from one form to another (kinetic to potential, chemical to thermal, etc.), it can never be destroyed. Furthermore, experience tells us that heat flows from hot to cold bodies, and never the reverse. The first observation, which concerns the conservation of energy, is embodied in the *first law of thermodynamics*, whereas the second one, which deals with the natural direction of processes, leads to the *second law of thermodynamics*. These laws can be expressed in simple mathematical forms, which can then be combined and manipulated to give useful functions from which the equilibrium conditions for a process or reaction can be calculated. In this way, it is possible, for example, to determine melting points of minerals, compositions of minerals crystallizing from magma, temperatures and pressures of metamorphic reactions, relative stabilities of minerals with respect to chemical weathering, and compositions of ore-forming solutions.

Little more than a descriptive treatment of petrology could be given if thermodynamics were to be omitted. However, an entire book would be required to fully develop all

thermodynamic relations encountered in the petrologic literature. In this and the following two chapters, only some of the more important fundamental concepts are covered. Standard physical chemistry texts will provide the reader with a more extensive coverage of the topic (e.g. Castellan, 1983, and Denbigh, 1957).

7.2 ENERGY IN THE FORM OF HEAT AND WORK

When discussing the energy of processes, it is important to specify the extent of the material being considered. This is done by using the term *system* to designate that part of space under consideration. A system may have real boundaries, such as the walls of a magma chamber, or imaginary ones, as did the small control volume used in Chapter 2 to derive the rate of flow of magma. The system is chosen to suit the particular problem. Systems are *isolated* if they have no interaction with the surroundings, *closed* if they exchange only heat, and *open* if they exchange both heat and material. Truly isolated systems are difficult to find, but their concept plays an important role in derivations of certain theoretical relations. Many geological systems can be considered closed, as, for example, a small rapidly cooling dike. A large batholith, on the other hand, might exchange considerable amounts of water and other mobile constituents with its surroundings while cooling and would be considered an open system. Many metamorphic reactions involve the loss of a volatile phase from the rock and are therefore open.

Energy can be expressed in the form of either heat or work, ignoring for the moment energy tied up with chemical reaction. *Heat* is the quantity of energy that flows across the boundary of a system in response to a temperature gradient. *Work* is the quantity of energy that crosses the boundary of a system and is converted entirely into mechanical work in the surroundings, such as the lifting of a weight (Fig. 7.1); a geological example would be the explosive removal of the top of Mount St. Helens. By convention, energy put into a system in the form of heat, Q , is positive, whereas that in the form of work, W , is negative. Positive work, then, is done on the surroundings. This convention is inherited from the early days of thermodynamics when there was interest in how much work a machine could do on its surroundings. Some texts (e.g. Kern and Weisbrod, 1967) have changed the sign convention for work, so that, like heat, it is positive when done on the system. Because the designation of sign is purely

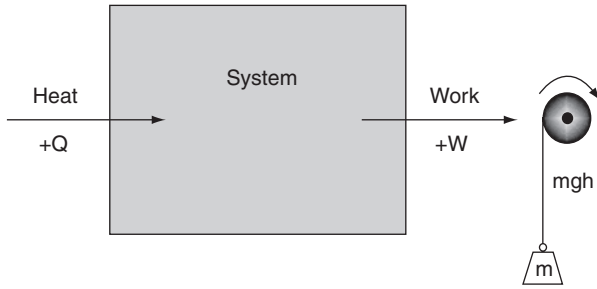


Fig. 7.1 Sign convention for energy transferred into or out of a thermodynamic system in the form of heat or work.

arbitrary, the sign convention does not affect thermodynamic conclusions. Care should be taken, however, in reading thermodynamic texts to ascertain the sign convention used.

The type of work most commonly encountered in petrologic processes is that known as *work of expansion*. For example, when a rock melts at some depth in the Earth, the approximate 10% expansion involved with the phase change results in work being done as the volume expands against the opposing pressure (P_{op}) of the surrounding rock. This work of expansion is given by

$$W_{\text{exp}} = (\text{force}) \times (\text{distance}) = (P_{\text{op}} \times \text{area}) \times (\text{distance}) = P_{\text{op}} \Delta V \quad (7.1)$$

where ΔV is the volume change. Other types of work include electrical and magnetic, but these are not normally involved in petrologic processes (now would be a good time to do Problem 7.1 and 7.2).

To appreciate work of expansion, consider a gas bubble with volume V_1 , pressure P_1 , and temperature T in a magma that is suddenly erupted onto the Earth's surface where the pressure is P_2 . The bubble expands to V_2 against the opposing pressure P_2 , but its temperature is kept constant by the thermal buffering of the surrounding hot magma. This change can be represented by the simple mechanical analog shown in Figure 7.2. The work of expansion done by this bubble on the surrounding magma is given by

$$W_{\text{exp}} = P_2(V_2 - V_1)$$

If the gas behaves ideally ($PV = nRT$), this isothermal expansion can be represented by the P versus V plot in Figure 7.2, in which the shaded area represents the amount of work done.

If the magma had stopped at some intermediate depth where the bubble could have expanded against an intermediate pressure P_i and then erupted onto the surface to complete its expansion, the work done in this two-stage decompression would be

$$W_{\text{exp}} = P_1(V_i - V_1) + P_2(V_2 - V_i)$$

This amount of work (Fig. 7.3 (A)) is greater than that done by the single-stage expansion. If the bubble had expanded in three stages, the work would have been still greater (Fig. 7.3 (B)). Clearly, the maximum amount of work that could be

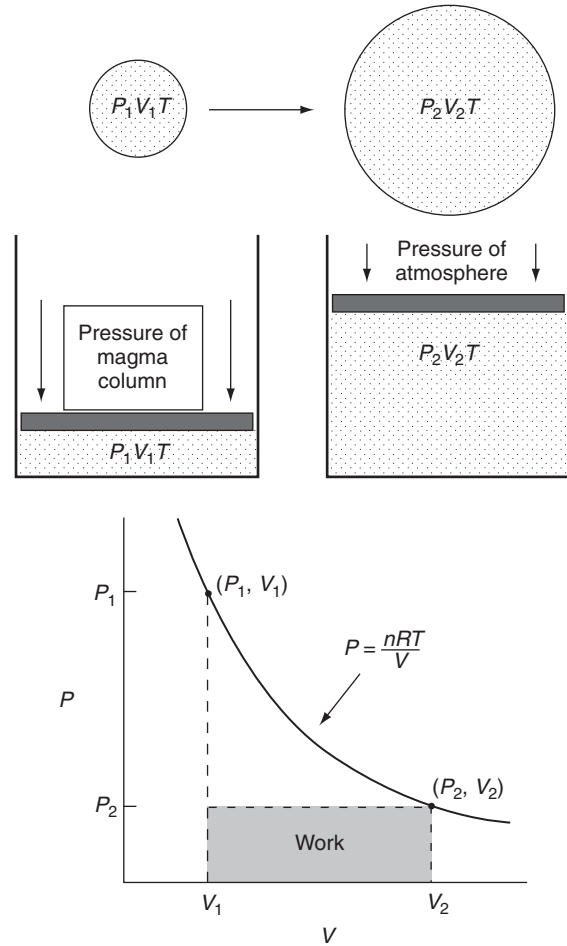


Fig. 7.2 Mechanical analog of a gas bubble expanding isothermally against a pressure of 1 atm (10^5 Pa), and a graphical representation of the amount of work done during expansion ($P\Delta V$) assuming that the gas behaves ideally ($PV = nRT$).

obtained from this expansion results from an infinite number of infinitesimal steps (Fig. 7.3(C)), in which case the work done would be

$$W_{\text{exp}}^{\text{max}} = \int_1^2 P_{\text{op}} dV$$

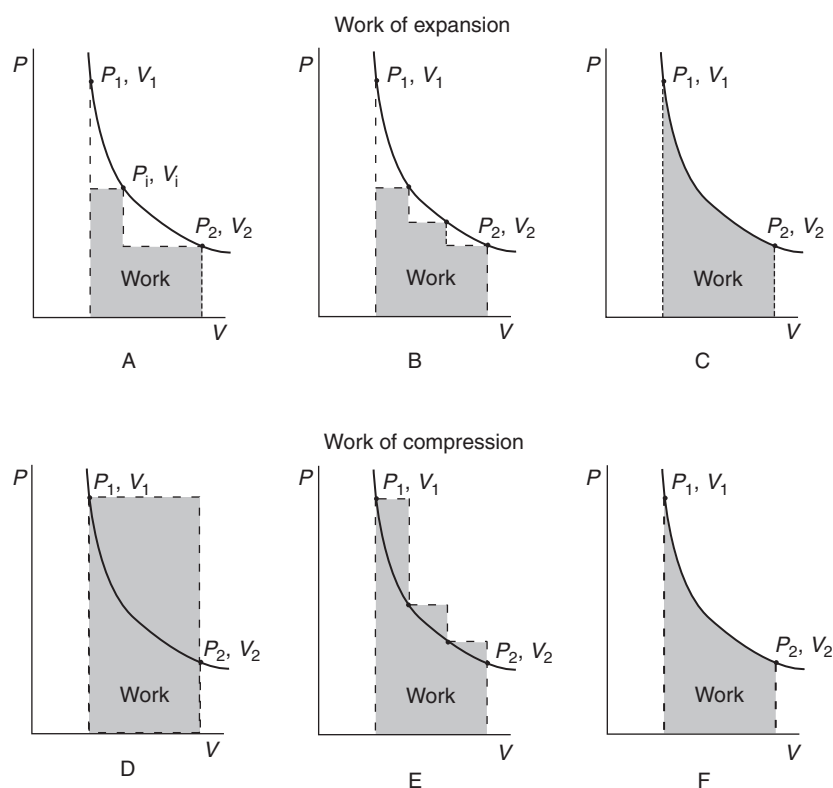
where P_{op} is the opposing pressure at any stage of expansion. If the gas is taken to be ideal, P_{op} can be replaced by nRT/V , in which case

$$W_{\text{exp}}^{\text{max}} = \int_1^2 \frac{nRT}{V} dV = nRT \int_1^2 \frac{dV}{V} = nRT \ln \frac{V_2}{V_1} \quad (7.2)$$

Supposing that the gas bubble were now to be compressed back to its original state, work would have to be done on the system. This could be done in a single stage of compression by suddenly increasing the pressure to P_1 , in which case the amount of work done (Fig. 7.3(D)) would be given by

$$W_{\text{comp}} = P_1(V_1 - V_2)$$

Fig. 7.3 Work of expansion (shaded area) produced when decompression of an ideal gas takes place in (A) two stages, (B) three stages, (C) an infinite number of infinitesimal steps, and the amount of work necessary to return this gas to its original state by isothermally compressing it in (D) one stage, (E) three stages, and (F) an infinite number of infinitesimal steps.



