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THE THERMODYNAMIC BASIS FOR THE MINERAL FACIES CONCEPT

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ABSTRACT. For a given petrologic system, the curves of univariant equilibrium on a P, T diagram may be regarded as a "petrogenetic grid" (Bowen, 1940) defining the mineral facies for that system.

If only crystalline solids are involved it can be shown that most curves of this sort are essentially straight lines through any geologically probable range of temperature and pressure.

Mineralogic reactions involving the so-called "volatile" components are herein treated by considering the system as "open" to these components. Four limiting cases are discussed and their geologic applications reviewed briefly. The limiting cases are:

1. The "volatile" component in question is present as a pure phase at the same pressure and temperature as the surrounding rock. This assumption yields a *maximum* equilibrium temperature for a given pressure, and is roughly equivalent to considering the system as closed with the volatile component present in excess.

2. The rock is in equilibrium with a fissure system containing a dilute aqueous solution. This method is most applicable when the "volatile" in question is water itself, and indicates, in general, a decrease in dehydration temperature with depth.

3. The gradient of chemical potential of the "volatile" components has reached a value such that there is no longer any tendency for their vertical diffusion.

4. The chemical potential of the "volatile" component is sufficiently low that no solid phase containing it is stable. This is analogous to a closed system devoid of the volatile component.

NOTATION

X any extensive property
E internal energy
H enthalpy
G Gibbs free energy
S entropy
V volume
T absolute temperature
P pressure
C_p heat capacity at constant pressure
α thermal expansion
β compressibility (isothermal)
ρ density

Subscripts

S solid phases
F fluid phases
a, *b*, *c*, individual phases
i, *j*, *k*, individual components

n_{ia} number of moles or gram-formula units of component i in phase a

$\overline{X}_{ia}$ partial molar X of component i in phase a
N_{ia} mole fraction of component i in phase a
ΔX X of products less X of reactants
μ_{ia} $(=\overline{G}_{ia})$ chemical potential of component i in phase a
g acceleration of gravity
R gas constant

INTRODUCTION

There is considerable textural and mineralogic evidence (Eskola, 1915. 1920; Tilley, 1924; Turner, 1948) that many rocks represent a state of chemical equilibrium, or at least a close approximation thereto, as of their time of formation. Where this is true, the mineralogy of a given rock should be the key, within limits, to the conditions prevailing when it formed. This is the basis of Eskola's concept (1920) of *mineral facies*. Bowen (1940) has suggested that a pressure-temperature diagram upon which have been plotted the curves of univariant equilibrium appropriate to a given bulk composition rock might serve as a "petrogenetic grid." The areas between the lines of univariant equilibrium would then be the fields of stability of the various *mineral facies* for that bulk composition. With this end in view experimental investigation of the field of stability of various mineral species has been under way for several years (Bowen and Tuttle, 1949; Yoder, 1950a, 1950b, 1951, 1952):

A simple P. T. grid of this sort, however, presupposes that the bulk composition of the rock may be regarded as fixed, an assumption that cannot be made safely with regard to highly mobile components such as water and carbon dioxide. Petrographic evidence indicates that these components are readily gained or lost in petrogenetic processes. Thermodynamically, this means that we must regard a rock or petrologic "system" as *open* to certain mobile components, notably water and carbon dioxide. The field of stability of a mineral containing a mobile component is then dependent not only upon temperature and pressure but also upon the chemical potential (partial molar free energy) of the mobile component in the immediate environment. In a completely closed system the chemical potential of any component is determined by the pressure, temperature, and bulk composition. If a system is open to a certain component, however, its chemical potential is independent of temperature and pressure, owing to the possibility of transfer of the mobile component between a given system and its environment. The field of stability of a mineral facies in a rock containing m mobile components is thus, in general, $(m + 2)$-variant, that is, dependent on pressure, temperature *and* the chemical potential of the mobile components. The boundary between two mineral facies is then no longer a univariant curve on a P-T diagram but an $(m + 1)$-variant surface or hypersurface in $(m + 2)$-dimensional space.

Fortunately, few metamorphic changes involve gain or loss of more than one mobile component at a time. Commonly the only mobile component involved is water or carbon dioxide. Such equilibria are *divariant surfaces* in a 3-dimensional diagram, where pressure, temperature, and the chemical potential of the mobile component are the coordinates. If, in any instance, the

chemical potential gradient of the mobile component may be regarded as dependent on the temperature and pressure distribution in the Earth's crust, the equilibrium may be regarded, to the extent that this is true, as univariant and dependent only on pressure and temperature. A possible mechanism by which this last might come about is through attainment of osmotic equilibrium with a hydrothermal fissure system. Another possibility is that free vertical diffusion of the mobile components has taken place so that an equilibrium chemical potential gradient has been attained for each. Both possibilities will be considered in the following pages, as well as certain features of univariant equilibria in closed systems.

