[AMERICAN JOURNAL OF SCIENCE, VOL. 251, APRIL 1953, PP. 299-308]

A NOTE ON THE STABILITY OF JADEITE

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ABSTRACT. By the use of certain simplifying assumptions the stability pressure, at various temperatures, for the formation of jadeite from nepheline and albite is calculated from thermal data. The pressure increases by about 18 bars per degree; and at 400° C. the pressure is estimated to be 4800 bars. From the known behavior of hydrates under high pressure it is suggested that under pressure analcite may melt incongruently to form jadeite and water, so that at a sufficiently high pressure jadeite rather than analcite would be produced from a mixture of the correct composition, even in presence of excess water.

THE EFFECT OF PRESSURE ON STABILITY

ONE of the comparatively rare minerals is jadeite, which is a hard, dense material having a composition that is represented by the formula $Na_2O \cdot Al_2O_3 \cdot 4SiO_2$ with varying amounts of diopside and other substances in solid solution. It is of especial interest because it has never been synthesized, despite much effort on the part of numerous investigators to accomplish this. One of the earliest attempts, which was inconclusive, was by Professor Pentti Eskola and the writer when the former was a guest investigator at the Geophysical Laboratory about twenty-five years ago. When natural jadeite is heated it begins to decompose at temperatures as low as 800° C., first forming a certain amount of glass (Greig and Barth, 1938) and then recrystallizing to a mixture of nepheline ($Na_2O \cdot Al_2O_3 \cdot 2SiO_2$) and albite ($Na_2O \cdot Al_2O_3 \cdot 6SiO_2$). Glass of jadeite composition, when held at 900° or 1000° crystallizes into nepheline and albite, but at 800° or lower the material seems to persist indefinitely as glass (Yoder, 1950). As reported by Yoder, the unpublished work of Morey and of Bowen and Tuttle shows that with a mixture of the composition of jadeite in the presence of water vapor at a pressure of 1000 or 2000 atmospheres and at temperatures of 600° to 700° nepheline and albite are produced, while at temperatures of 400° to 550° the hydrated compound analcite, $Na_2O \cdot Al_2O_3 \cdot 4SiO_2 \cdot 2H_2O$, forms promptly. Further experimental work by Yoder (1950) at pressures extending to somewhat more than 2000 bars yielded a definite pressure-temperature curve for the decomposition of analcite into nepheline plus albite plus water. The equilibrium pressure increases rapidly with temperature, the relation being approximately linear, except possibly at the lower pressures. Representative points on the line are 500 bars at 538° and 2000 bars at 563°.

If we consider the reaction

$$\tfrac{1}{2}\,\mathrm{Ne} + \tfrac{1}{2}\,\mathrm{Ab} = \mathrm{Jd} \qquad (1)$$

in which the symbols, in order, stand for nepheline, albite, and jadeite respectively, with the formulas written as above, we note that the reaction proceeds with a diminution of volume. The respective densities of synthetic nepheline, natural albite, and natural jadeite at room temperatures and atmospheric pressure are 2.619, 2.605, and 3.328, from which it is readily calculated that the reaction as written proceeds with a volume change of -33.4 cm^3. It is a well known principle of thermodynamics that high pressure favors the formation of dense materials. If, for example, a substance such as jadeite is unstable at atmospheric pressure with respect to nepheline and albite (which definitely seems to be the case at high temperatures), then, without knowing any properties of the materials except their densities or specific volumes, we may be sure that at a sufficiently high pressure jadeite will be the stable form at the temperature to which the measurements pertain. Quantitatively, the situation may be described by the well known equation

$$\delta\,(\Delta\,F) = \Delta\,V\,\delta\,P \qquad (2)$$

in which $\Delta\,F$ is the free energy for the reaction, $\Delta\,V$ is the volume change, and P the pressure. The equation states that the variation in the free energy change is equal to the difference in volume of the products and the reactants multiplied by the variation in pressure. This relation is important because if the product of the reaction does not tend to form spontaneously at ordinary pressures—that is to say, if the product is unstable and thus $\Delta\,F$ for the reaction is positive—then in the event that $\Delta\,V$ is negative (i.e., the reaction proceeds with a decrease in volume), we may readily calculate from $\Delta\,V$ and $\Delta\,F$ the pressure required to reduce the positive $\Delta\,F$ to zero or beyond—the fundamental condition of thermodynamic stability.