If the bubble were compressed in a series of stages (Fig. 7.3 (E)) the amount of work required would obviously be less, and the minimum amount of work (Fig. 7.3(F)) would be done when the pressure at each stage was increased infinitesimally, giving

$$W_{\text{comp}}^{\text{min}} = \int_2^1 P_{\text{op}} dV = nRT \int_2^1 \frac{dV}{V} = nRT \ln \frac{V_1}{V_2} \quad (7.3)$$

$$= -nRT \ln \frac{V_2}{V_1}$$

We have followed a bubble through an isothermal cycle of expansion and compression. During the first half of the cycle, the bubble did work on the surroundings, but during the second part, work was done on the bubble to restore it to its initial state. From Figure 7.3, the amount of work produced during expansion in a finite number of steps is clearly less than the amount of work that has to be performed on the system to restore it to its former state. Therefore, processes such as this, carried out in a finite number of steps, always result in work having to be done on the system. On the other hand, if the cycle of decompression and compression could be carried out in an infinite number of infinitesimal steps, the work of expansion (Eq. (7.2)) would equal exactly the work required to compress the gas (Eq. (7.3)); that is, the areas under the PV curves ($\int PdV$) would be equal. Because the compression part of the cycle carried out in this manner is the exact reverse of the decompression part of the cycle, processes of this type are described as *reversible*, whereas processes carried out in a finite number of steps are *irreversible*. All natural processes are irreversible; reversible processes are

unnatural because they would require an infinite amount of time to take place. The concept of a reversible reaction, however, plays an important role in determining conditions of equilibrium, as will be seen later in this chapter.

7.3 FIRST LAW OF THERMODYNAMICS

In the isothermal cyclic process described above, irreversible expansion or compression of the bubble results in turbulence in the gas, which can be equated with heat. For the temperature to remain constant, this heat has to be liberated into the surroundings. Hence, all natural cycles (natural = irreversible), in addition to requiring work to be done on the system, produce heat in the surroundings. Experience tells us that these two quantities of energy are always equal. This fact was first clearly enunciated by the German physicist Mayer in 1842 and eight years later was quantified in Joule's classic experiment on the *mechanical equivalent of heat*. Observations such as these led to the formulation of the *first law of thermodynamics*, which states that *for any cyclical process (reversible or irreversible), the work produced in the surroundings is equal to the heat removed from the surroundings*.

Mathematically the first law can be expressed as

$$\oint dW = \oint dQ$$

or

$$\oint (dQ - dW) = 0 \quad (7.4)$$

where dQ and dW are the differentials of heat and work involved in the cyclic process, and the symbol \oint indicates a cyclic integral; that is, the sum of all the dQ and dW around the cycle. Note that d is used to indicate an inexact differential, because the integrals of dQ or dW have no definite values unless the path is specified (Figure 7.3). Equation (7.4), however, reveals that although $\oint dQ$ and $\oint dW$ by themselves do not have definite values, $\oint (dQ - dW)$ does have a definite value, which for a cyclic process is zero. This means that although the quantities of work and heat taken separately can have various values depending on the path followed by the process, the value of their combination is independent of the path; its value is determined only by the initial and final states of the system. Because of this behavior, $dQ - dW$ is said to be a **state property; that is, a property which is dependent only on the state of the system and not on the path followed**. For convenience, this state property is given the name *internal energy*, E , and is defined as

$$dE \equiv dQ - dW \quad (7.5)$$

Note that the internal energy is not an independent quantity that can be equated with heat and work; it is simply the sum of the energy put into the system in the form of heat (dQ) and work ($-dW$). Note also that it is defined in differential form; only changes in the internal energy can be measured, not absolute amounts. Integration of Eq. (7.5) results in a constant of integration that cannot be evaluated. This lack of knowledge of the absolute value of internal energy is of no importance because all thermodynamic calculations eventually deal only with differences, and thus the constant of integration disappears. For example, the change in internal energy associated with a reaction going from state 1 to state 2 is given by

$$\int_1^2 dE = \int_1^2 dQ - \int_1^2 dW$$

or

$$E_2 - E_1 = \Delta E = Q - W \quad (7.6)$$

So far, we have used, for illustrative purposes, the purely physical process of the expansion and compression of a gas bubble. Equation (7.5), however, is equally applicable to any process in which there is a change in energy, whether it is physical or chemical. The process could, for example, involve a change of state from solid to liquid or from one mineral polymorph to another, or a chemical reaction between several minerals. Each of these processes will involve the transfer of energy in the form of both heat and work and must obey Eq. (7.5).

Many reactions of interest to petrologists involve work of expansion ($P\Delta V$) at constant pressure – for example, the melting of a rock at a specific depth in the Earth. In such a case, Eq. (7.6) can be expressed as

$$E_2 - E_1 = Q_P - P(V_2 - V_1)$$

where Q_P is the heat involved with the reaction at constant pressure. On rearranging, we obtain

$$Q_P = (E_2 + PV_2) - (E_1 + PV_1) \quad (7.7)$$

which shows that the heat involved with a reaction taking place at constant pressure is the difference between two groups of terms which describe the energy, pressure, and volume of the final and initial states of the system. We have already seen that the internal energy is a state property. But PV is also a state property; for example, in the case of an ideal gas it would be equal to nRT . Consequently, $E + PV$ must also be a state property. It is therefore given a special name, *enthalpy* (H), which is defined as

$$H \equiv E + PV \quad (7.8)$$

Equation (7.7) now becomes

$$Q_P = H_2 - H_1 = \Delta H \quad (7.9)$$

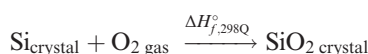
The enthalpy change in a reaction is, therefore, the heat withdrawn from the surroundings at constant pressure.

If heat is given out during a reaction it is said to be **exothermic** and ΔH is negative. An **endothermic** reaction is one that takes heat from the surroundings and hence ΔH is positive. For example, if forsterite were to react with quartz at 298 K (25 °C) to form enstatite, 7.4 kJ mol⁻¹ of forsterite would be liberated, and hence $\Delta H_{298} = -7.3$ kJ mol⁻¹. In contrast, the reaction from low quartz (α) to high quartz (β) at 848 K (575 °C) is endothermic, and $\Delta H_{848} = +1.2$ kJ mol⁻¹.

7.4 STANDARD HEATS OF FORMATION

Because enthalpy involves the internal energy (Eq. (7.8)), absolute values cannot be known. This, however, is not a problem because thermodynamic calculations deal only with changes in enthalpy. For example, in the reaction above where forsterite reacts with quartz to form enstatite, the absolute values of the enthalpies of the minerals cannot be known, but the enthalpy change ($\Delta H = -7.4$ kJ mol⁻¹) accompanying the reaction can be determined and used to calculate the conditions under which this reaction will occur.

Although absolute values of enthalpy cannot be known, it is convenient to think of substances as having such values. By convention, then, we assign an arbitrary “absolute” value of zero to the enthalpy of each of the elements in their standard stable form at 298.15 K (25 °C) and a pressure of 10⁵ Pa (1 bar). This is represented by $H_{298, \text{element}}^\circ \equiv 0$, where the superscript ° indicates 10⁵ Pa pressure. With this arbitrary base level, it is then possible to define the enthalpy of a mineral in terms of the enthalpy change accompanying the formation of that mineral from the elements at 298 K and 10⁵ Pa pressure. **An enthalpy defined in this way is referred to as the standard heat (enthalpy) of formation of the mineral, $H_{f, 298}^\circ$.** For example, the reaction to form quartz would be



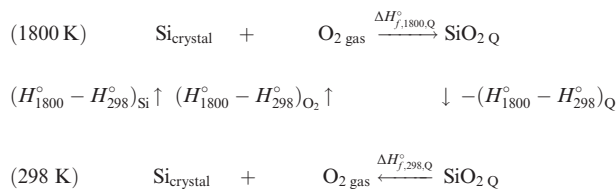
and the standard heat of formation would be given by

$$\Delta H_{f,298,Q}^{\circ} = H_{298,Q}^{\circ} - (H_{298,\text{Si}}^{\circ} + H_{298,\text{O}_2}^{\circ})$$

But the terms in parentheses have values of zero, since they refer to the elements in their stable states at 298 K and 10^5 Pa pressure. The enthalpy of quartz under these conditions is therefore equal to the enthalpy change of the reaction, which is $-910.83 \text{ kJ mol}^{-1}$. Note that in this reaction the stable form of silicon under these conditions is a crystalline metal, whereas the stable form of oxygen is the diatomic gas (O_2). Standard heats of formation of minerals are given in Table 7.1.

Although the heat of formation of quartz in the previous reaction was given for a temperature of 298 K, this reaction is not likely to proceed rapidly at this temperature – if it did, pocket calculators and computers would have a very short life expectancy. High temperatures are required before silicon metal will react rapidly with oxygen. Therefore, if we were interested in measuring the heat involved with this reaction, it would be necessary to carry out the experiment at high temperatures. How, then, would we determine, from the high-temperature experiments, the enthalpy change associated with the reaction at 298 K?