Earlier work.—The work of Johnston and Niggli (1913) and V. M. Goldschmidt (1912) is notable among early investigations of the physico-chemical principles involved in metamorphic processes. A revival of interest in such matters has been indicated by the chapters on chemical thermodynamics in recent texts on petrology and geochemistry, chiefly those by Turner and Verhoogen (1951), Mason (1952), Barth (1952), and Ramberg (1952). Certain important aspects of phase equilibrium in open systems have been discussed by Korzhinsky (1936, 1950). The calcite-wollastonite equilibrium has been restudied by Danielsson (1951) from the point of view of osmotic equilibrium, and Ramberg (1944, 1952) has considered free vertical diffusion of mobile components as a factor in metamorphic processes.

Recent experiments in hydrothermal systems, notably by Bowen and Tuttle (1949), Roy and Osborne (1950), and Yoder (1950a, 1950b, 1952), has also provided much-needed data and stimulated interest in the rôle of water in petrologic processes. Yoder and Weir (1951) have considered the effect of pressure on metamorphic processes, and Yoder (1952) has considered the fields of stability of certain hydrous minerals from the point of view of closed systems with "excess" or "deficient" water.

Readers familiar with the above literature are probably aware of fundamental differences in the approaches of the various authors, and of the difficulties involved in correlating field observations with either experimental data or theoretical discussions. It is the hope of the present author to be able, in this paper, to resolve some of the inconsistencies in the current literature and to narrow somewhat the existing gaps between isograds, P-T curves, and differential equations.

UNIVARIANT EQUILIBRIUM

Solid phases of fixed composition.—The equation of univariant equilibrium for reactions at constant pressure and temperature may be written

$$\Delta G = 0 = \Delta E + P\Delta V - T\Delta S \qquad (1)$$

or

$$\Delta G = 0 = \Delta H - T\Delta S \qquad (1a)$$

The reaction is written so that ΔS is positive. From the first and second laws of thermodynamics we have, for a reversible process

$$d(\Delta E) = Td(\Delta S) - Pd(\Delta V) \qquad (2)$$

hence, maintaining equilibrium, we have

$$\left(\frac{dP}{dT}\right)_{\Delta G = 0} = \frac{\Delta S}{\Delta V} \qquad (3)$$

or, alternatively,

$$\left(\frac{dP}{dT}\right)_{\Delta G=0} = \frac{\Delta H}{T\Delta V} \tag{3a}$$

a relationship commonly known as the Clapeyron equation.

For most solid-solid reactions at moderate (room temperature) and high temperatures it can be shown that equation (1) is, for most practical purposes, the equation of a straight line on a P-T diagram, the slope of this line, for a given reaction, being given by (3).

The volume of most solids varies little with temperature and pressure. From available data (Birch et al., 1942, p. 30-37) we find that, at 25°C. and one atmosphere, the volume expansion, α, defined by the relation

$$\alpha = \frac{1}{V}\left(\frac{\partial V}{\partial T}\right)_P \tag{4},$$

is between 1 x 10^{-5} per degree and 4 x 10^{-5} per degree for most rock-forming minerals, and that the isothermal compressibility, β, defined by the relation

$$\beta = -\frac{1}{V}\left(\frac{\partial V}{\partial P}\right)_T \tag{5},$$

is between 0.5 x 10^{-6} per bar and 3 x 10^{-6} per bar. The variation of α and β with temperature and pressure has been discussed at some length by Birch (1952), both quantities, in general, increasing slightly with rising temperature and decreasing slightly with rising pressure. Nevertheless, these variations, as well as the initial values of α and β, are so small that we may neglect them for most "chemical" purposes despite their importance in geophysical calculations. Since most solids have about the same thermal expansion and compressibility, it is evident that we are even safer in assuming constancy of ΔV for any univariant equilibrium than of V for any of the individual participating phases. The volume changes of the reactants, in short, are largely cancelled by corresponding volume changes on the part of the products, so that ΔV is virtually constant. This constancy has, in fact, been effectively demonstrated by Yoder and Weir (1951) for the specific reaction: 2 jadeite = nepheline + albite.[1] Available compressibility and thermal expansion data indicate that it is probably a safe assumption for any univariant equilibrium involving only solid phases.

Molar volumes may be determined readily and with considerable accuracy, when necessary, from either specific gravity or unit cell measurements. The minerals in table 1 are listed in order of increasing volume per gm-atom. The volumes, per gram-atom, of most mineral oxides, oxy-salts, and silicates lie in the range 4.5 to 9.0 cc (table 1). Values of 7.5 cc/gm-atom or more are found chiefly in silicates with tetrahedral frameworks (feldspars, feldspathoids, silica minerals, and cordierite), and values of 5.0 cc/gm-atom or less

[1] Although demonstrating the virtual constancy of ΔV, Yoder and Weir draw therefrom an erroneous conclusion. Specifically, the constancy of ΔV, and hence of the effect of pressure on ΔG, does not mean that the effect itself is zero or negligible. ΔV, for the reaction: 2 jadeite = nepheline + albite, although virtually constant, is neither zero nor negligible.

occur chiefly in hydroxides. Volume changes accompanying solid-solid transitions are commonly on the order of 0.5 to 1.0 cc/gm-atom. Extreme examples are the reaction *diamond → graphite*, and the reaction *2 jadeite → albite + nepheline*. Among polymorphous pairs, that form which lies highest on the list in table 1, is the one favored by an increase in pressure. The greater the volume-difference, the more marked the effect of a given increase in pressure.