There are now data at hand from which, by application of the principle stated above, we can draw useful conclusions as to the stability of jadeite not merely at room temperature but also, as we shall see later, at those higher temperatures that are known to be favorable to mineral formation. To determine ΔF at atmospheric pressure we use the well known relation

$$\Delta F = \Delta H - T \Delta S \qquad (3)$$

in which ΔH is the enthalpy difference, i.e., the negative of the heat of reaction as ordinarily defined, T is the temperature on the absolute scale, and ΔS the entropy difference. By averaging the results obtained by Kracek, Neuvonen, and Burley (1951) for the reaction heat determined from the heats of solution of various samples of the pertinent minerals in hydrofluoric acid, we find that ΔH is -6120 calories at 25° C. The entropy may be determined by measuring the heat capacities (i.e., specific heats) down to temperatures close to absolute zero. From the unpublished measurements of Kelly and Todd, quoted by Kracek, Neuvonen, and Burley (1951), it is found that ΔS for the reaction (1) is -14.7 cal/deg at 25° or 298° K. It follows that $T \Delta S$ is -4380 cal at 298° K; and that, by equation (3), ΔF is -1740 cal at 289° K. The negative sign means that jadeite is stable with respect to nepheline and albite *at room temperature*, but of course we want to know about ΔF at elevated temperatures.

THE EFFECT OF TEMPERATURE

The variation of ΔF with T may be expressed in several ways. A useful relation is as follows:

$$d(\Delta F)/d T = -\Delta S. \qquad (4)$$

In the limiting case for which ΔC_p, the difference in heat capacities of the products and reactants, is zero, ΔS, being dependent on ΔC_p, is constant; and by integration we obtain immediately the simple form

$$\Delta F = \Delta H + IT \qquad (5)$$

in which I is a constant. It should be carefully noted that equation (5) is to be used *only in the temperature for which* $\Delta C_p = 0$. In this particular case I is equal to $-\Delta S$, which is constant because ΔC_p is assumed to vanish for the particular range of temperature throughout which equation (5) is applicable. (Of course, in general, and especially at temperatures below room temperature, ΔC_p may be very far from zero, and ΔS may thus be very far from being constant.)

If ΔC_p is finite but constant, the variation of ΔF with T takes the familiar form

$$\Delta F = \Delta H_0 - \Delta C_p \ln T - IT \qquad (6)$$

in which $\Delta \vec{H}_0$ may be considered to be a constant determined by the equation

$$\Delta H = \Delta H_0 + T \Delta C_p \qquad (7)$$

which expresses the variation of ΔH with T through the temperature range for which ΔC_p is constant. Equation (6) applies *only* to that same temperature range.

The value of these simplified expressions for the problem in hand will become apparent when we tabulate, as is done in table 1, the unpublished results obtained by Kelly and Todd (mentioned above) for the heat capacities of nepheline, albite, and jadeite. It is evident that ΔC_p decreases numerically with increasing T, reaching the low value, — 0.66 cal., at room temperature. A reasonable assumption is that ΔC_p is becoming assymptotic to zero and then maintains that value at higher temperatures. This assumption would be equivalent to the assertion that at high temperatures the molecular heat capacities of the silicates under consideration are additive functions of the atomic properties, there being, of course, the same assemblages of atoms on the two sides of equation (1).

TABLE 1

ΔC_p for the Reaction ½ Ne + ½ Ab = Jd (Kelly and Todd)

T	Cp (cal/deg)			ΔC_p
	½ Ne	½ Ab	Jd	
50	4.56	7.80	5.10	— 7.26
75	8.35	13.74	13.10	— 8.99
100	11.74	19.31	22.68	— 8.37
125	14.80	24.52	32.40	— 6.92
150	17.46	29.22	41.28	— 5.40
175	19.86	33.46	49.02	— 4.30
200	21.98	37.26	55.86	— 3.38
225	23.88	40.26	62.10	— 2.04
250	25.60	43.74	67.62	— 1.72
275	27.14	46.52	72.54	— 1.12
298	28.38	48.96	76.68	— 0.66

Utilizing this assumption that at the higher temperatures ΔC_p is 0, we apply equation (5), noting that $\Delta H = -6120$

cal., $T \Delta S = -4380$, $(\Delta F)_{298} = -1740$, from which it is readily found that $I = 14.7$; and we calculate ΔF for the basic reaction at various temperatures up to $T = 900°$. It turns out that ΔF steadily increases (algebraically), reaching a value of several thousand calories (positive) at the upper end of this temperature range. At the higher temperatures, therefore, jadeite is unstable unless a certain amount of pressure is applied. To calculate this pressure for each temperature, we turn to equation (2), noting that in this equation, if ΔV is in cm^3 and P is in bars, ΔF will be in decijoules. In order to convert calories to decijoules we multiply by 41.84; and one practical form of equation (2) is therefore