To answer this we make use of the fact that enthalpy is a state property, and therefore its value is independent of the path followed by the reaction. For instance, instead of trying to react oxygen with silicon at 298 K, we can heat these materials to a high temperature, 1800 K for example. Quartz forms rapidly at this temperature. Once the reaction is complete, the quartz can be cooled to 298 K. Thus, the temperature of the starting materials and end product will both be 298 K, even though the reaction took place at 1800 K. The enthalpy change between starting materials and end product at 298 K will be the same whether the reaction proceeded directly at 298 K or followed the high-temperature path. These two possible ways of carrying out this reaction can be illustrated as follows:



Because enthalpy is a state property, its integral around a cyclic process must be zero. Thus, if we were to heat Si and O_2 from 298 K to 1800 K, react them together to form quartz, cool the quartz to 298 K, and then break down the quartz to form Si and O_2 again, the sum of the enthalpy changes of all of the steps around this cycle would be zero; that is,

$$(H_{1800}^{\circ} - H_{298}^{\circ})_{\text{Si}} + (H_{1800}^{\circ} - H_{298}^{\circ})_{\text{O}_2} + \Delta H_{f,1800,Q}^{\circ} + [-(H_{1800}^{\circ} - H_{298}^{\circ})_{\text{Q}}] + [-(\Delta H_{f,298,Q}^{\circ})] = 0$$

By rearranging this, we obtain the standard heat of formation of quartz at 298 K,

$$\begin{aligned} \Delta H_{f,298,Q}^{\circ} &= \Delta H_{f,1800,Q}^{\circ} - (H_{1800}^{\circ} - H_{298}^{\circ})_{\text{Q}} \\ &+ [(H_{1800}^{\circ} - H_{298}^{\circ})_{\text{Si}} + (H_{1800}^{\circ} - H_{298}^{\circ})_{\text{O}_2}] \quad (7.10) \end{aligned}$$

Most of the enthalpy data presented in Table 7.1 have been collected at temperatures other than 298 K and have had to be corrected to this standard temperature. Moreover, many of the reactions have followed more complicated paths than ones simply requiring heating and cooling. Some have involved dissolving the elements and minerals in acid or high-temperature metallic melts. The heats of solution in these solvents have then been used to calculate the $\Delta H_{f,298}^{\circ}$. Again, because enthalpy is a state function, the actual path taken in the reaction does not affect the enthalpy change of the overall reaction, which depends only on the initial and final states.

The enthalpy data presented in Table 7.1 are normally used to calculate the enthalpy of formation of a mineral at a particular temperature of interest. For example, we might wish to know the enthalpy of formation of quartz at 1800 K and 10^5 Pa pressure. This can be determined by rearranging Eq. (7.10) and inserting the value for the heat of formation of quartz at 298 K obtained from thermodynamic tables. This gives

$$\begin{aligned} \Delta H_{f,1800,Q}^{\circ} &= \Delta H_{f,298,Q}^{\circ} + (H_{1800}^{\circ} - H_{298}^{\circ})_{\text{Q}} \\ &- [(H_{1800}^{\circ} - H_{298}^{\circ})_{\text{Si}} + (H_{1800}^{\circ} - H_{298}^{\circ})_{\text{O}_2}] \quad (7.11) \end{aligned}$$

High-temperature heats of formation can also be read directly from thermodynamic tables, but care must be exercised in doing this. Enthalpy data are commonly presented in two different ways. One lists values calculated according to Eq. (7.11) (Robie *et al.*, 1978). The other also uses Eq. (7.11), but the enthalpy terms for the elements (those in square brackets) are dropped (Helgeson *et al.*, 1978); enthalpies calculated this way are referred to as **apparent enthalpies of formation from the elements**. A simple example will illustrate the justification for dropping these terms. To determine the enthalpy change associated with the transformation from low to high quartz at 848 K we need know only the difference in the heats of formation from the elements of these two forms of quartz at this temperature. Values obtained from Eq. (7.11) for the two polymorphs will have identical terms for the elements (those in brackets) because the same elements are involved in both minerals. These terms, therefore, cancel when we take the difference in the enthalpies of formation of the two polymorphs. The same argument applies to other more complicated reactions, because the same elements are present on both sides of the reaction.

To calculate a high-temperature heat of formation from Eq. (7.11), the change in enthalpy associated with changes in temperature (e.g. $(H_{1800}^{\circ} - H_{298}^{\circ})_{\text{Q}}$ in Eq. (7.11)) must be evaluated. This can be determined from the heat capacity of the mineral at constant pressure (C_P), because

$$\int_{H_{298}^{\circ}}^{H_T^{\circ}} dH = \int_{298}^T C_P dT \quad (7.12)$$

Table 7.1 *Molar thermodynamic data for common minerals at standard temperature and pressure, i.e. 298.15 K and 10⁵ Pa (1 bar)*