TABLE 1
Volumes (25°C.)

Mineral	Formula	Molar Volume (cc)	Gram-atomic Volume (cc)
Diamond	C	3.4	3.4
Diaspore	$HAlO_2$	17.6	4.4
Gibbsite	$Al(OH)_3$	32	4.6
Brucite	$Mg(OH)_2$	24.2	4.8
Corundum	Al_2O_3	26	5.2
Graphite	C	5.3	5.3
Staurolite	$Fe(OH)_2 \cdot Al_4(SiO_4)_2O_2$	111	5.3
Kyanite	$Al_2(SiO_4)O$	44	5.5
Lawsonite	$CaAl_2(Si_2O_7)\ (OH)_2 \cdot H_2O$	104	5.5
Chloritoid	$Fe(OH)_2 \cdot Al_2(SiO_4)O$	72.5	5.6
Periclase	MgO	11.2	5.6
Pyrope	$Mg_3Al_2(SiO_4)_3$	113	5.7
Almandine	$Fe_3Al_2(SiO_4)_3$	115	5.8
Kaolinite	$Al_2(Si_2O_5)\ (OH)_4$	99	5.8
Chlorite	$Mg_5Al(AlSi_3O_{10})\ (OH)_8$	211	5.9
Jadeite	$NaAl(Si_2O_6)$	60	6.0
Serpentine	$Mg_3(Si_2O_5)\ (OH)_4$	109	6.1
Sillimanite	$Al(AlSiO_5)$	44	6.1
Forsterite	$Mg_2(SiO_4)$	44	6.3
Enstatite	$Mg(SiO_3)$	31.5	6.3
Grossularite	$Ca_3Al_2(SiO_4)_3$	126	6.3
Clinozoisite	$Ca_2Al_3(SiO_4)_3(OH)$	141	6.4
Pyrophyllite	$Al_2(Si_4O_{10})\ (OH)_2$	128	6.4
Talc	$Mg_3(Si_4O_{10})\ (OH)_2$	136	6.5
Andalusite	$AlAl(SiO_4)O$	52	6.5
Muscovite	$KAl_2(AlSi_3O_{10})\ (OH)_2$	142	6.8
Phlogopite	$KMg_3(AlSi_3O_{10})\ (OH)_2$	150	6.8
Aragonite	$Ca(CO_3)$	34	6.8
Calcite	$Ca(CO_3)$	37	7.4
Quartz (Low)	SiO_2	22.4	7.5
Analcite	$Na(AlSi_2O_6) \cdot H_2O$	98	7.5
Gehlenite	$Ca_2(Al_2SiO_7)$	91	7.6
Anorthite	$Ca(Al_2Si_2O_8)$	101	7.8
Albite	$Na(AlSi_3O_8)$	102	7.8
Wollastonite	$Ca(SiO_3)$	39.5	7.9
Nepheline	$Na(AlSiO_4)$	56.5	8.1
Orthoclase	$K(AlSi_3O_8)$	105	8.1
Cordierite	$Mg_2(Al_4Si_5O_{18})$	236	8.1
Tridymite (Low)	SiO_2	25.5	8.5
Cristobalite (Low)	SiO_2	26.0	8.7

Volumes for garnets are based on unit-cell dimensions given by Fleischer (1937), all others are based on unit-cell volumes listed by Fairbairn (1943).

The molar and gram-atomic entropies (at 25°C. and 1 atm.) of some minerals have been listed in table 2. The listing is in order of increasing entropy per gram-atom. The relation of entropy to temperature is analogous (but opposite in sign) to that of volume to pressure. Among polymorphous pairs, that form which is *lowest* on the list is the one most favored by an increase in temperature. The magnitude of this effect is proportional to the entropy-difference. At room temperature and atmospheric pressure the gram-atomic entropies of most rock-forming minerals are between 100 and 225 decijoules.

Materials of low gram-atomic entropy are commonly materials of low gram-atomic volume, as is evident from comparison of tables 1 and 2. There are exceptions, an important one being andalusite-sillimanite, but these exceptions are limited chiefly to cases where the volume and entropy changes are relatively slight. This means that an increase in pressure generally has an effect, on a solid-solid transition, opposite to that produced by an increase in temperature. The point should be emphasized because it is contrary to the impression given in many discussions of metamorphic processes. Most equilibrium curves for solid-solid reactions will thus have positive slopes on a P-T diagram. The exceptions, in fact, are sufficiently rare that it is fairly safe to assume, until shown otherwise, that the phase or "facies" with the smaller volume will also have a smaller entropy and hence be the "low-temperature" form. This is particularly so if the volume change per gram-atom is relatively large, and is true in all instances known to the writer where ΔV exceeds 0.5 cc/gm-atom.

TABLE 2
Entropies (25°C.)

