

Thermodynamics of a pure substance at the triple point

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A thermodynamic study of a pure substance at the triple point is presented. In particular, we show that the mass fractions of the phases coexisting at the triple point obey lever rules in the specific entropy-specific volume diagram, and the relative changes in the mass fractions present in each phase along reversible isochoric and adiabatic processes of a pure substance at the triple point are governed by the relative sizes of the segments of the triple-point line in the pressure-specific volume diagram and in the temperature-specific entropy diagram. Applications to the ordinary triple point of water and to the triple point of Al_2SiO_5 polymorphs are presented. © 2007 American Association of Physics Teachers.

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I. INTRODUCTION

The number of independent intensive variables, r , which determine the state of a heterogeneous system is given by the Gibbs's phase rule,

$$r = c - \phi + 2, \quad (1)$$

where c is the number of independent components and ϕ is the number of phases in the system. The phase rule (1) establishes that for a pure substance ($c=1$), the maximum number of phases that can coexist in equilibrium is three ($\phi=3$). The states where three phases coexist are called triple points. Most pure substances have a triple point in which solid, liquid, and vapor phases coexist, but other triple points involving any three phases (for example, polymorphic solids and ^4He) can be formed. The essential feature of a triple point is that $r=0$, that is, there are no independent intensive variables at the triple point. The pure substance is then said to have zero degrees of freedom and the system is invariant, which means that its intensive state is given by fixed values of the temperature and pressure. Therefore, the triple points are isolated points in the pressure-temperature (PT) phase diagram, and are reproducible under the same conditions. This invariance explains the usefulness of triple points as fixed thermometric points.

There are six triple points among the 17 defining thermometric fixed points of the International Temperature Scale of 1990 (ITS-90).¹ The study of PT phase diagrams, where the triple points play a fundamental role, are of paramount importance in the thermodynamics of materials, including geomaterials.^{2,3} For example, the region of the PT phase diagram that includes the triple point of the Al_2SiO_5 polymorphs provides a fundamental pattern (petrogenetic grid) for estimating the conditions of pressure and temperature under which an Al_2SiO_5 metamorphic rock⁴ crystallizes.^{5,6}

The aim of this paper is two-fold. We will show that the mass fractions of the phases coexisting at the triple point follow lever rules in the specific (per unit mass) entropy-specific volume (sv) diagram, generalizing familiar lever rules for a two-phase system. We also show that the relative changes in the mass fractions of each phase along reversible isochoric (constant volume) and adiabatic (isentropic) processes of a pure substance at the triple point are governed by the relative sizes of the segments of the triple-point line in

the pressure-specific volume (Pv) diagram and in the temperature-specific entropy (Ts) diagram, respectively. These results are applied to the triple points of water (ice I-liquid-vapor) and Al_2SiO_5 (andalusite-kyanite-sillimanite). The interest in the triple point of water rests mainly on the fact that the definition of the Kelvin is based on this point and its practical realization in triple point cells. The main interest in the triple point of Al_2SiO_5 polymorphs arises from the fact that the use of this system as a primary geothermobarometer is related to the frequent occurrence of the three polymorphs in fine-grained mudstones, siltstones, and shales with different metamorphic grade (metapelitic rocks).^{3,5,6}

II. LEVER RULES AT THE TRIPLE POINT

Let v and s be the specific volume and the specific entropy of a three-phase (α , β , and γ) state of a substance at the triple point. We consider a mass m of a pure substance at the triple point so that m_α is the mass in the phase α , m_β is the mass in the phase β , and m_γ is the mass in the phase γ ($m=m_\alpha+m_\beta+m_\gamma$). If $x_\alpha \equiv m_\alpha/m$, $x_\beta \equiv m_\beta/m$, and $x_\gamma \equiv m_\gamma/m$ are the mass fractions associated with the phases α , β , and γ , we have

$$x_\alpha + x_\beta + x_\gamma = 1, \quad (2)$$

$$v_\alpha x_\alpha + v_\beta x_\beta + v_\gamma x_\gamma = v, \quad (3)$$

$$s_\alpha x_\alpha + s_\beta x_\beta + s_\gamma x_\gamma = s, \quad (4)$$

where v_α , v_β , and v_γ are the specific volumes of the three phases at the triple point, and s_α , s_β , and s_γ are the corresponding specific entropies. Equations similar to Eqs. (3) and (4) also hold for specific internal energies or specific enthalpies. From Eqs. (2)–(4), we obtain