Mineral	Formula	Formula wt (kg)	Volume (J bar ⁻¹)	ΔH_f° (kJ)	S° (J K ⁻¹)	ΔG_f° (kJ)	a (kJ K ⁻¹)	$b \times 10^5$ (kJ K ⁻²)	c (kJ K)	d (kJ K ^{-1/2})
Acmite	NaFeSi ₂ O ₆	0.23101	6.459	-2586.65	170.6	-2419.31	0.3071	1.6758	-1685.5	-2.1258
Akermanite	Ca ₂ MgSi ₂ O ₇	0.27264	9.254	-3866.36	212.5	-3668.89	0.3854	0.3209	-247.5	-2.8899
Albite	NaAlSi ₃ O ₈	0.262224	10.006	-3934.56	210.1	-3711.91	0.452	-1.3364	-1275.9	-3.9536
Almandine	Fe ₃ Al ₂ Si ₃ O ₁₂	0.49775	11.511	-5263.52	340	-4939.8	0.6773	0	-3772.7	-5.044
Analcite	NaAlSi ₂ O ₆ ·H ₂ O	0.220155	9.74	-3309.9	232	-3090.97	0.6435	-1.6067	9302.3	-9.1796
Andalusite	Al ₂ SiO ₅	0.162046	5.153	-2588.8	92.7	-2440.97	0.2773	-0.6588	-1914.1	-2.2656
Andradite	Ca ₃ Fe ₂ Si ₃ O ₁₂	0.505184	13.204	-5768.13	318	-5424.33	0.6386	0	-4955.1	-3.9892
Annite	KFe ₃ (AlSi ₃ O ₁₀)(OH) ₂	0.51189	15.432	-5151.67	418	-4796.02	0.8157	-3.4861	19.8	-7.4667
Anorthite	CaAl ₂ Si ₂ O ₈	0.27821	10.079	-4233.48	200	-4007.51	0.3716	1.2615	-4110.2	-2.0384
Anthophyllite	Mg ₇ Si ₈ O ₂₂ (OH) ₂	0.780872	26.54	-12069.2	536	-11342.22	1.2773	2.5825	-9704.6	-9.0747
Antigorite	Mg ₄₈ Si ₃₄ O ₈₅ (OH) ₆₂	4.536299	175.48	-71424.31	3591	-70622.39	9.621	-9.1183	-35941.6	-83.0342
Aragonite	CaCO ₃	0.100089	3.415	-1207.58	89.5	-1128.03	0.1923	-0.3052	1149.7	-2.1183
Brucite	Mg(OH) ₂	0.058327	2.463	-924.92	64.5	-834.31	0.1584	-0.4076	-1052.3	-1.1713
Calcite	CaCO ₃	0.100089	3.689	-1207.47	92.5	-1128.81	0.1409	0.5029	-950.7	-0.8584
Carbon dioxide	CO ₂	0.04401	2478.920	-393.51	213.7	-394.3	0.0878	-0.2644	706.4	-0.9989
Carbon monoxide	CO	0.02801	2478.920	-110.53	197.67	-137.13	0.0457	-0.0097	662.7	-0.4147
Chloritoid (Fe)	FeAl ₂ SiO ₅ (OH) ₂	0.25191	6.98	-3215.38	155	-2973.74	0.4846	-1.3808	-198.9	-4.7622
Chloritoid (Mg)	MgAl ₂ SiO ₅ (OH) ₂	0.22037	6.875	-3551.42	140	-3313.56	0.4644	-1.2654	-1147.2	-4.341
Chrysotile	Mg ₃ Si ₂ O ₅ (OH) ₄	0.277134	10.746	-4359.03	221.3	-4030.75	0.6247	-2.077	-1721.8	-5.6194
Clinocllore	Mg ₅ Al ₂ Si ₃ O ₁₀ (OH) ₄	0.48777	21.09	-8912.41	430.5	-8263.35	1.1618	1.0133	-7657.3	-9.6909
Clinzoisite	Ca ₂ Al ₃ Si ₃ O ₁₂ (OH)	0.622882	13.63	-6898.15	301	-6502.98	0.567	1.8063	-7034	-2.603
Coesite	SiO ₂	0.060085	2.064	-905.47	40.8	-850.89	0.0965	-0.0577	-444.8	-0.7982
Cordierite	Mg ₂ Al ₃ (AlSi ₅ O ₁₈)	0.584969	23.322	-9163.37	407.5	-8653.24	0.8213	4.3339	-8211.2	-5.00
Cordierite hydrous	Mg ₂ Al ₃ (AlSi ₅ O ₁₈)·H ₂ O	0.602984	23.322	-9446.98	487.3	-8891.08	0.8697	5.1995	-7723.7	-5.2512
Corundum	Al ₂ O ₃	0.101961	2.558	-1675.25	50.9	-1581.72	0.1395	0.589	-2460.6	-0.5892
Cristobalite	SiO ₂	0.060085	2.61	-905.99	46.5	-853.12	0.0979	-0.335	-636.2	-0.774
Daphnite	Fe ₅ Al ₂ Si ₃ O ₁₀ (OH) ₄	0.64548	21.34	-7134.85	565	-6535.56	1.2374	1.3594	-3743	-11.25
Diamond	C	0.012011	0.342	2.07	2.3	3.13	0.0243	0.6272	-377.4	-0.2734
Diopside	CaMg(SiO ₃) ₂	0.21656	6.619	-3202.76	142.7	-3027.8	0.3145	0.0041	-2745.9	-2.0201
Dolomite	CaMg(CO ₃) ₂	0.184411	6.434	-2324.43	156	-2161.51	0.3589	-0.4905	0	-3.4562
Enstatite	Mg ₂ (SiO ₃) ₂	0.200792	6.262	-3090.47	132.5	-2915.53	0.3562	-0.299	-596.9	-3.1853
Epidote	Ca ₂ FeAl ₂ Si ₃ O ₁₂ (OH)	0.651747	13.91	-6463.21	328	-6076.41	0.5446	2.4781	-11230	-1.1921
Fayalite	Fe ₂ SiO ₄	0.203778	4.631	-1478.15	151	-1378.98	0.2011	1.733	-1960.6	-0.9
Ferrosilite	Fe ₂ (SiO ₃) ₂	0.263862	6.592	-2388.63	190.6	-2234.53	0.3987	-0.6579	1290.1	-4.058
Forsterite	Mg ₂ SiO ₄	0.140708	4.366	-2172.2	95.1	-2052.75	0.2333	0.1494	-603.8	-1.8697
Gehlenite	Ca ₂ Al ₂ SiO ₇	0.274205	9.024	-3986.88	202	-3784.82	0.4057	-0.7099	-1188.3	-3.1744
Glaucophane	Na ₂ Mg ₃ Al ₂ Si ₈ O ₂₂ (OH) ₂	0.78355	26.05	-11969.47	535	-11233.99	1.7175	-12.107	7075	-19.272
Graphite	C	0.012011	0.53	0	5.85	0	0.051	-0.4428	488.6	-0.8055
Grossular	Ca ₃ Al ₂ Si ₃ O ₁₂	0.450454	12.535	-6644.15	255	-6280.94	0.626	0	-5779.2	-4.0029
Hedenbergite	CaFe(SiO ₃) ₂	0.248106	6.795	-2844.16	174.2	-2680.39	0.3402	0.0812	-1047.8	-2.6467
Hematite	Fe ₂ O ₃	0.159692	3.027	-825.71	87.4	-743.73	0.1639	0	-2257.2	-0.6576
Hercynite	FeAl ₂ O ₄	0.173809	4.075	-1959.15	107.5	-1843.85	0.2833	-0.5376	609.8	-2.7136
Hydrogen	H ₂	0.002016	2478.920	0	130.7	0	0.0233	0.4627	0	0.0763
Ilmenite	FeTiO ₃	0.151745	3.169	-1231.3	108.9	-1154.63	0.1389	0.5081	-1288.8	-0.4637
Jadeite	NaAl(SiO ₃) ₂	0.20214	6.04	-3027.85	133.5	-2849.1	0.3011	1.0143	-2239.3	-2.0551
Kalsilite	KAlSiO ₄	0.158167	6.04	-2121.92	134	-2005.98	0.242	-0.4482	-895.8	-1.9358
Kaolinite	Al ₂ Si ₂ O ₅ (OH) ₄	0.258161	9.934	-4122.18	203.7	-3801.72	0.4367	-3.4295	-4055.9	-2.6991
Kyanite	Al ₂ SiO ₅	0.162046	4.414	-2593.11	83.5	-2442.59	0.2794	-0.7124	-2055.6	-2.2894
Laumontite	CaAl ₂ Si ₄ O ₁₂ ·4H ₂ O	0.470441	20.37	-7268.47	457	-6707.45	1.0134	-2.1413	-2235.8	-8.8067
Lawsonite	CaAl ₂ Si ₂ O ₇ (OH) ₂ ·H ₂ O	0.3142	10.132	-4869.14	230	-4513.04	0.6878	0.1566	375.9	-7.1792
Leucite	KAlSi ₂ O ₆	0.218248	8.828	-3029.16	200	-2866.19	0.3698	-1.6332	684.7	-3.6831
Magnesite	MgCO ₃	0.084321	2.803	-1111.36	65.1	-1027.74	0.1864	-0.3772	0	-1.8862
Magnetite	Fe ₃ O ₄	0.231539	4.452	-1115.51	146.1	-1012.31	0.2625	-0.7204	-1926.2	-1.6557
Margarite	CaAl ₂ (Al ₂ Si ₂ O ₁₀)(OH) ₂	0.398187	12.964	-6241.23	267	-5856.99	0.7444	-1.68	-2074.4	-6.7832
Merwinite	Ca ₃ Mg(SiO ₄) ₂	0.328719	9.847	-4546.42	253.1	-4317.73	0.4175	0.8117	-2923	-3.3203
Methane	CH ₄	0.016043	2478.920	-74.81	186.26	-50.66	0.1501	0.2062	3427.7	-2.6504
Microcline	KAlSi ₃ O ₈	0.278337	10.892	-3975.11	216	-3750.19	0.4488	-1.0075	-1007.3	-3.9731
Monticellite	CaMgSiO ₄	0.156476	5.148	-2253.05	108.1	-2134.63	0.2507	-1.0433	-797.2	-1.9961
Muscovite	KAl ₂ (AlSi ₃ O ₁₀)(OH) ₂	0.398313	14.083	-5984.18	292	-5603.71	0.7564	-1.984	-2170	-6.9792
Nepheline	NaAlSiO ₄	0.145227	5.419	-2095.08	124.4	-1980.35	0.2727	-1.2398	0	-2.7631
Oxygen	O ₂	0.031999	2478.920	0	205.2	0	0.0483	-0.0691	499.2	-0.4207
Paragonite	NaAl ₂ (AlSi ₃ O ₁₀)(OH) ₂	0.382201	13.211	-5946.34	276	-5565.09	0.803	-3.158	217	-8.151
Pargasite	NaCa ₂ Mg ₄ Al(Al ₂ Si ₆ O ₂₂)(OH) ₂	0.835858	27.19	-12720.65	601	-11986.81	1.2802	2.2997	-12359.5	-8.0658
Periclase	MgO	0.040311	1.125	-601.6	26.9	-569.34	0.0605	0.0362	-535.8	-0.2992
Phlogopite	KMg ₃ (AlSi ₃ O ₁₀)(OH) ₂	0.417286	14.964	-6219.16	328	-5837.42	0.7703	-3.6939	-2328.9	-6.5316
Prehnite	Ca ₂ Al(AlSi ₃ O ₁₀)(OH) ₂	0.412389	14.026	-6203.18	292.8	-5825.13	0.7249	-1.3865	-2059	-6.3239
Pyrope	Mg ₃ Al ₂ Si ₃ O ₁₂	0.40313	11.318	-6284.72	266.3	-5933.62	0.6335	0	-5196.1	-4.3152
Pyrophyllite	Al ₂ Si ₄ O ₁₀ (OH) ₂	0.360316	12.81	-5640.64	239.4	-5266.87	0.7845	-4.2948	1251	-8.4959
Pyroxene Ca–Al	CaAl ₂ SiO ₆	0.218125	6.356	-3307.03	138	-3129.29	0.3476	-0.6974	-1781.6	-2.7575
Quartz	SiO ₂	0.060085	2.269	-910.83	41.5	-856.46	0.1107	-0.5189	0	-1.1283
Rutile	TiO ₂	0.079899	1.882	-944.18	50.6	-888.92	0.0904	0.29	0	-0.6238
Sanidine	KAlSi ₃ O ₈	0.277337	10.9	-3964.96	230	-3744.21	0.4488	-1.0075	-1007.3	-3.9731
Silica liquid	SiO ₂	0.060085	2.64	-920.85	16.5	0.0825	0	0	0	
Sillimanite	Al ₂ SiO ₅	0.162046	4.986	-2585.68	95.5	-2438.93	0.2802	-0.69	-1375.7	-2.3994
Spessartine	Mn ₃ Al ₂ Si ₃ O ₁₂	0.40313	11.792	-5646.4	367	-5326.31	0.5846	-0.1593	-7516.7	-2.7501
Spinel	MgAl ₂ O ₄	0.142273	3.978	-2300.72	81.5	-2175.64	0.2427	-0.6037	-2315.1	-1.6781
Staurolite (Fe)	Fe ₄ Al ₁₈ Si _{7.5} O ₄₈ H ₄	1.69170	44.88	-23753.93	1010	-22282.23	2.88	-5.6595	-10642	-25.373
Stishovite	SiO ₂	0.060085	1.401	-875.63	24.5	-816.2	0.0681	0.601	-1978.2	-0.0821
Talc	Mg ₃ Si ₄ O ₁₀ (OH) ₂	0.379289	13.625	-5897.1	260	-5516.73	0.6222	0	-6385.5	-3.9163
Tremolite	Ca ₂ Mg ₅ Si ₈ O ₂₂ (OH) ₂	0.81241	27.27	-12310.38	550	-11581.42	1.2602	0.383	-11455	-8.2376
Tridymite	SiO ₂	0.060085	2.7	-906.69	46.1	-853.69	0.0979	-0.335	-636.2	-0.774
Ulvöspinel	Fe ₂ TiO ₄	0.22359	4.682	-1497.49	175	-1401.79	-0.1026	14.252	-9144.5	5.2707
Wairakite	CaAl ₂ Si ₄ O ₁₂ ·H ₂ O	0.434411	19.04	-6666.42	375	-6220.05	0.8383	-2.146	-2272	-7.2923
Water (steam)	H ₂ O	0.0180153	2478.920	-241.81	188.8	-228.59	0.0401	0.8656	487.5	-0.2512
Wollastonite	CaSiO ₃	0.116164	3.993	-1634.06	82.5	-1548.47	0.1593	0	-967.3	-1.0754
Zoisite	Ca ₂ Al ₃ Si ₃ O ₁₂ (OH)	0.622882	13.575	-6898.61	297	-6502.25	0.5957	6.2297	-5921.3	-3.3947

The coefficients a , b , c , and d are from the heat capacity polynomial $C_p = a + bT + cT^{-2} + dT^{-1/2}$ (Note that values of b have been multiplied by 10^5 . The unit of volume, J bar⁻¹ = 10 cm³ = 10⁻⁵ m³). From Holland and Powell (1998) and from the Thermocalc web page at www.earthsci.unimelb.edu.au/tpg/thermocalc.