Mineral	Formula	Molar Entropy (dj/deg)	Gram-atomic Entropy (dj/deg)
Diamond	C	24.4±0.2	24.4±0.2
Graphite	C	56.9±0.2	56.9±0.2
Gibbsite	$Al(OH)_3$	701±4.0	100.1±0.6
Corundum	Al_2O_3	523±6.0	104.6±1.2
Kyanite	$Al_2(SiO_4)O$	838±3.0	104.7±0.4
Andalusite	$AlAl(SiO_4)O$	932±4.0	116.5±0.5
Sillimanite	(Al_2SiO_5)	961±4.0	120.1±0.5
Brucite	$Mg(OH)_2$	631±2.0	126.2±0.4
Jadeite	$NaAl(Si_2O_6)$	1331±8.0	133.1±0.8
Enstatite	$Mg(SiO_3)$	679±4.0	135.8±0.8
Forsterite	$Mg_2(SiO_4)$	952±8.0	136.0±1.1
Periclase	MgO	274±6.0	137±3.0
Quartz (Low)	SiO_2	418±4.0	139±1.3
Cristobalite (Low)*	SiO_2	426±4.0	142±1.3
Tridymite (Low)*	SiO_2	433±8.0	144±2.7
Portlandite	$Ca(OH)_2$	730±40.0	146±8.0
Albite	$Na(AlSi_3O_8)$	2059±13.0	158.4±1.0
Wollastonite	$CaSiO_3$	820±8.0	164±1.6
Nepheline	$Na(AlSiO_4)$	1218±8.0	174±1.1
Aragonite	$Ca(CO_3)$	887±13.0	177±2.6
Calcite	$Ca(CO_3)$	929±8.0	186±1.6
Lime	CaO	410±8.0	205±4.0
Water (liq.)	H_2O	701±13.0	234±4.0

Entropy of Nepheline from Kracek et al. (1951), all other data from Kelley (1950). Data converted to decijoules/deg (1 dj = 41.84 cal.).

* Relative positions reversed for "high" forms.

ΔS for most solid-solid transitions is commonly between 5 and 10 decijoules per gram-atom per degree. Extreme examples, again, are 32.5 decijoules/gm-atom/degree for diamond → graphite and 30.8 decijoules/gm-atom/degree for 2 jadeite → nepheline + albite. The thermochemical data (table 2) indicates that the uncertainty in ΔS may be from $\pm$ 1 to $\pm$ 5 decijoules/gm-atom/degree. This should be borne in mind in all instances where ΔS /gm-atom is relatively small.

The entropy of a crystalline solid, as given in thermochemical tables, is based upon low-temperature heat capacity measurements and, strictly speaking, is an entropy difference; it is the entropy of the crystal at 25°C. less its entropy at absolute zero. It is commonly assumed, for chemical purposes, that the latter is zero, but this is not necessarily so. Although the vibrational entropy of a crystal drops to zero as the temperature approaches absolute zero, other contributions to the entropy (as, for example, the disordering of aluminum and silicon, in high-temperature feldspars) may readily be "frozen in." If this has happened, and is not taken into account, the heat capacity measurements will give too low a value by that part of the total entropy which had been "frozen in." Similarly, heat capacity measurements on a mix-crystal such as an intermediate olivine will neglect the entropy of mixing. Fortunately it is possible in most instances to anticipate difficulties of this sort from a knowledge of the crystal structure, and to make a reasonable estimate of the entropy-difference involved, though this is beyond the scope of the present paper.

The effect of pressure on entropy at constant temperature is given by the relation

$$\left(\frac{\partial S}{\partial P}\right)_T = -\left(\frac{\partial V}{\partial T}\right)_P = -V\alpha \tag{6}$$

Since the thermal expansion of solids is negligible for our purposes, it is clear that pressure has little effect on S, and even less on the ΔS of a reaction inasmuch as the thermal expansions of reactants and products will be similar.

The variation of entropy with temperature is given by the relation

$$\left(\frac{\partial S}{\partial T}\right)_P = \frac{1}{T}\left(\frac{\partial H}{\partial T}\right)_P = \frac{C_P}{T} \tag{7}$$

where C_p is the heat capacity at constant pressure. At room temperature and one atmosphere the heat capacity of most rock-forming minerals is between 150 and 210 decijoules/gm-atom/degree. At lower temperatures heat capacities decrease rapidly, approaching zero as the temperature approaches absolute zero. At higher temperatures the heat capacities of virtually all solids approach, asymptotically, values of about 250 decijoules/gm-atom/degree. In other words, the gram-atomic heat capacities of solids approach, at high temperatures, the value of 3R (249.42 decijoules/gm-atom/degree) indicated by the empirical law of Dulong and Petit (Slater, 1939, p. 213-214) as well as by the later theories of Einstein and Debye (Slater, p. 222-255). Strictly speaking, the Einstein and Debye theories predict that the heat capacity at

constant volume, C_v, rather than C_p, should approach 3R/gm-atom, but as we can see from the relation

$$C_P = C_V + TV\frac{\alpha^2}{\beta} \tag{8}$$

these do not differ greatly in solids. The gram-atomic heat capacities of most rock-forming minerals approach 3R in the temperature range from 600 to 1000°C. Since

$$\left(\frac{\partial \Delta S}{\partial T}\right)_P = \frac{\Delta C_P}{T} \tag{9}$$

it is clear that ΔS for an isochemical solid-solid transition may be regarded as constant at temperatures above 1000°C. Actually this is sufficiently true even at room temperature inasmuch as the deviations from 3R are about the same for any two polymorphs or isochemical aggregates, and T is a relatively large number. For most reactions that concern us $\frac{\Delta C_P}{T}$ is less than .05 deci-joules/gm-atom/degree[2] and becomes rapidly less with rising T, owing to both the increase in T itself and the fact that ΔC_P approaches zero. We could take this into account in the equations of univariant equilibrium, but in view of the initial uncertainty in determining ΔS there is little point in so doing.