$$x_\alpha = \frac{v_\beta \gamma (s - s_\beta) - s_\beta \gamma (v - v_\beta)}{v_\beta \gamma s_{\beta\alpha} - v_\beta \alpha s_{\beta\gamma}}, \quad (5)$$

$$x_\beta = \frac{v_\gamma \alpha (s - s_\gamma) - s_\gamma \alpha (v - v_\gamma)}{v_\beta \gamma s_{\beta\alpha} - v_\beta \alpha s_{\beta\gamma}}, \quad (6)$$

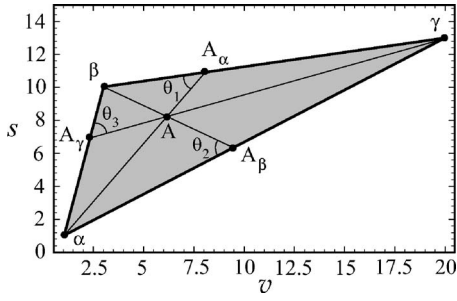


Fig. 1. The sv -diagram at the triple point for a pure substance with phases α , β , and γ . The specific entropies and specific volumes are taken in arbitrary units to be $v_\alpha=1$, $v_\beta=3$, $v_\gamma=20$, $s_\alpha=1$, $s_\beta=10$, and $s_\gamma=13$. A is an arbitrary point either within the triangle or on a side.

$$x_\gamma = \frac{v_{\alpha\beta}(s - s_\alpha) - s_{\alpha\beta}(v - v_\alpha)}{v_{\beta\gamma}s_{\beta\alpha} - v_{\beta\alpha}s_{\beta\gamma}}, \quad (7)$$

where we have used the notation $f_{ij} \equiv f_j - f_i$. Two remarks can be made from Eqs. (5)–(7). From Duhem's theorem,^{7,8} if the total mass m is known, a three-phase state is completely specified by two specific variables that can be chosen, for example, from the set $(v, s, x_\alpha, x_\beta, x_\gamma)$, and the mass fractions are linear functions of both v and s .

If we choose s and v as the two specific variables that specify the state of the system at the triple-point and use Eq. (5), we find that the line $s = s_\beta + s_{\beta\gamma}(v - v_\beta)/v_{\beta\gamma}$ defines the states for which $x_\alpha = 0$. Similarly, if we use Eqs. (6) and (7), we find the lines that define the states for which $x_\beta = 0$ and $x_\gamma = 0$, respectively. These three lines form a triangle in the sv -diagram (see Fig. 1) whose sides correspond to states in which only two phases are present.^{9,10} The vertices of the triangle correspond to states in which only one phase is present, for example $(x_\beta = 1, x_\gamma = x_\alpha = 0)$ corresponds to the vertex β ; the points inside the triangle correspond to states in which the three phases are present ($x_\beta \neq 0, x_\gamma \neq 0, x_\alpha \neq 0$). In these diagrams the loci of constant values of a given specific variable are straight lines of the same slope. In particular, the loci of constant values of a mass fraction are straight lines parallel to that side of the triangle along which this mass fraction takes the zero value. Because of the Clapeyron-Clausius equation,

$$\left(\frac{dP}{dT}\right)_{\alpha\beta} = \frac{s_{\beta\alpha}}{v_{\beta\alpha}}, \quad (8)$$

the slope of a side such as $\alpha\beta$ of the triangle in the sv diagram of a triple-point system coincides with the slope of the corresponding coexistence curve ($\alpha\beta$) at the triple point in the PT phase diagram.