Heat capacities, however, vary with temperature; thus C_P must be expressed as a function of T before Eq. (7.12) can be integrated. Variations in the heat capacity of most minerals can be fitted to an expression of the form

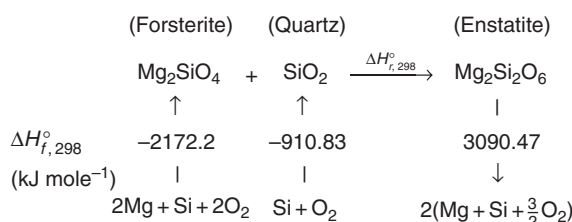
$$C_P = a + bT + \frac{c}{T^2} + \frac{d}{T^{1/2}} \quad (7.13)$$

Values of these coefficients are given in Table 7.1 for the common minerals (note that the values of b in Table 7.1 have been multiplied by 10^5). Substitution of Eq. (7.13) into Eq. (7.12) gives, on integration,

$$H_T^\circ - H_{298}^\circ = a(T - 298) + \frac{b}{2}(T^2 - 298^2) - c\left(\frac{1}{T} - \frac{1}{298}\right) + 2d(T^{1/2} - 298^{1/2}) \quad (7.14)$$

Calculation of the high-temperature enthalpy of formation of a mineral is therefore a simple matter using Eqs. (7.11) and (7.14) and the data in Table 7.1 (Problem 7.3). Because the calculations are tedious, they are best carried out by computer; they can be handled easily on the simple spreadsheet.

The actual reactions involved in forming minerals from the elements are of little interest in themselves, as most do not occur in nature. Elemental silicon, for example, is never found reacting with oxygen to form quartz. The enthalpies of these reactions, however, can be used to calculate the enthalpies of reaction (ΔH_r°) between other minerals, and herein lies the value of the standard heats of formation. To illustrate this, consider the petrologically important reaction of olivine with quartz to form orthopyroxene:



For each of these minerals it is possible to write a reaction for their formation from the elements. The enthalpies of these reactions are obtained directly from Table 7.1. These reactions provide another path between the reactants and products. Enstatite, for example, could be broken down into its constituent elements; these elements could then be recombined to form forsterite and quartz; reaction of forsterite with quartz returns us to enstatite. Because enthalpy is a state property, its integral around this cycle must be zero. We can determine the enthalpy change of the reaction ($\Delta H_{r,298}^\circ$), then, by summing all of these terms as we proceed around the cycle in one direction – clockwise, for example. In doing this, care must be taken to keep the signs of the enthalpy changes correct. Table 7.1 indicates that the enthalpy of formation of a mineral from the elements is negative; that is, heat is liberated into the surroundings when elements are combined to form the mineral. If the reaction takes place in

the opposite direction, that is, the mineral breaks down into the elements, the enthalpy change must be positive. For this cycle we can write

$$\Delta H_{r,298}^\circ + 3090.47 + (-910.83) + (-2172.2) = 0$$

from which it follows that $\Delta H_{r,298}^\circ = -7.4 \text{ kJ mol}^{-1}$ of olivine. The enthalpy change of this reaction at higher temperatures can be calculated using the enthalpies of formation of the minerals at higher temperatures (Problem 7.4).

7.5 SECOND LAW OF THERMODYNAMICS

Determination of the enthalpy change accompanying a reaction is the first step to understanding the conditions under which a reaction will take place. There remains the important question of the direction of the reaction. Will mineral A change into B, or will B change into A? We know from experience that many everyday processes have a definite direction to them. When cream is stirred in coffee, mixing occurs; if the direction of stirring is reversed, the coffee and cream do not unmix. It is therefore a matter of experience that the process of stirring results in mixing; the opposite is never observed. This implies that some fundamental principle governs the direction of the process. If this principle can be determined, it could be used to indicate the directions of reactions with which we do not have everyday experience, such as those occurring in the Earth. This principle is embodied in the second law of thermodynamics, and it involves an obscure property of material known as entropy (S).

In discussing the first law of thermodynamics it was emphasized that the heat involved with a change from one state to another has no definite value unless the path is specified. This can be illustrated by considering different ways in which a gas can be expanded from one state to another. Imagine that this is done reversibly, although we know, in reality, such a process would take infinite time. Consider first the isothermal expansion of the gas from an initial state A to a final state B (Fig. 7.4). During this expansion a quantity of heat, Q_4 , is absorbed from the surroundings in order to keep the temperature constant. If the temperature is not maintained constant during the expansion, many other paths can be followed between A and B . For example, the gas could expand in an insulated container where no heat would be absorbed from the surroundings, and as a result its temperature would fall, for example to T_1 (C in Fig. 7.4). Such a change, in which no heat is transferred in or out of the system, is *adiabatic*. From point C , the gas could expand isothermally to point D with the absorption of a quantity of heat Q_1 . Adiabatic compression would then take the gas to point B . The expansion of the gas from A to B could also involve several isothermal steps, such as the path $AEFGHB$, in which two quantities of heat, Q_3 and Q_2 , are absorbed along the isothermal lines T_3 and T_2 , respectively. Even when the path does not follow adiabatic or isothermal lines, as along the irregular curve in Figure 7.4, the path can be treated as a large number of infinitesimal adiabatic and isothermal steps, with

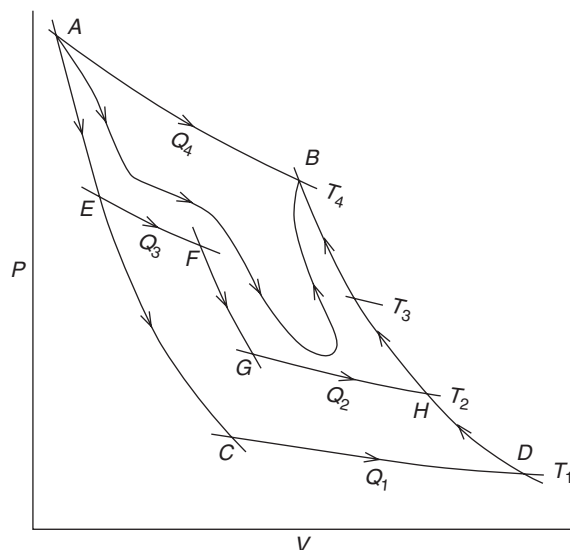


Fig. 7.4 Various paths that can be followed by a gas changing its pressure and volume from state *A* to *B*. The curves labeled T_1 to T_4 are isothermal lines arranged in order of increasing temperature, whereas the steeper curves are adiabatic lines.

each of the latter involving the absorption of a quantity of heat, dQ , so that the total heat absorbed between *A* and *B* is $\int_A^B dQ_{\text{rev}}$. The subscript rev indicates that the process takes place reversibly.

Each one of the paths between *A* and *B* in Fig. 7.4 involves a different quantity of heat; that is,

$$Q_4 \neq Q_1 \neq (Q_3 + Q_2) \neq \int_A^B dQ_{\text{rev}}$$

Because the amount of heat involved in the change from *A* to *B* depends on the path followed, heat cannot be a state property. If, however, the various quantities of heat are divided by the absolute temperatures at which the heat absorption takes place, a function is created that is independent of the path followed. This function must, therefore, be a state function. Thus,

$$\frac{Q_4}{T_4} = \frac{Q_1}{T_1} = \frac{Q_3}{T_3} + \frac{Q_2}{T_2} = \int_A^B \frac{dQ_{\text{rev}}}{T}$$

This state property is given the name *entropy* and symbol *S*. It is defined by the equation

$$dS \equiv \frac{dQ_{\text{rev}}}{T} \quad (7.15)$$

As with any state property, the total change in entropy accompanying a reversible cycle is zero; that is,

$$\oint dS = \oint \frac{dQ_{\text{rev}}}{T} = 0$$

A reversible cycle, however, is not a natural one. In an irreversible or natural cycle the amount of heat generated in the surroundings is greater than in a reversible one (review the sign convention in Fig. 7.1). Consequently, we can write

$$\oint \frac{dQ_{\text{irrev}}}{T} < \oint \frac{dQ_{\text{rev}}}{T} = \oint dS = 0 \quad (7.16)$$

or in general form

$$dS \geq \frac{dQ}{T} \quad (7.17)$$

where the equality sign applies to the reversible case and the inequality sign to the irreversible one. For a real reaction to take place (irreversible), dQ/T must be less than dS . Also, for a process taking place in an isolated system, dQ_{irrev} must be zero, and therefore $dS > 0$. That is, for a real reaction to occur in an isolated system entropy must increase. The reaction will continue until equilibrium is attained, at which point dS becomes zero and the entropy is a maximum. This statement is but one of many different ways of expressing the *second law of thermodynamics*.

It is important to emphasize that in Eq. (7.15), entropy is defined using the heat involved in a *reversible* reaction. The fact that a reversible reaction is not possible does not invalidate the definition. Entropy is a state function, and therefore its change in value depends only on the initial and final states and not on the path of the reaction or whether it was carried out reversibly or irreversibly. All natural reactions are irreversible, and this simply means that $dQ_{\text{irrev}}/T < dS$.