It is evident, then, that if we restrict the discussion to temperatures above 25°C. (safe enough geologically) we may assume, as a first approximation, that both ΔS and ΔV are constant for solid-solid reactions, despite the fact that the entropy of any one of the participating phases is dependent on temperature.

It can also be shown that the ratio $\Delta S/\Delta V$ for a solid-solid reaction may also be regarded as constant, since,

$$\left[\frac{\partial\left(\frac{\Delta S}{\Delta V}\right)}{\partial P}\right]_T = \frac{\Delta S}{\Delta V}\left[\frac{\Delta(V\beta)}{\Delta V} - \frac{\Delta(V\alpha)}{\Delta S}\right] \tag{10}$$

and

$$\left[\frac{\partial\left(\frac{\Delta S}{\Delta V}\right)}{\partial T}\right]_P = \frac{\Delta S}{\Delta V}\left[\frac{\Delta C_P}{T\Delta S} - \frac{\Delta(V\alpha)}{\Delta V}\right] \tag{11}$$

For most reactions, the bracketed terms on the right hand side of each of these relations tend to cancel each other because entropy and volume vary sympathetically. The largest of these bracketed terms, at least at low temperatures, will generally be the heat-capacity term in equation (11). This means that we may anticipate that some solid-solid equilibrium curves will show, at relatively low temperatures, a slight concavity toward the pressure axis, since the high-entropy phase has, in general, the higher heat capacity.

From equation (1) and equation (3) it is evident that constancy of ΔS

and ΔV implies constancy of ΔE, at least along the equilibrium curve. This is also evident from the relations

$$\left(\frac{\partial E}{\partial P}\right)_T = PV\beta - TV\alpha \tag{12}$$

and

$$\left(\frac{\partial E}{\partial T}\right)_P = C_P - PV\alpha \tag{13}$$

From equations (7) and (9) it is further evident that ΔH may be regarded as independent of temperature at constant pressure. This suggests that if ΔH and ΔS at 25°C. and one atmosphere are known we might obtain the transition temperature at one atmosphere by means of equation (1a). Unfortunately, however, relative enthalpies, as determined from heats of solution, are generally not of sufficient accuracy to make such a calculation worthwhile, and equation (1a) is useful chiefly as a way to determine the latent heat of a reaction when the entropy change and transition temperature are known, at least until more accurately determined heats of solution are forthcoming. Most measurements of heats of solution of minerals are given as good to about the nearest hundred calories per gram-atom, that is, to within ±50 calories (2000 decijoules) per gram-atom. ΔH is then good to within ±4000 decijoules per gram-atom. If ΔS is 10 decijoules/gm-atom/degree (30 decijoules/gm-atom/degree is an exceptionally large value) this means an uncertainty of ±400°C. in determining the transition temperature by equation (1a), neglecting any error in ΔS. For an exceptionally accurate heat of solution, or an exceptionally high ΔS, or both, this uncertainty is reduced. With present data, then, it is often better to estimate the *position* of an equilibrium curve by an "educated geological guess" than to employ equation (1a), although, since the errors in $\Delta S/\Delta V$ are considerably less, we may estimate its *slope* with some accuracy by means of equation (3).

Non-first-order transitions.—Certain transitions in solids, notably those of the order-disorder type, may take place with no discontinuity in the first-order derivatives of the free energy, that is, without discontinuities in entropy and volume, though these properties may change rapidly over a narrow range of temperature or pressure. In such an instance ΔS and ΔV are both zero, and the Clapeyron equation (3) is indeterminate. When discontinuities appear in second- or higher-order derivatives of the free energy, the pressure dependence of the transition temperature may be determined from equations derived by Ehrenfest (Guggenheim, 1950, p. 775), but practical difficulties arise in measuring such discontinuities.