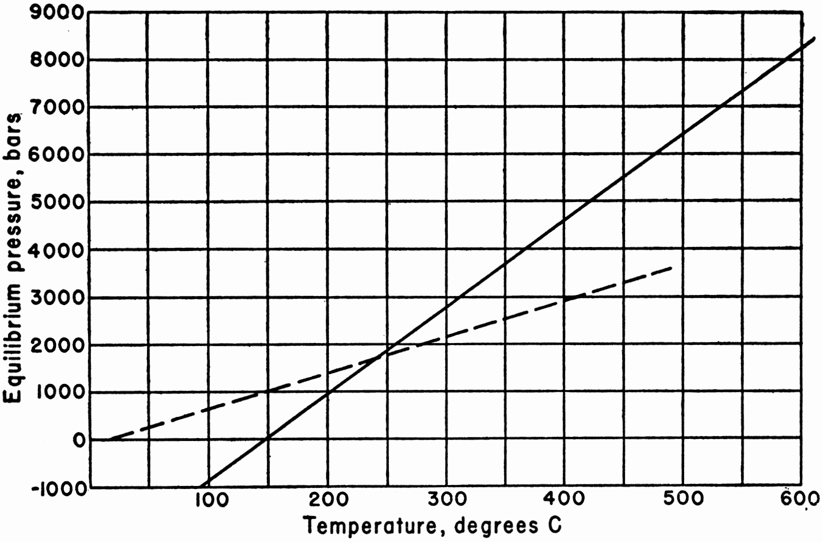

Fig. 1. The solid line shows, as a function of temperature, the equilibrium pressure for the formation of jadeite from nepheline and albite. Temperatures in the Earth corresponding to a gradient of 35 deg/km and a crustal density of 2.7 are given by the dashed line.

$$P = -41.84\ (\Delta F)/\Delta V \qquad (2a)$$

in which P, the pressure required to reduce the positive ΔF to zero, is expressed in bars, ΔF is in calories, and ΔV in cm^{-3}. Finally, because ΔV is -33.4 cm^3, we simply multiply the (positive) values of ΔF obtained from equation (5) by 1.25 to obtain the equilibrium pressures (in bars) at the various temperatures.

These equilibrium pressures are plotted against temperature in figure 1. The most interesting range is from 400° C. to 600°. At lower temperatures mineral formation is usually sluggish, and at higher temperatures improbably high pressures would be required. It may be seen from the curve that at 400°, 500°, and 600° C. the equilibrium pressures are respectively 4700, 6500, and 8300 bars.

It is interesting to calculate the differences in the results that would be obtained if ΔC_p should have a high temperature value, -0.5, rather than zero. In this case equation (6) is applicable. With $\Delta C_p = -0.5$, ΔH_0 is -5970, and I is found to be 11.2. (Note that I is no longer to be identified with $-\Delta S$.) At 400° C. this equation yields a value of P about 100 bars higher than is obtained on the assumption that ΔC_p equals zero—an insignificant difference.

Similar considerations permit the calculation of the stability pressure for the formation of one formula weight (as here defined) of jadeite and two formula weights of quartz from one formula weight of albite at various temperatures. Here again, ΔC_p seems to be practically zero at room temperature and above; and ΔV is nearly the same as before, namely -34.4 cm^3. Taking -1210 cal. as the average of Kracek, Neuvonen and Burley's results for ΔH and -4420 from Kelly's results for $T \Delta S$ at 25°, we may readily calculate that the stability pressures at 300° and 400° are respectively about 9000 and 10,800 bars.

EFFECTS OF COMPRESSIBILITY AND EXPANSIBILITY

It is obvious that strictly the proper volumes to use in the thermodynamic relation are those pertaining to the equilibrium pressures and temperatures. The effects of compressibility and thermal expansibility have been studied by Yoder and Weir (1951) using their own data on compression and the unpublished data by J. L. Rosenholtz and D. T. Smith on thermal expansion. From the equation of Yoder and Weir showing the combined effect of temperature and pressure on the volume change of the reaction in equation (1), it may be seen that this effect is not very important—as recognized by Yoder and Weir. As an example, a pressure of 5000 bars causes the volume change at room temperature to decrease numerically by 1.1, that is, from -33.4 to -32.3; and an increase of temperature from 25° C. to 400° C. at atmospheric pressure causes the volume change to increase numerically by 1.0. The two effects thus tend to offset each other. Because of this, since the compressibility of the pertinent minerals is still not known at high temperatures (or, what amounts to the same thing, the thermal expansibility at high pressures), and because of the apparently inevitable uncertainties in the basic thermal measurements leading to ΔH, ΔS, and ΔF, it thus appears that at present the effects of compressibility and expansibility can be ignored for the purposes of solving the jadeite problem. Similarly, as indicated above, the high-temperature heat capacities seem to be unimportant in this connection. Rather, for progress in the final solution of the problem, experimental effort should be concentrated on attempts to synthesize jadeite at higher pressures than have yet been tried, and perhaps also on improving somewhat the accuracy of measurements leading to the heat of reaction.