We will see later how entropy can be measured. But first, we will investigate the physical significance of entropy.

7.6 ENTROPY

Thermodynamic terms such as pressure, work, and heat are familiar from everyday experiences, but entropy, despite its importance, is not. But our expectations that stirring cream in coffee will cause mixing, or that oxygen in the air is unlikely suddenly all to move to one end of a room, or that heat will flow from high to low temperatures, are based on processes in which entropy strives for a maximum. This suggests that entropy is a measure of the degree of randomness in a system. This relation was first formalized by the Austrian physicist Boltzmann, who showed that entropy can be defined in terms of the number of possible arrangements of the particles constituting a system. Entropy, so defined, is given by

$$S = k \ln \Omega \quad (7.18)$$

where k is the Boltzmann constant (gas constant per molecule, $R/N_0 = 1.3806 \times 10^{-23} \text{ J K}^{-1}$) and Ω is the number of possible arrangements. From this relation, entropy is clearly related to the amount of disorder or randomness in a system.

To illustrate this relation, we will consider the entropy change accompanying the transformation from low- to high-temperature albite. Albite is a framework silicate with four asymmetric tetrahedral sites, three occupied by silicon and one by aluminum. In the low-temperature form, aluminum enters one specific site, but at high temperature, it may be in any of the four sites. Consequently, the high-temperature form has a greater capacity for randomness and should therefore have the higher entropy.

In low-temperature albite, the atoms can be arranged in only one way. Admittedly, the silicon atoms could be switched around in the silicon sites, but silicon atoms are indistinguishable, and thus this would not result in distinguishable arrangements. The entropy due to occupancy of the tetrahedral sites in low albite is therefore

$$S_{\text{LowAb}} = k \ln 1 = 0$$

At high temperature, the aluminum can enter any of the tetrahedral sites. But 1 mole of albite ($\text{NaAlSi}_3\text{O}_8$) contains N_0 (Avogadro's number = 6.022×10^{23}) atoms of aluminum and $3N_0$ atoms of silicon that must be distributed over $4N_0$ tetrahedral sites. The number of possible ways of arranging these is

$$\Omega = \frac{(4N_0)!}{(N_0)!(3N_0)!}$$

Hence,

$$S_{\text{HighAb}} = k[\ln(4N_0)! - \ln(N_0)! - \ln(3N_0)!]$$

Because N is very large, we can use Stirling's approximation, that is,

$$\ln N! = N \ln N - N$$

The entropy of the high-temperature form is then

$$S_{\text{HighAb}} = kN_0[4 \ln 4 - 3 \ln 3]$$

but $kN_0 = R$, the gas constant ($8.31443 \text{ J K}^{-1} \text{ mol}^{-1}$), so that

$$S_{\text{HighAb}} = 18.70 \text{ J mol}^{-1} \text{ K}^{-1}$$

Therefore, the entropy change due to the disordering of the aluminum and silicon in the tetrahedral sites is $S_{\text{HighAb}} - S_{\text{LowAb}}$, which is $18.70 \text{ J mol}^{-1} \text{ K}^{-1}$.

It should be emphasized that this calculated entropy change is a maximum because no account is taken of any crystal chemical restrictions on the possible groupings of ions. In addition, this calculation pertains only to the change in the configuration of the aluminum and silicon in the tetrahedral sites. The albite structure may have other sources of randomness that contribute to the absolute entropy of this mineral (see Problem 7.5).

7.7 THIRD LAW OF THERMODYNAMICS AND THE MEASUREMENT OF ENTROPY

The third law of thermodynamics states that *the entropy of a pure, perfectly crystalline substance is zero at the absolute zero of temperature*. The entropy of such a substance at temperature T is then

$$S_T = \int_0^T \frac{dQ_{\text{rev}}}{T} = \int_0^T \frac{C_p}{T} dT \quad (7.19)$$

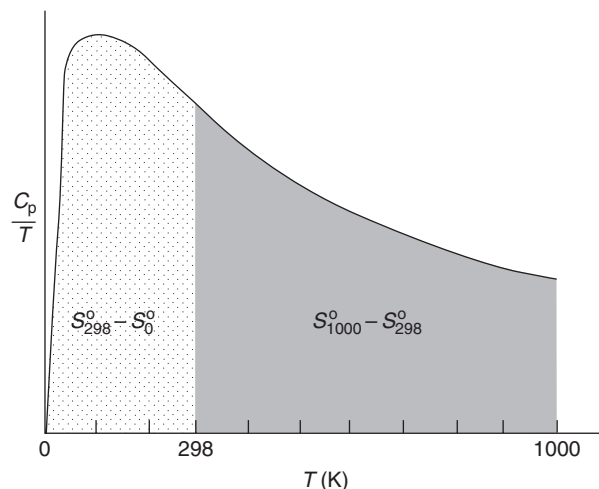


Fig. 7.5 The entropy of a substance is given by the area under the curve in a plot of C_p/T versus T . Entropies of substances at 298 K and 10^5 Pa (1 bar) pressure (stippled area) are listed in Table 7.1. Higher temperature entropies can be obtained by adding the area under the higher-temperature part of the curve (darker shaded area).

where C_p , the heat capacity at constant pressure, is a readily measured physical property. Entropy is normally determined by graphically evaluating the integral in Eq. (7.19). This is done by plotting C_p/T versus T and measuring the area under the curve (Fig. 7.5).

The terms *pure* and *perfectly crystalline* in the third law are very important. Substances such as glass or intermediate composition plagioclase would still have entropy at absolute zero because of their randomness in structure (*configurational entropy*). For any substance, the entropy can be thought of as consisting of two parts, one thermal and the other configurational; that is,

$$S = S_{\text{thermal}} + S_{\text{configurational}}$$

The S_{thermal} becomes zero at the absolute zero of temperature for all substances, but the $S_{\text{configurational}}$ becomes zero at this temperature only for pure, perfectly crystalline substances. This need not concern us, however, for the entropy data at 298 K in Table 7.1 take this into account.

The entropy of a substance at high temperature and 10^5 Pa pressure can be calculated from the data in Table 7.1 through the following relation:

$$S_T^{\circ} = \int_{298}^T \frac{C_p}{T} dT + S_{298}^{\circ} \quad (7.20)$$

The heat capacities at high temperatures, however, are given by Eq. (7.13), with the coefficients being listed in Table 7.1. Integration of Eq. (7.20), therefore, gives

$$S_T^{\circ} = \left[a \ln T + bT - \frac{c}{2T^2} - \frac{2d}{T^{1/2}} \right] \Big|_{298}^T + S_{298}^{\circ} \quad (7.21)$$

7.8 GIBBS EQUATION: THERMODYNAMIC POTENTIALS

The first law of thermodynamics gives the relations between the various forms of energy, whereas the second law gives the sense of direction for reactions by introducing the concept of entropy, which is given absolute values by the third law. These can now be combined into a general relation governing reactions and equilibrium.

Rearranging Eq. (7.5) gives

$$-dE - dW + dQ = 0$$

From the second law (Eq. (7.17)) $T dS \geq dQ$; hence,

$$-dE - dW + T dS \geq 0$$

The work can be expressed as work of expansion ($P dV$) plus any other form of work (dU). Thus,

$$-dE - PdV - dU + TdS \geq 0 \quad (7.22)$$

This is a general relation indicating that at equilibrium, which is equivalent to the reversible situation, the left-hand side of the equation must be zero, and for a spontaneous reaction, it must be greater than zero.

Let us consider a reaction that takes place under constant pressure and constant temperature, a common condition encountered in petrologic problems. In this case, PdV and TdS can be written as $d(PV)$ and $d(TS)$. Equation (7.22) therefore becomes

$$-dE - d(PV) + d(TS) \geq dU$$

or

$$-d(E + PV - TS) \geq dU \quad (7.23)$$

The combination of terms $(E + PV - TS)$ is a state variable and is given the name *Gibbs free energy* (G); that is,

$$G \equiv E + PV - TS = H - TS \quad (7.24)$$

Equation (7.23) becomes

$$-dG \geq dU$$

and in the case where only work of expansion is done, which is the most common geological situation,

$$-dG \geq 0 \quad (7.25)$$

Thus, for a spontaneous reaction (irreversible) to occur at constant P and T , $-dG$ must be positive; that is, the free energy must decrease. The reaction will proceed until equilibrium is attained (reversible), at which point $-dG=0$, and the free energy is a minimum.