An alternate approach is to consider the rapid changes in entropy and volume as taking place abruptly rather than over an interval. This is, in effect, considering a hypothetical equilibrium between (in the case of an order-disorder transition) the disordered state and a partially ordered state. Both phases in such an equilibrium are metastable or even unstable relative to some state with an intermediate degree of order, but this is of no consequence for our purposes. Such an approximation is useful because the pressure-de-

TABLE 3

Solid-Solid Reactions

Reaction	ΔS (dj/deg/gm-atom)	ΔV (cc/gm-atom)	$\frac{\Delta S}{\Delta V}$ (bars/deg) $\left[= = \left(\frac{dP}{dT}\right)_{\Delta G = 0} \right]$
*Diamond → Graphite	32.5 ± 0.4	1.9	17
Aragonite → Calcite	9.0 ± 5.0	0.6	15
Kyanite → Andalusite	11.8 ± 0.9	1.0	12
Kyanite → Sillimanite	15.4 ± 0.9	0.6	26
Andalusite → Sillimanite	3.6 ± 1.0	-0.4	-9
2 Jadeite → Nepheline + Albite	30.8 ± 2.0	1.9	16
Jadeite + Quartz → Albite	23.8 ± 2.0	2.0	12
Jadeite + Enstatite → Albite + Forsterite	16.1 ± 2.0	1.15	14

* ΔC_P not negligible for this reaction.

pendence of such a metastable equilibrium can be evaluated, and because the P-T curve for the metastable or unstable transition must always be *within* the band representing the actual transition interval. The value of this method is greatest for relatively abrupt transitions, specifically those for which the transition band on a P-T diagram is relatively narrow.

Phases of variable composition.—An analagous situation occurs when, with phases of variable composition, a given mineralogic change takes place over an interval rather than at a fixed P or T. Examples are common and are to be anticipated wherever an intermediate member of a solid solution series or a liquid phase is involved, and where the total number of phases involved is *less* than the maximum permissible for univariant equilibrium. Thus the reaction:

orthopyroxene → clinopyroxene

takes place over a temperature interval, for intermediate Fe-Mg ratios (Bowen and Schairer, 1935), but the reaction:

olivine + orthopyroxene + tridymite → olivine + clinopyroxene + tridymite

is abrupt at constant pressure owing to the phase-rule restrictions. In the first reaction the transition interval for any given composition would be a band on a P-T diagram analogous to that for order-disorder transitions.

A mineral aggregate, on passing through such a transition interval, with maintenance of equilibrium, undergoes two second-order transitions, one on entering the interval and one on leaving it, but no first-order transition. The discontinuities in heat capacity and thermal expansion may be used as in other second-order transitions, but it is more convenient, for most purposes, to consider a related metastable or unstable equilibrium. In the above example it would be the P-T curve along which an orthopyroxene has the same molar free energy as a clinopyroxene of identical composition. This can be no more than a partial equilibrium since the chemical potentials of the pyroxene end-members must be different in the two phases, but this does not prevent its being defined thermodynamically. The partial equilibrium always lies within the actual transition interval.

In this paper the equations for most reactions will be written in terms of pure mineral end members. An actual reaction involving mix crystals will in general behave differently owing to the effects of mixing upon the thermodynamic properties. In some minerals, notably in the Fe-Mg olivines and orthopyroxenes (Sahama and Torgeson, 1949) and in the plagioclase feldspars (Bowen, 1928, p. 179), there is evidence that the solid solutions are ideal or nearly ideal. In an ideal mixture, a, the free energy of the mixture may be given in terms of the chemical potentials (μ_i°) of the pure end members by the equation

$$G = \Sigma_i n_{ia}\mu_{ia} = \Sigma_i n_{ia} \quad (\mu_i^\circ + RT\ln N_{ia}) \tag{14}$$

It is probably not safe to assume, however, that many solid solutions are ideal mixtures.

The effect of non-hydrostatic stress.—For most chemical purposes equa-

tions (1) and (2) are adequate starting points. Both carry the assumption, however, that the work done in a chemical process is solely that involved in changes of volume against hydrostatic pressures. This cannot always be justified in a petrologic system inasmuch as the pressure on a solid is not necessarily hydrostatic. In any vanishingly small volume in a solid in which the pressure is non-hydrostatic, the pressure acting upon a plane passing through that volume depends upon the orientation of the plane. In the terminology of Harker (1939) the solid is under a "shearing-stress." If non-hydrostatic stresses are involved, the work done in any process is related not only to changes in volume (dilatation), but also to changes in shape (distortion). The pressure-volume terms in equations (1) and (2) must be replaced, in this event, by a more complicated expression taking into account the vectorial properties of the stresses and the resulting strains. For simplicity, however, we may consider the free energy of a substance under non-hydrostatic stress by comparing it with that of the same substance, at the same temperature and *mean hydrostatic pressure*, but not under non-hydrostatic stress. The mean hydrostatic pressure, P_m, is defined as the arithmetic mean of the three principal stresses. We may then, for convenience, define a quantity, D, by the following equation

$$D = G_{st} - G_u \tag{15}$$

where G_{st} is the free energy of the stressed solid and G_u is the free energy of the same solid, unstressed, but at the same temperature and acted upon by a hydrostatic pressure equal to the mean hydrostatic pressure acting upon the stressed solid.