An alternative way to determine the sv -diagram is by considering the Gibbs's surface of the pure substance.^{11–14} This surface represents the specific internal energy u as a function of the variables s and v ; that is, the fundamental equation (or characteristic function) in the energy representation, $u = u(s, v)$, which contains all thermodynamic information about the system.¹⁵ Because $T = (\partial u / \partial s)_v$ and $P = -(\partial u / \partial v)_s$, the temperature and the pressure at any point on the Gibbs's surface are determined by the two slopes of the plane tangent to the surface at that point. In the regions representing a unique phase, a definite temperature and pressure determine one definite volume, so that the tangent plane touches such

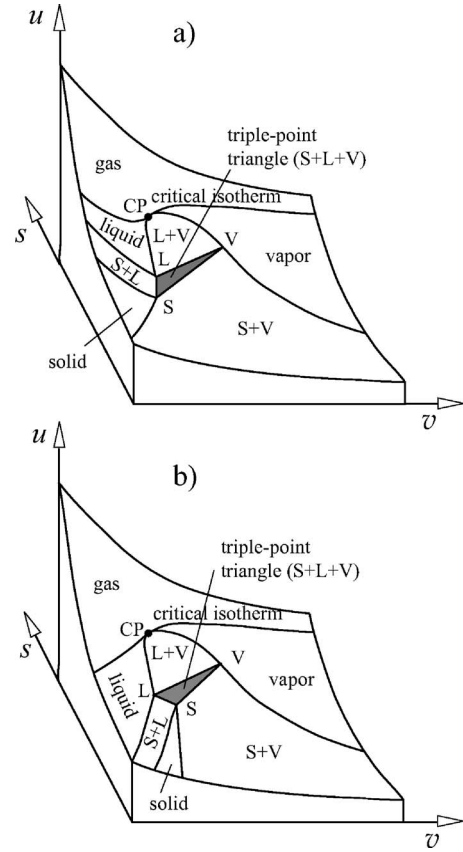


Fig. 2. The Gibbs's surface of a pure substance that (a) contracts upon freezing and (b) expands upon freezing. The triple point region has the shape of a triangle with vertices corresponding, respectively, to the pure phases solid (S), liquid (L), and vapor (V). CP is the critical point.

regions at only one point (these regions are *skew surfaces*). In the regions representing equilibrium between two phases, the temperature and the pressure are related and do not determine a unique volume, and a tangent plane touches a two-phase region along a line (these regions are *ruled surfaces*). At the triple point, because all proportions of the three phases are in equilibrium at the same temperature and pressure, the tangent plane touches the surface at all of these points; that is, this region is a plane triangle whose vertices correspond to the pure phase α , β , and γ . Typical Gibbs's surfaces for two pure substances in their solid, liquid, and vapor phases are shown in Fig. 2. Figure 2(a) corresponds to a substance for which the liquid contracts upon freezing, and Fig. 2(b) corresponds to a substance for which the liquid expands upon freezing. In particular, the projection onto the sv -plane of the triple-point triangle in Fig. 2(a) provides a triple point sv -diagram of the kind plotted in Fig. 1.

An sv -diagram allows for a simple geometrical interpretation of Eqs. (5)–(7). Consider a state A with coordinates (v, s) in the triangle $\alpha\beta\gamma$ (see Fig. 1). The area of a triangle with vertices at (v_1, s_1) , (v_2, s_2) , and (v_3, s_3) is given by

$$\text{Area}(123) = \pm \frac{1}{2} \begin{vmatrix} v_1 & s_1 & 1 \\ v_2 & s_2 & 1 \\ v_3 & s_3 & 1 \end{vmatrix} = \pm \frac{1}{2} (v_1 s_2 + v_2 s_3 + v_3 s_1 - v_1 s_3 - v_2 s_1 - v_3 s_2), \quad (9)$$

where the sign is chosen so that one takes the positive result. Then Eqs. (5)–(7) become (see Fig. 1)

$$x_\alpha = \frac{\text{Area}(\alpha\beta\gamma)}{\text{Area}(\alpha\beta\gamma)} = \frac{\frac{1}{2}\overline{\beta\gamma} \overline{A_\alpha A} \sin \theta_1}{\frac{1}{2}\overline{\beta\gamma} \overline{A_\alpha \alpha} \sin \theta_1} = \frac{\overline{A_\alpha A}}{\overline{A_\alpha \alpha}}, \quad (10)$$

$$x_\beta = \frac{\text{Area}(\alpha A \gamma)}{\text{Area}(\alpha\beta\gamma)} = \frac{\frac{1}{2}\overline{\alpha\gamma} \overline{A_\beta A} \sin \theta_2}{\frac{1}{2}\overline{\alpha\gamma} \overline{A_\beta \beta} \sin \theta_2} = \frac{\overline{A_\beta A}}{\overline{A_\beta \beta}}, \quad (11)$$