Although various forms of energy are transferred during a reaction proceeding at constant P and T , it is the Gibbs free energy that controls the feasibility and direction of the reaction. This is illustrated graphically in Figure 7.6. The change in internal energy (ΔE) accompanying a reaction taking place at a particular pressure and temperature consists of the work

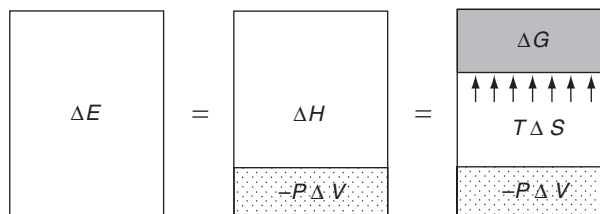


Fig. 7.6 Energy changes involved with a reaction at constant pressure and temperature. The reaction continues spontaneously until ΔG is reduced to zero.

done on the system ($-P\Delta V$) and the enthalpy change (ΔH). The enthalpy change can be further subdivided into thermal energy due to the entropy change ($T\Delta S$) and the change in free energy (ΔG). As the reaction proceeds, entropy is always increasing and striving for a maximum consonant with the state of the system; hence, $T\Delta S$ is also increasing and does so at the expense of ΔG . The free-energy change is therefore that part of the heat removed from the surroundings that can be used to increase the randomness of the system. As the reaction proceeds and the system becomes more random, this fraction of the enthalpy change decreases and becomes zero at equilibrium. At this point it is clear from Figure 7.6 that $T\Delta S = \Delta H$. This also follows directly from Eq. (7.24), which, for an infinitesimal change, would be

$$dG = dE + PdV + VdP - TdS - SdT \quad (7.26)$$

But, if P and T are constant,

$$dG = dE + PdV - TdS$$

which, from Eq. (7.8), gives

$$dG = dH - TdS$$

which, in turn, for a finite change, becomes

$$\Delta G = \Delta H - T\Delta S \quad (7.27)$$

At equilibrium $\Delta G=0$; hence,

$$T\Delta S = \Delta H$$

or

$$T_{\text{equil}} = \Delta H / \Delta S \quad (7.28)$$

Equation (7.28) gives a simple means of determining the equilibrium temperature for a reaction. Consider, for example, the reaction of cristobalite melting at 10^5 Pa pressure to form silica liquid. Data for this reaction at high temperature indicate that ΔH is $+8071 \text{ J mol}^{-1}$ and ΔS is $+4.05 \text{ J mol}^{-1} \text{ K}^{-1}$. Therefore, the equilibrium temperature or melting point would be $T_{\text{equil}} = \Delta H / \Delta S = 1993 \text{ K}$ or 1720°C .

The equilibrium temperature for any reaction, such as that for the melting of cristobalite, is the temperature at which $\Delta G=0$. This is shown in Figure 7.7 as the point of intersection of the free-energy curves for cristobalite and silica liquid (glass at low temperature). At higher temperatures, ΔG is

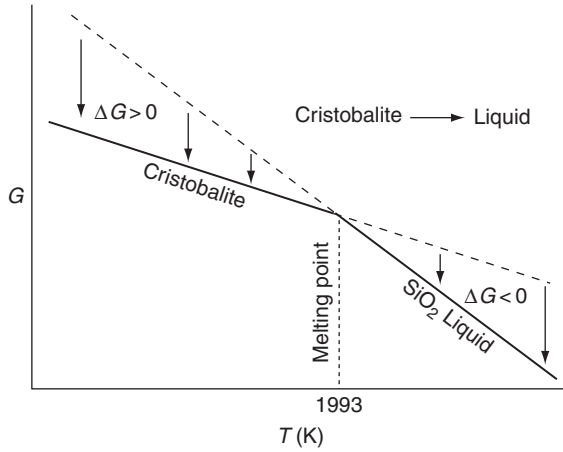


Fig. 7.7 Free energy versus temperature plots at constant pressure for cristobalite and silica liquid. The intersection of the two curves is the melting point of cristobalite. Below the melting point, cristobalite has a lower free energy than does the silica liquid and is therefore the stable phase; above the melting point, the liquid has a lower free energy and is therefore stable.

negative; hence, the reaction proceeds with the melting of cristobalite. Below this temperature, ΔG is positive, so the reaction can proceed only in the opposite direction, causing cristobalite to crystallize. The most stable form is always the one with the lowest free energy. Of course, thermodynamics indicates only what the equilibrium state should be, but kinetic factors may prevent this from being achieved. Volcanic glasses, for example, could lower their free energy by crystallizing, but the kinetics of this process are slow at low temperatures.

For many petrologic problems, we need to calculate the ΔG of reaction under conditions different from those for which the data in Table 7.1 are applicable. To do this it is necessary to know how free energy changes with temperature and pressure. From Eq. (7.22) it is clear that for a reversible reaction involving only work of expansion, dE is equivalent to $TdS - PdV$, which can be substituted for dE in Eq. (7.26), giving

$$dG = TdS - PdV + PdV + VdP - TdS - SdT$$

which reduces to

$$dG = -SdT + VdP \quad (7.29)$$

In a closed system – that is, one in which no matter is transferred in or out – G is a function only of temperature and pressure [$G = f(T, P)$]. We can express the total change in G (dG) resulting from a change in T and P as the sum of the change due to T and the change due to P . This is known as a *total differential* of the function, and it is represented as follows:

$$dG = \left(\frac{\partial G}{\partial T}\right)_P dT + \left(\frac{\partial G}{\partial P}\right)_T dP \quad (7.30)$$

The terms in parentheses are known as *partial derivatives*, as they denote the variation in G with respect to only one of the

two variables, while the other variable, shown as a subscript outside the parentheses, is held constant. Comparison of Eqs. (7.30) and (7.29) reveals that

$$\left(\frac{\partial G}{\partial T}\right)_P = -S \quad (7.31)$$

and

$$\left(\frac{\partial G}{\partial P}\right)_T = \bar{V} \quad (7.32)$$

The bar over the \bar{V} signifies molar volume. This is introduced because values of G are typically given as molar quantities. Because all substances have positive entropy, free energy always decreases with increasing temperature at constant pressure, and because liquids have higher entropies than corresponding solids, their free energy decreases more rapidly than that of solids (Fig. 7.7). Molar volumes are also always positive, therefore increasing pressure at constant temperature causes the free energy to rise.

Similar relations can be derived for the free-energy change of a reaction. The change in the ΔG of a reaction with temperature is

$$\left(\frac{\partial \Delta G}{\partial T}\right)_P = -\Delta S \quad (7.33)$$

and the change with pressure is

$$\left(\frac{\partial \Delta G}{\partial P}\right)_T = \Delta V \quad (7.34)$$

In these cases, the change in the ΔG of the reaction is determined by the entropy change and volume change of the reaction. Both of these terms can be either positive or negative, so generalizations about the variation of the ΔG of a reaction cannot be made. However, in the case of reactions that evolve a gas such as many metamorphic reactions, ΔS and ΔV will both be positive, and therefore the ΔG of reaction will decrease with increasing temperature and increase with increasing pressure.

Other useful relations can be derived from Eq. (7.30) simply by utilizing two properties of a total differential, that is the *cross-derivative rule* and the *cyclic rule*. We have seen by comparing Eqs. (7.29) and (7.30) that

$$\left(\frac{\partial G}{\partial T}\right)_P = -S \quad \text{and} \quad \left(\frac{\partial G}{\partial P}\right)_T = \bar{V}$$

If we take derivatives of these expressions with respect to the variable held constant, we obtain

$$\left[\frac{\partial}{\partial P} \left(\frac{\partial G}{\partial T}\right)_P\right]_T = -\left(\frac{\partial S}{\partial P}\right)_T \quad \text{and} \quad \left[\frac{\partial}{\partial T} \left(\frac{\partial G}{\partial P}\right)_T\right]_P = \left(\frac{\partial V}{\partial T}\right)_P$$

But, from the *cross-derivative rule* for a total derivative that is exact,

$$\left[\frac{\partial}{\partial P} \left(\frac{\partial G}{\partial T} \right)_P \right]_T = \left[\frac{\partial}{\partial T} \left(\frac{\partial G}{\partial P} \right)_T \right]_P \quad (7.35)$$

Therefore,

$$-\left(\frac{\partial S}{\partial P} \right)_T = \left(\frac{\partial V}{\partial T} \right)_P$$

but from Eq. (2.2), $(\partial V/\partial T)_P = \alpha V$, where α is the isobaric coefficient of thermal expansion. Therefore,

$$\left(\frac{\partial S}{\partial P} \right)_T = -\alpha V \quad (7.36)$$

This allows us to evaluate the variation in entropy with pressure from two easily measured physical properties, α and V .

Similarly, by differentiating Eq. (7.32) we obtain

$$\left(\frac{\partial^2 G}{\partial P^2} \right)_T = \left(\frac{\partial V}{\partial P} \right)_T$$

but from Eq. (2.8) $(\partial V/\partial P)_T = -\beta V$, where β is the isothermal coefficient of compressibility. Therefore,

$$\left(\frac{\partial^2 G}{\partial P^2} \right)_T = -\beta V \quad (7.37)$$

And by differentiating Eq. (7.31) we obtain

$$\left(\frac{\partial^2 G}{\partial T^2} \right)_P = -\left(\frac{\partial S}{\partial T} \right)_P$$

but $(\partial S/\partial T)_P = C_p/T$. Thus,

$$\left(\frac{\partial^2 G}{\partial T^2} \right)_P = -\frac{C_p}{T} \quad (7.38)$$

The *cyclic rule* for total differentials states that if any three variables, x , y , and z , for example, are connected by a functional relation, then the three partial derivatives satisfy the following relation:

$$\left(\frac{\partial x}{\partial y} \right)_z \left(\frac{\partial y}{\partial z} \right)_x \left(\frac{\partial z}{\partial x} \right)_y = -1 \quad (7.39)$$

This rule is easily remembered by writing the three variables in any order in a row, and then repeating them below so that none of the vertical columns match. These vertical pairs give the partial derivatives, with the subscripted variable, which is held constant, being the third variable. For example,

$$\begin{array}{ccc} z & y & x \\ x & z & y \end{array} \quad \text{becomes} \quad \left(\frac{\partial z}{\partial x} \right)_y \left(\frac{\partial y}{\partial z} \right)_x \left(\frac{\partial x}{\partial y} \right)_z = -1$$

If the cyclic rule is applied to the three variables P , T , and V , we obtain

$$\left(\frac{\partial P}{\partial T} \right)_V \left(\frac{\partial T}{\partial V} \right)_P \left(\frac{\partial V}{\partial P} \right)_T = -1 \quad (7.40)$$

But from Eq. (2.2), $(\partial V/\partial T)_P = \alpha V$, and from Eq. (3.1), $(\partial V/\partial P)_T = -\beta V$, which, when substituted into Eq. (7.40), give

$$\left(\frac{\partial P}{\partial T} \right)_V \left(\frac{1}{\alpha V} \right) (-\beta V) = -1$$

Hence,

$$\left(\frac{\partial P}{\partial T} \right)_V = \frac{\alpha}{\beta} \quad (7.41)$$

Thermodynamic relations, then, can be manipulated with the cyclic and cross-derivative rules into useful forms for specific applications.