A theoretical investigation of the probable magnitude of D, compared with the other factors affecting the free energy of a solid, has been made by Verhoogen (1951) who concluded that in general it should be negligible. To the extent that Verhoogen's conclusion is correct this means that equations (1) and (2) may be applied to solids under non-hydrostatic stress as well as to substances under simple hydrostatic pressure, if "P" represents the arithmetic mean of the three principal stresses, when the pressure is non-hydrostatic. This means, further, that at a given temperature and mean hydrostatic pressure, the free energy of a solid should be independent of "shearing stress," a conclusion obviously in conflict with Harker's concept (1939) of "stress" and "antistress" minerals. This concept implies that D is not only significant but varies significantly from mineral to mineral, being relatively large (if positive) in antistress minerals and relatively small (if positive) in stress minerals. Experimental evidence (Larsen and Bridgman, 1938) on the matter is sparse and negative, in that no significant effect of non-hydrostatic stress upon chemical equilibria has yet been demonstrated, other than what can be related to the effect of the mean hydrostatic pressure involved.

A few further comments might be made. One is that it is to be anticipated that D, if other than zero, should, when the crystal is anisotropic, depend upon the orientation of the crystal relative to the principal stresses. Such variations, furthermore, might be fully as great as those between different minerals, as, for example, are variations in hardness and optical properties.

A consequence of this is that stress-sensitive anisotropic minerals should show preferred orientation when formed under non-hydrostatic stress. Actually the most commonly cited anisotropic stress (kyanite, staurolite, chloritoid) or antistress (andalusite, cordierite) minerals show preferred orientation less commonly than do minerals such as mica, chlorite and quartz which are generally regarded as relatively insensitive to non-hydrostatic stress.

A second point is that the occurrence of a mineral in a highly *deformed* rock does not necessarily mean that it grew under strong non-hydrostatic stress, even where it can be demonstrated conclusively that the mineral formed during the deformation. Extreme deformation might as well be interpreted as evidence of extreme plasticity as of a strong non-hydrostatic stress. The more plastic a material is, in fact, the less capable it is of supporting a non-hydrostatic stress. It is also true that strong non-hydrostatic stresses may be set up without large scale deformation, as, for example, when a crystalline aggregate is subjected to a sudden change in temperature. This might happen in thermal metamorphism at an igneous contact. Such stresses would, of course, differ in orientation from grain to grain but might nevertheless be great enough to bring about rupture of relict minerals, and are supposedly responsible (Harker, 1939) for the decussate (criss-cross) texture of hornfelses. In short, it would seem that the assumptions that the minerals of thermally metamorphosed rocks grew in the absence of non-hydrostatic stress, and that those in the regionally metamorphosed rocks of orogenic belts grew under relatively strong non-hydrostatic stress, are open to question. All considered, the writer is inclined to believe that the burden of the proof lies with the stress-mineral concept. The catalytic effects of non-hydrostatic stress are, of course, well known and have been discussed at some length by Eskola (1934). Significant displacements of chemical equilibria, however, are still unproven, and the writer proposes to show in the following discussion that many of the effects commonly attributed to non-hydrostatic stress are amenable to alternative explanation.

In accord with the above remarks, then, we shall return to equations (1) and (2), bearing in mind, owing to our neglect of non-hydrostatic stress, that under some conditions they may not be entirely adequate.

Equilibria involving a fluid phase.—If a fluid phase is involved in the reaction we cannot assume constancy of ΔS and ΔV unless the fluid is known to be a liquid or in a liquid-like super-critical state. The thermal expansion and compressibility of most liquids is small and their heat capacities do not differ greatly from those of the corresponding solids. Slopes of equilibrium curves on a P-T diagram are likely to be steep (at a high angle to the temperature axis) relative to those of solid-solid transitions owing to the considerable increase in entropy in passing from the solid to the liquid state. The volume changes per gram-atom are comparable to those in solid-solid transitions. The slopes are generally positive although the ice-water transition is an obvious exception.

If a gas is involved, however, thermal expansion and compressibility are no longer negligible and ΔC_p may also be large. Owing chiefly to the large molar volumes and high compressibilities of gases at low pressures, an

equilibrium curve involving production of a gas phase generally has a gentle positive slope at low pressures. With rising pressure the curve becomes both steeper and straighter as the gas becomes more like a liquid in its properties. Several equilibria of this type have been investigated experimentally (Bowen and Tuttle, 1949; Yoder, 1952). The slopes at the highest pressures at which investigations have been carried out (2-3000 bars) are steep, relative to most solid-solid transitions, and apparently positive (table 4), but the data are not sufficiently detailed to determine the slopes in the high-pressure region within very narrow limits.

TABLE 4
Slopes of Dehydration Curves at High Pressures

Reaction	Slope (bars/deg)
Brucite + Serpentine → Forsterite + Vapor	53 to 210
Serpentine → Talc + Forsterite + Vapor	49 to 240
Talc + Forsterite → Enstatite + Vapor	26 to 103
Talc → Enstatite + Quartz + Vapor	21 to 68
Brucite → Periclase + Vapor	−34 to 34
Chlorite → Forsterite + Cordierite + Spinel + Vapor	26 to 52

Slopes are from experimental data of Bowen and Tuttle (1949) and Yoder (1952). The range represents the greatest and least possible slopes consistent with runs at pressures greater than 5000 PSI (350 bars).