$$x_\gamma = \frac{\text{Area}(\alpha\beta A)}{\text{Area}(\alpha\beta\gamma)} = \frac{\frac{1}{2}\overline{\alpha\beta} \overline{A A_\gamma} \sin \theta_3}{\frac{1}{2}\overline{\alpha\beta} \overline{\gamma A_\gamma} \sin \theta_3} = \frac{\overline{A A_\gamma}}{\overline{\gamma A_\gamma}}, \quad (12)$$

respectively, where we have used the formula for the area of a triangle. Three points on the same straight line form a triangle of zero area and, thus, if the state A lies on one side of the shaded triangle in Fig. 1, the mass fraction of the phase associated with the vertex opposite to the line is zero. For example, if the state A lies on the side $\beta\gamma$, we have $\text{Area}(\alpha\beta\gamma)=0$, and Eqs. (10)–(12) give

$$x_\alpha = 0, \quad (13)$$

$$x_\beta = \frac{\text{Area}(\alpha A \gamma)}{\text{Area}(\alpha\beta\gamma)} = \frac{\overline{\gamma A}}{\overline{\gamma \beta}} = \frac{v_\gamma - v}{v_{\beta\gamma}} = \frac{s_\gamma - s}{s_{\beta\gamma}}, \quad (14)$$

$$x_\gamma = \frac{\text{Area}(\alpha\beta A)}{\text{Area}(\alpha\beta\gamma)} = \frac{\overline{A\beta}}{\overline{\gamma\beta}} = \frac{v - v_\beta}{v_{\beta\gamma}} = \frac{s - s_\beta}{s_{\beta\gamma}}. \quad (15)$$

Equations (14) and (15) are the well-known lever rules for a pure substance when only two phases (in this case, β and γ) are present.^{16–19} Equations (10)–(12) can be considered as generalized lever rules for a pure substance at the triple point.

III. TRANSFERRING ENERGY TO A SUBSTANCE AT THE TRIPLE POINT

By heating (cooling) and/or by compressing (expanding) reversibly a substance, we can change the relative masses of the three coexisting phases, while the pressure and the temperature remain constant at their triple point values. To analyze these changes, we consider a mass m of a pure substance at the triple point, so that x_α , x_β , and x_γ are the mass fractions in the α , β , and γ phases, respectively. Assume that an amount of heat $Q = T_{\text{tp}}\Delta S$ is transferred reversibly to the substance, and that the volume of the substance changes by ΔV due to an amount of work $W = -P_{\text{tp}}\Delta V$ done reversibly on the substance, where T_{tp} is the triple point temperature and P_{tp} is the triple point pressure. Then, from Eqs. (5)–(7), the changes of the mass fractions are given by

$$\Delta x_\alpha = \frac{v_{\beta\gamma}q - h_{\beta\gamma}\Delta v}{v_{\beta\gamma}h_{\beta\alpha} - v_{\beta\alpha}h_{\beta\gamma}}, \quad (16)$$

$$\Delta x_\beta = \frac{v_{\gamma\alpha}q - h_{\gamma\alpha}\Delta v}{v_{\beta\gamma}h_{\beta\alpha} - v_{\beta\alpha}h_{\beta\gamma}}, \quad (17)$$

$$\Delta x_\gamma = \frac{v_{\alpha\beta}q - h_{\alpha\beta}\Delta v}{v_{\beta\gamma}h_{\beta\alpha} - v_{\beta\alpha}h_{\beta\gamma}}, \quad (18)$$

where $q = Q/m$, $\Delta v = (\Delta V)/m$, and $h_{ij} = T_{\text{tp}}s_{ij}$ are the change in the specific enthalpy associated with the transition from

phase i to phase j . Equations (16)–(18) are very interesting because they give us information about the energy (transferred as heat and/or work) necessary to determine the mass fractions of the coexisting phases. For example, we can determine the heat and/or the work necessary for a phase to disappear. Furthermore, from Eqs. (16)–(18) we can easily check the mass conservation in the system

$$\Delta x_\alpha + \Delta x_\beta + \Delta x_\gamma = 0. \quad (19)$$

From Eq. (19) we have

$$\frac{\Delta x_\gamma}{\Delta x_\alpha} = -1 - \frac{\Delta x_\beta}{\Delta x_\alpha} \quad \text{and} \quad \frac{\Delta x_\gamma}{\Delta x_\beta} = -1 - \left(\frac{\Delta x_\beta}{\Delta x_\alpha}\right)^{-1}, \quad (20)$$

so that a knowledge of the relative fraction $\Delta x_\beta/\Delta x_\alpha$ lets us determine the two remaining relative fractions, $\Delta x_\gamma/\Delta x_\alpha$ and $\Delta x_\gamma/\Delta x_\beta$.