HYDRATES UNDER PRESSURE

As mentioned above, when a mixture of jadeite composition is heated under pressure and in the presence of water, the hydrate analcite is formed at pressures above the equilibrium pressure corresponding to the particular temperature (e.g. 2000 bars at 538°); and at lower pressures a mixture of nepheline and albite is produced. Analcite, thus, appears to form whenever sufficient water to produce the hydrate is present and when the proper pressure is applied. This circumstance has raised serious doubts among some investigators as to whether jadeite can ever be synthesized except with a deficiency of water. If Yoder's curve for the decomposition of analcite is plotted in the same diagram with the curve of figure 1, it may be seen that the two curves (extrapolated) cross at about 650° and 9000 bars. Accordingly, it might seem that except at very high pressures the analcite curve is the significant one.

In this connection it is interesting to consider the effect of pressure on hydrates. This subject was discussed by Adams (1938) and it was shown that, depending on circumstances, a hydrate subjected to pressure may melt, or the appropriate solution under high pressure may solidify to a hydrate. Figures 3 and 6 in the contribution cited illustrate the general appearance of the equilibrium curves for various types of congruent and incongruent melting at constant temperature and variable pressure, and figure 5 of that paper, which is the actual equilibrium diagram for the system Na_2SO_4—H_2O, shows the incongruent melting of $Na_2SO_4 \cdot 10H_2O$ at 4600 bars and 25°.

Such a melting under pressure will usually take place when the products (solution plus anhydrous material) have a lower agregate volume than the hydrate. Now let us consider the reaction

$$\text{Analcite} = \text{Jadeite} + 2H_2O. \qquad (8)$$

If the reaction proceeds with a diminution in volume, then pressure should favor it. It is difficult to estimate precisely the volume change in the most interesting region of temperature and pressure, but from the density at room temperature of analcite (2.285) and from an extrapolation of the curves presented by Kennedy (1950) for the specific volume of water at elevated temperatures and pressures, it is probable that at 4000 bars and at 400°, 500° and 600° the volume changes are respectively -30 cm^3, -27 cm^3, and -23 cm^3 for the reaction as written. The circumstance that these values of ΔV are strongly negative suggests that at pressures no higher than the equilibrium pressures (as shown in figure 1 for the formation of jadeite from nepheline and albite) analcite would melt incongruently to form jadeite and water or jadeite plus a saturated solution. (For temperatures above the critical point of water some persons might prefer to call such a process *incongruent sublimation.*) Thus even with excess water a mixture under a sufficiently high pressure might form jadeite rather than analcite. To determine the transition pressure by the thermodynamic method, it would be sufficient to know, in addition to the information already in hand, the thermal properties of analcite and (probably) also the specific volume of water, in the range from 400° to 600°, at somewhat higher pressures than have been applied previously to such experimentation.

CONCLUDING REMARKS

In figure 1 the temperatures in the crust of the Earth corresponding to a thermal gradient of 35 deg/km and a rock density of 2.7 are shown by the dashed line. It may be seen that this line crosses at about 240° the line for the equilibrium pressure of jadeite formation from nepheline and albite, and that at the higher temperatures the pressures given by this line are below the equilibrium pressures. Therefore, with what may be called a normal temperature gradient the pressures are apparently not high enough, in the range of temperature favorable to mineral growth, for jadeite to be stable. If figure 1 gives a true picture of the equilibrium conditions for the formation of jadeite under anhydrous conditions, and if the temperature gradient is "normal," then we should be obliged to conclude that only at temperatures below 240° could jadeite be stable. It should be noted, however, that there is unfortunately an uncertainty of considerable amount in the measured heat of reaction, one of the principal factors used in the calculation of the stability pressure. The measurement of the heats of solution of silicates in hot hydrofluoric acid involves many experimental difficulties; and it is therefore not surprising that the results of measurement show a spread that indicates that the average for the heat of reaction may be in error by several hundred calories, corresponding to perhaps a thousand bars. Furthermore, the thermal gradient in the Earth's crust is known to vary over a wide range. In some regions the gradient is much smaller than 35 deg/km, and in others larger. If the gradient were as low as 22 deg/km, then the pressures corresponding to given temperatures would be sufficiently high for the line expressing temperature as a function of pressure in the Earth to cross the jadeite equilibrium-pressure line of figure 1 at 400°; and at this temperature or below and at depths of about 17 km or less, jadeite would be stable.

We may conclude either (1) that the temperature gradient in regions where jadeite is found is lower than normal (or alternatively that the value taken for the heat of reaction should be numerically higher); or (2) that jadeite has been produced in the Earth as an unstable phase and has persisted unchanged despite the insufficient pressure in comparison with the pressure required for stability.

Finally, it is suggested that further attempts at synthesis in the presence of water and at pressures higher than have been used heretofore for this purpose would be worth while.

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