7.9 FREE ENERGY OF FORMATION AT ANY TEMPERATURE AND PRESSURE

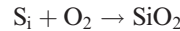
Finally, we will derive an expression for the free energy of formation of a phase at any temperature and pressure. We define the molar free energy of formation of a phase from the elements at 298.15 K and 10^5 Pa (1 bar) as

$$\begin{aligned} \text{Free energy of formation} &= \Delta \bar{G}_{f,298}^\circ \\ &= \Delta H_{f,298}^\circ - 298 \Delta S_{298}^\circ \end{aligned} \quad (7.42)$$

The ΔS in this expression refers to the difference in entropies of the phase and its constituent elements in their standard states ($S_{\text{phase}} - \sum S_{\text{elements}}$). Values of $\Delta \bar{G}_{f,298}^\circ$ in column 7 of Table 7.1 are calculated according to Eq. (7.42). In Section 7.4 it was shown that if the ΔH_r° is used to calculate the ΔH of a reaction between phases, the terms for the enthalpy of the elements on the reactant and product sides of a reaction cancel. The same is true for the entropies of the elements, and in some compilations of thermodynamic data, $\Delta \bar{G}_{f,298}^\circ$ is calculated ignoring the entropies of the elements. A value calculated in this manner is known as the *apparent free energy of formation*; it is given by

$$\Delta \bar{G}_{f,298}^\circ = \Delta H_{f,298}^\circ - 298.15 \times S_{298}^\circ \quad (7.43)$$

where S_{298}° is the entropy of the phase only. For example, the reaction to form quartz from the elements in their standard states is



According to Eq. (7.42), the $\Delta \bar{G}_{f,298}^\circ$ for quartz would be

$$\begin{aligned} \Delta \bar{G}_{f,298}^\circ &= \Delta H_{f,298}^\circ - 298.15 \left(S_{298, \text{Qtz}}^\circ - (S_{298, \text{Si}}^\circ + S_{298, \text{O}_2}^\circ) \right) \\ &= -856.46 \text{ kJ} \end{aligned}$$

The apparent free energy of formation (Eq. (7.43)) would be

$$\Delta \bar{G}_{f,298}^\circ = \Delta H_{f,298}^\circ - 298.15 \times S_{298, \text{Qtz}}^\circ = -923.06 \text{ kJ}$$

Readers should take care to ascertain which type of free energy of formation is being used when they consult other texts.

The reason for using the apparent free energy of formation is that it reduces the amount of calculation necessary when determining the free energy of formation of a phase at elevated temperatures and pressures. It eliminates having to calculate the changes in the enthalpies and entropies of the elements when the temperature and pressure are raised above standard conditions. We will illustrate this by deriving the expression for the apparent free energy of formation of a phase at any temperature T (K) and pressure P (Pa).

We first determine $\Delta\bar{G}_{f,298}^\circ$ at standard conditions from Eq. (7.43). If the temperature is to be raised, appropriate terms must be added for changes in enthalpy, $\int dH$ (Eq. (7.12)), and entropy, $\int dS$ (Eq. (7.20)). If the pressure is to be changed, the free energy must also be adjusted according to Eq. (7.32). Combining all these terms into one expression gives

$$\Delta\bar{G}_{f,T,P} = \left(\Delta H_{f,298}^\circ + \int_{298}^T C_p dT \right) - T \left(S_{298}^\circ + \int_{298}^T \left(\frac{C_p}{T} \right) dT \right) + \int_{10^5}^P V dP \quad (7.44)$$

Substituting the polynomial expression for C_p (Eq. (7.13)) and integrating, we obtain

$$\begin{aligned} \Delta\bar{G}_{f,T,P} = & \Delta H_{f,298}^\circ - TS_{298}^\circ + a(T - 298) + \frac{b}{2}(T^2 - 298^2) \\ & - c \left(\frac{1}{T} - \frac{1}{298} \right) + 2d \left(T^{1/2} - 298^{1/2} \right) \\ & - T \left[a \ln \left(\frac{T}{298} \right) + b(T - 298) \right. \\ & \left. - \frac{c}{2} \left(\frac{1}{T^2} - \frac{1}{298^2} \right) - 2d \left(\frac{1}{T^{1/2}} - \frac{1}{298^{1/2}} \right) \right] \\ & + \int_{10^5}^P V dP \end{aligned} \quad (7.45)$$

If a computer has not yet been used in solving problems in this text, Eq. (7.45) will rapidly convince the reader of its advantages. The last term in this equation has not been integrated. If pressure remains constant, the term becomes zero. Because the compressibilities of minerals and magmas are extremely small, V can be considered a constant, so when pressure does vary, this term becomes $V(P - 10^5)$. But for a gas, V is certainly not a constant, and the variation of V with P must be known before we can integrate this term. This problem is dealt with in Section 8.3.

7.10 PROBLEMS

7.1 If the molar volume of a peridotite is $5 \times 10^{-5} \text{ m}^3$, and its volume increase on totally melting is 10%, how much work is done when 1 mol of peridotite melts at a depth where the pressure is 2 GPa? Note that the system being considered is the 1 mol of rock. Be certain to get the sign convention correct (see Fig. 7.1).

7.2 If the molar volume of granitic magma is $7 \times 10^{-5} \text{ m}^3$, and on crystallizing it decreases by 10%, compare the work done by magma crystallizing near the top of a batholith, where the pressure is 0.05 GPa, with magma crystallizing near the base of the batholith, where the pressure is 0.5 GPa. Be careful of the sign convention.

7.3 From data in Table 7.1, and using Eq. (7.14), determine the enthalpy of formation of kyanite and andalusite at 466 K and 10^5 Pa (1 bar). If kyanite were to change into andalusite under these conditions, what would be the enthalpy of reaction? Is the reaction exothermic or endothermic? (Be careful of the sign convention; write the reaction kyanite \rightarrow andalusite, then ΔH_r is the final enthalpy minus the initial.)

7.4 Using the ΔH_f° at 298.15 K and heat capacity data in Table 7.1, calculate the enthalpy of reaction at 10^5 Pa and 1500 K for the reaction forsterite + quartz \rightarrow enstatite.

7.5 In dolomite, calcium has two different possible sites to occupy at high temperatures, but at low temperatures it preferentially enters one of these sites, and magnesium occupies the other. Calculate the configurational entropy associated with the complete disordering of dolomite.

7.6 If entropy is a function of temperature and pressure, that is, $S = S(T, P)$, (a) write the total differential of $S(T, P)$, and (b) show that the total differential of $S(T, P)$ is given by

$$dS = \left(\frac{C_p}{T} \right) dT - \alpha V dP$$

where α is the coefficient of thermal expansion (Eq. (2.2)). [Hint: Use derivatives of $G(T, P)$.]

7.7 Convection within the mantle or within a magma chamber causes the thermal gradient to approach the adiabatic gradient ($dQ = 0$ and $dS = 0$). Using the expression for dS in Problem 7.6b, along with the cyclical rule for partial derivatives, show that the adiabatic gradient is given by

$$\left(\frac{\partial T}{\partial P} \right)_S = \frac{T \bar{V} \alpha}{C_p}$$

7.8 The granitic magma in Problem 7.2, which has a molar volume of $7 \times 10^{-5} \text{ m}^3$, has a molecular weight of 0.168 kg ($\rho = 2.4 \text{ Mg m}^{-3}$), a coefficient of thermal expansion, α , of $2 \times 10^{-5} \text{ K}^{-1}$, a heat capacity, C_p , of $0.8 \text{ kJ kg}^{-1} \text{ K}^{-1}$, and a temperature of 900 °C (1173 K).

(a) If magmatic convection has established an adiabatic temperature gradient within the body, calculate the value of $(\partial T / \partial P)_S$ from the relation in Problem 7.7. (Note $1 \text{ J} = 1 \text{ Pa m}^3$.)

(b) Using the relation $dP = \rho g dz$ (Eq. (1.1)), calculate the adiabatic temperature gradient, $(\partial T / \partial z)_S$, in this convecting body of magma, and compare this value with a typical geothermal gradient in the upper continental crust.

7.9 From the data in Table 7.1 and using Eq. (7.21), calculate the entropies of kyanite and andalusite at 466 K and

- 10^5 Pa. What entropy change accompanies the change of kyanite to andalusite under these conditions?
- 7.10** Using the results for ΔH° and ΔS° from Problem 7.3 and 7.9 respectively, calculate the free energy change, ΔG_r (Eq. (7.27)), for the reaction of kyanite to andalusite at 466 K and 10^5 Pa. From the value of the ΔG_r° , what can you conclude about this reaction under these conditions of temperature and pressure?
- 7.11** For the reaction kyanite \rightarrow andalusite at 466 K and 10^5 Pa calculated in Problem 7.10, determine the change in the ΔG_r if the pressure is increased to 10^8 Pa at 466 K. Which of the minerals will be more stable under these new conditions? (Recall that $1 \text{ J} = 1 \text{ Pa m}^3$.)
- 7.12** For the reaction kyanite \rightarrow andalusite calculated in Problem 7.11, calculate how much the temperature would have to be increased at a pressure of 10^8 Pa in order to return the value of ΔG_r to zero, that is, to reestablish equilibrium. Assume that the entropy change for the reaction remains constant and is equal to the value calculated in Problem 7.9.
- 7.13** Using Eq. (7.45), calculate the ΔG_f of calcite and of aragonite at 800 K and 10^5 Pa. Which phase is more stable under these conditions?
- 7.14** Using Eq. (7.45), calculate the ΔG_f of calcite and of aragonite at 298.15 K and 0.5 GPa. Which phase is more stable under these conditions?