Let us consider that heat is transferred reversibly to a pure substance at the triple point, but its volume is kept fixed ($\Delta v = 0$). Then, from Eqs. (16) and (17) we obtain

$$\left(\frac{\Delta x_\beta}{\Delta x_\alpha}\right)_{\Delta v=0} = -\frac{v_{\alpha\gamma}}{v_{\beta\gamma}}. \quad (21)$$

Equation (21) shows that when we reversibly supply heat (by thermal contact with a heat reservoir at temperature T_{tp}) to a constant-volume substance at the triple point, the changes in the mass fractions are governed by the relative sizes of the segments $v_{\alpha\gamma}$ and $v_{\beta\gamma}$ of the triple point line in the Pv -diagram.

Now, suppose that we change ($\Delta S = 0$), the volume, reversibly and adiabatically (that is, work is done reversibly on or by the system and may, thus, be positive or negative) of a substance at the triple point. From Eqs. (16) and (17) we obtain

$$\left(\frac{\Delta x_\beta}{\Delta x_\alpha}\right)_{q=0} = -\frac{h_{\alpha\gamma}}{h_{\beta\gamma}} = -\frac{s_{\alpha\gamma}}{s_{\beta\gamma}}. \quad (22)$$

Equation (22) shows that, when the volume of a substance at the triple point is changed reversibly and adiabatically, the changes in the mass fractions are governed by the relative sizes of the segments $s_{\alpha\gamma}$ and $s_{\beta\gamma}$ of the triple point line in the Ts diagram.

IV. APPLICATIONS

Now we apply the results of the Sec. III to water at its ordinary triple point and to the triple point of the polymorphs of Al_2SiO_5 , with the objective of analyzing the relative changes of the coexisting phases when there is only reversible heat transfer or only reversible work done with a three-phase system.

Water. Water has a triple point at $T_{\text{tp}} = 273.16$ K and $P_{\text{tp}} = 611.3$ Pa. At this point solid (S) liquid (L), and vapor (V) coexist with values of specific volumes and specific entropies given in Table I. If we use the Clapeyron–Clausius equation (9), the slopes of the coexistence curves in the PT phase diagram are given by

Table I. Triple-point thermodynamic data of the phases for water (Ref. 20) and Al_2SiO_5 polymorphs (Ref. 21).

Water			Al_2SiO_5		
Phase	v ($\text{m}^3 \text{kg}^{-1}$)	s ($\text{kJ kg}^{-1} \text{K}^{-1}$)	Phase	v ($\text{m}^3 \text{kg}^{-1}$)	s ($\text{kJ kg}^{-1} \text{K}^{-1}$)
solid (S)	1.0908×10^{-3}	-1.221	kyanite (K)	2.7467×10^{-4}	1.4702
liquid (L)	1.000×10^{-3}	0.000	andalusite (A)	3.2056×10^{-4}	1.5263
vapor (V)	206.14	9.1562	sillimanite (S)	3.0860×10^{-4}	1.5408

$$\left(\frac{dP}{dT}\right)_{\text{SL}} = -13447.1 \frac{\text{kPa}}{\text{K}}, \quad (23a)$$

$$\left(\frac{dP}{dT}\right)_{\text{LV}} = 44.41 \frac{\text{Pa}}{\text{K}}, \quad (23b)$$

$$\left(\frac{dP}{dT}\right)_{\text{SV}} = 50.34 \frac{\text{Pa}}{\text{K}}. \quad (23c)$$

Using these values, the PT phase diagram of water near its triple point is shown in Fig. 3(a), and the sv diagram of the triple-point triangle is plotted in Fig. 3(b). We note that the slopes of the triangle sides are also given by Eq. (23).

Figure 3(b) allows for a qualitative analysis of the evolution of water at the triple point after reversible heat transfer and/or work is done. For example, a reversible heating process at constant volume (upward vertical process) increases the liquid + vapor fraction until the solid disappears, and an adiabatic reversible expansion process (horizontal process to the right) increases the solid + vapor fraction until the liquid disappears. A quantitative study requires the calculation of the mass fraction changes. This quantitative analysis can be of practical interest for controlling the relative amounts of solid, liquid, and vapor inside water triple-point cells. For example, we use the data from Table I and Eq. (16) and obtain

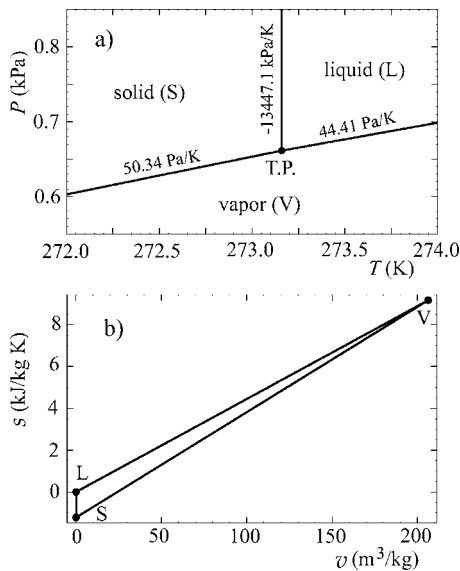


Fig. 3. (a) Water PT phase diagram in the neighborhood of its triple point. (b) Triple point triangle for water in the sv plane. The data from Table I for water are used.

$$(\Delta x_S)_{\Delta v=0} = \frac{v_{\text{LV}}}{T_{\text{tp}}(v_{\text{LV}}s_{\text{LS}} - v_{\text{LS}}s_{\text{LV}})} q = -2.998 \times 10^{-3} q, \quad (24)$$

with q given in kJ kg^{-1} , and from Eqs. (21) and (20),

$$\left(\frac{\Delta x_L}{\Delta x_S}\right)_{\Delta v=0} = -\frac{v_{\text{SV}}}{v_{\text{LV}}} = -0.999\,999\,56 \approx -1 \quad (25)$$

and

$$\left(\frac{\Delta x_V}{\Delta x_S}\right)_{\Delta v=0} = -1 - \left(\frac{\Delta x_L}{\Delta x_S}\right)_{\Delta v=0} = -4.4 \times 10^{-7} \approx 0. \quad (26)$$

Equations (24)–(26) show that, when heat is transferred ($q > 0$) reversibly to a fixed volume of water at the triple point, the mass in the liquid phase increases at the expense of the mass in the solid phase while the mass in the vapor phase increases very slightly (remaining almost constant). From Eq. (16) we have

$$(\Delta x_S)_{q=0} = -\frac{s_{\text{LV}}}{v_{\text{LV}}s_{\text{LS}} - v_{\text{LS}}s_{\text{LV}}} \Delta v = 3.638 \times 10^{-2} \Delta v, \quad (27)$$

with Δv given in $\text{m}^3 \text{kg}^{-1}$, and from Eqs. (22) and (20),

$$\left(\frac{\Delta x_L}{\Delta x_S}\right)_{q=0} = -\frac{s_{\text{SV}}}{s_{\text{LV}}} = -1.133, \quad (28)$$

$$\left(\frac{\Delta x_V}{\Delta x_S}\right)_{q=0} = -1 - \left(\frac{\Delta x_L}{\Delta x_S}\right)_{q=0} = 0.133. \quad (29)$$

Equations (27)–(29) show that, when work is reversibly and adiabatically done by compression ($\Delta v < 0$) at the triple point, the mass in the liquid phase increases at the expense of both the mass in the solid and vapor phases, and the decrease in the mass fraction of the solid phase is about 7.5 times that of the vapor phase.

Al_2SiO_5 polymorphs. Metamorphosed aluminous rocks contain Al_2SiO_5 polymorphs: kyanite (K), andalusite (A), and sillimanite (S). The triple point of this system defines a very useful fixed point in metamorphic petrology. Although there are several estimates of the pressure and temperature of the triple point among the polymorphs of Al_2SiO_5 , the values of $P_{\text{tp}} = 3.87 \pm 0.3$ kbar and $T_{\text{tp}} = 784 \pm 20$ K are currently preferred by petrologists.²¹ The specific volume and entropy values for this system at the triple point are given in Table I. These values have been calculated by us from an internally consistent thermodynamic data set for kyanite, andalusite, and sillimanite given in Ref. 22. From the Clapeyron–Clausius equation (9) the slopes of the coexistence curves in the PT phase diagram are given by

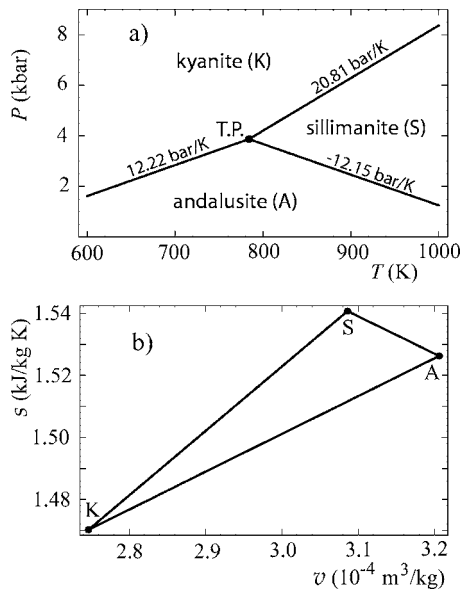


Fig. 4. (a) PT phase diagram for the system Al_2SiO_5 in the neighborhood of its triple point. (b) Triple point triangle for Al_2SiO_5 polymorphs in the sv plane. The data from Table I for Al_2SiO_5 polymorphs are used.

$$\left(\frac{dP}{dT}\right)_{KS} = 20.81 \text{ bar/K}, \quad (30a)$$

$$\left(\frac{dP}{dT}\right)_{KA} = 12.22 \text{ bar/K}, \quad (30b)$$

$$\left(\frac{dP}{dT}\right)_{SV} = -12.15 \text{ bar/K}. \quad (30c)$$

Using these values, the PT phase diagram of Al_2SiO_5 is shown in Fig. 4(a), while the sv diagram of the associated triple-point triangle is plotted in Fig. 4(b).

Figure 4(b) allows for a qualitative analysis of the evolution of coexisting kyanite, andalusite, and sillimanite samples as a consequence of thermodynamic processes due to the movement of magma toward the earth's surface (magmatic activity). In particular, we can see that reversible heating events produce sillimanite, and reversible cooling events produce kyanite + andalusite. Also, reversible high pressure (compression) events produce kyanite + sillimanite, and reversible low-pressure (decompression) events produce andalusite. Therefore, the occurrence of coexisting kyanite, andalusite, and sillimanite at the intersections of andalusite-kyanite and kyanite-sillimanite zones suggests a magmatic activity characterized by heating and decompression events. A quantitative study requires the calculation of the mass fraction changes. If we use the data from Table I, from Eq. (16) we have

$$(\Delta x_S)_{\Delta v=0} = \frac{v_{KA}}{T_{tp}(v_{KA}s_{KS} - v_{KS}s_{KA})} q = 4.377 \times 10^{-2} q, \quad (31)$$

with q given in kJ kg^{-1} . From Eqs. (21) and (20) we have

$$\left(\frac{\Delta x_K}{\Delta x_S}\right)_{\Delta v=0} = -\frac{v_{SA}}{v_{KA}} = -0.261 \quad (32)$$

and

$$\left(\frac{\Delta x_A}{\Delta x_S}\right)_{\Delta v=0} = -1 - \left(\frac{\Delta x_K}{\Delta x_S}\right)_{\Delta v=0} = -0.739. \quad (33)$$

Equations (31)–(33) show that when heat is supplied ($q > 0$) reversibly to a fixed volume of Al_2SiO_5 at the triple point, the presence of sillimanite increases at the expense of both kyanite and andalusite, and the decrease in the mass fraction of andalusite is about 2.8 times that of kyanite.

From Eq. (16) we have

$$(\Delta x_S)_{q=0} = -\frac{s_{KA}}{v_{KA}s_{KS} - v_{KS}s_{KA}} \Delta v = -41931.5 \Delta v, \quad (34)$$

with Δv given in $\text{m}^3 \text{kg}^{-1}$, and from Eqs. (22) and (20) we have

$$\left(\frac{\Delta x_K}{\Delta x_S}\right)_{q=0} = -\frac{s_{SA}}{s_{KA}} = 0.259, \quad (35)$$

$$\left(\frac{\Delta x_A}{\Delta x_S}\right)_{q=0} = -1 - \left(\frac{\Delta x_K}{\Delta x_S}\right)_{q=0} = -1.259. \quad (36)$$

Equations (34)–(36) show that, in reversible adiabatic compression ($\Delta v < 0$) processes of Al_2SiO_5 at the triple point, the presence of sillimanite and kyanite increases while andalusite decreases, and the increase in the mass fraction of sillimanite is about four times that of kyanite.

V. SUMMARY

In summary, the possible states of a pure substance at the triple point can be represented by a triangle in a sv -diagram. The vertices of the triangle are single-phase states, the sides of the triangle are two-phase states, and the points inside the triangle are three-phase states. Then the relative mass amount in each phase can be obtained by using simple lever rules. Furthermore, by reversibly exchanging heat and/or doing work with a substance at the triple point, we can change the amount of the substance that exists in each of the three phases. In particular, if the substance is kept at constant volume or is surrounded by adiabatic walls, the relative changes of the mass fractions when energy is reversibly transferred to the substance are given by the ratio between the portions of the triple-point line in the Pv -diagram and in the Ts -diagram, respectively. These results are a consequence of the linearity of the mass fraction in each phase versus the total specific entropy and the total specific volume of a pure substance at the triple point.

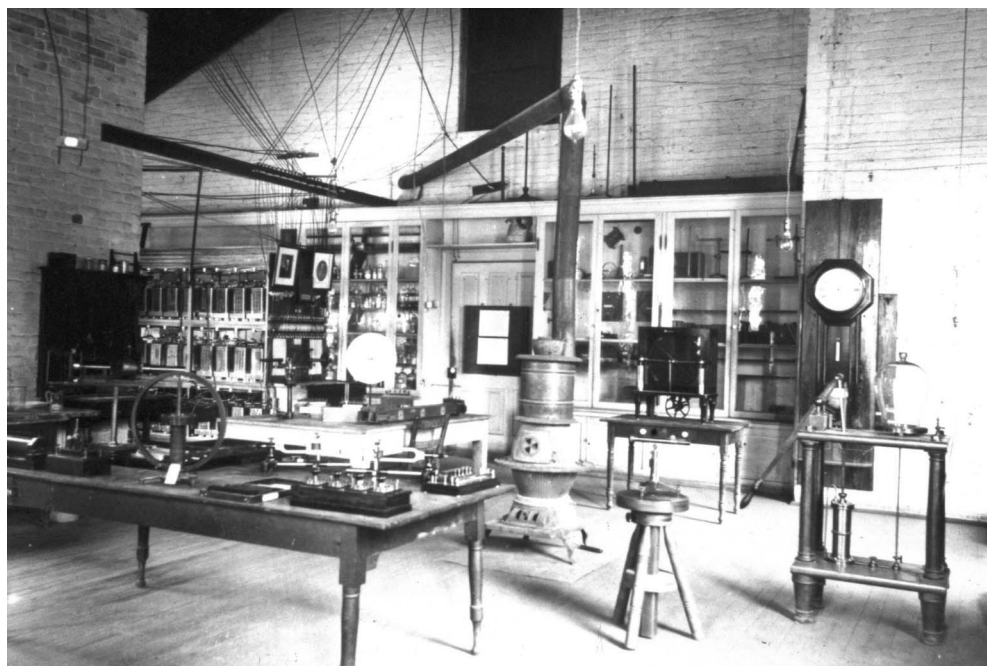
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Apparatus at Washington and Lee. This picture was taken of the apparatus collection at Washington and Lee College ca. 1900. On the stool is a seven-mirror device for spectrum recombination. At the right hand side is a large "American"-style vacuum pump with a bell jar. An electrostatic machine is on the small table to the right of the stove. A set of chemical cells (probably Edison cells) is on the back wall on the left hand side. On the right-hand side of the large table is a pair of driven tuning forks for demonstrating Lissajous figures, and to the left is the large circular coil of a tangent galvanometer. A spectrometer can be seen below the two hanging portraits. (Notes by Thomas B. Greenslade, Jr., Kenyon College)