There is, however, reason to question the applicability of these curves to analogous reactions taking place in an actual geologic environment. We cannot assume that naturally occurring fluid phases, when present, are "pure components," nor can we assume that they were subjected to the same mean hydrostatic pressure as that acting on the adjacent solids. Pure or nearly pure water is a possibility, but pure carbon dioxide is less likely, and we cannot assume that the molar properties of pure carbon dioxide in any way approximate the partial molar properties of carbon dioxide in a dilute aqueous solution at the same temperature and pressure. The chemical potential (partial molar free energy) of any component in a solution *must* be *less* than the molar free energy of the pure component at the same P and T. Otherwise, the component in question would separate as a distinct phase, the system thereby attaining a lower free energy. If a stable solution exists it is thus evident that the chemical potentials of the various components are lower than the molar free energies of these components were they to occur as pure phases at the same pressure and temperature. This means that if the "volatile" component does not occur as a pure phase, the actual transition temperature at any given pressure will be lower than that given by the experimental results mentioned above. It can be shown that, as the mole fraction or concentration of a given component approaches zero, its chemical potential must decrease indefinitely. As the concentration of the critical component in the fluid approaches zero, in other words, the equilibrium temperature must approach absolute zero, whatever the pressure.

Even if the critical component does occur as a pure fluid phase its molar free energy will decrease, at any given temperature, as the pressure upon it is lowered. This means that even where the critical component can be assumed

"pure" we will overestimate the transition temperature from the above curves if the pressure upon it is less than that on the adjacent solids.

It is evident, then, that the curves discussed above are useful only as limiting cases, and tell us for a given "rock-pressure" only the maximum possible transition temperature. They are applicable only where the fluid contains only the "volatile" component in question and is acted upon by the same pressure as the adjacent solids.

A further complication arises in that we cannot assume that a true fluid phase is always present when reactions of this type take place in actual rocks. Geologic and petrographic evidence suggests that in many instances the "volatile" or mobile components have been removed by diffusion as rapidly as produced, or supplied by diffusion as rapidly as consumed. True fluids of course exist in fissures and other large openings, but "volatilizations" and "devolatilizations" have clearly not been restricted to those portions of the rock in direct contact with such openings. The "intergranular film," furthermore, is believed to be quite unlike a liquid or gas in its properties. The water in any subcapillary opening is strongly bonded by adsorption to the adjacent surfaces and probably best regarded as solid — analogous, structurally, to zeolitic water or water of hydration. The intergranular film is also quantitatively inadequate to account for the vast quantities of water given off in the metamorphism of a shale to a sillimanite gneiss, or for the carbon dioxide produced in the conversion of a siliceous dolomite to a calc-silicate granulite. It appears, then, that a rock must be regarded as an open system, permeable to certain relatively mobile components such as water and carbon dioxide.

OPEN SYSTEMS

Partial molar properties.—Partial molar properties may be defined by equations of the type:

$$\overline{X}_{ia} = \left(\frac{\partial X_a}{\partial n_{ia}}\right)_{P,T,n_{ja},n_{ka},\ldots} \qquad (16)$$

where X may be any extensive property of phase *a* such as V, S, E or G, *i* refers to the component in question, and *j* to all *other* components of *a*. Thus, X_{ia} is to be read: "partial molar X of *i* in *a*."

The partial molar Gibbs free energy, however, is commonly referred to as the *chemical potential* and denoted by the symbol μ, so that

$$\mu_{ia} = \left(\frac{\partial G_a}{\partial n_{ia}}\right)_{P,T,n_{ja},n_{ka},\ldots} \qquad (16a)$$

For two phases sharing a given component *i* to be in equilibrium, μ_i in each must be the same. Otherwise the free energy of the system may be lowered by appropriate transfer of *i*.

Significance of chemical potential in open systems.—Similarly if a *system* in thermal equilibrium with its surroundings is open with regard to a mobile component *i*, then μ_i must be the same in both the system and its immediate surroundings in order that there be no tendency for transfer of *i* to or from the system. The free energy of the "megasystem" consisting of the open system plus its environment is at a minimum with regard to distribution of component *i* when such a distribution has been attained. It is interest-

ing to note that the megasystem as defined above is a closed system even though both its component parts (open system and environment) are not. The distinction between a closed and open system is thus dependent in large part on what one chooses to *define* as the limits of the system. Although closed systems are easier to treat thermodynamically, it is impractical in many instances to hunt about for a "megasystem" large enough to remain "closed" through a given process. We might be forced in certain instances to consider not only a large portion of the Earth's crust but the hydrosphere or atmosphere as well. A system of such size is not only cumbersome but also rarely, if ever, in a state of complete internal equilibrium. For these and other reasons we shall find it simpler to regard rocks as open system with regard to certain mobile or "volatile" components.

Multivariant equilibrium.—If a rock with a *given* content of fixed components is an open system with regard to a mobile component, *i*, its most stable state (mineral facies) will be dependent not only on pressure and temperature but also upon the value of μ_i in its immediate environment. A state of equilibrium between two different facies may now be expressed by the equation

$$\Delta G = 0 = \Delta E_S + P\Delta V_S - T\Delta S_S + \mu_i \Delta n_i \qquad (17)$$

Where ΔG refers to the megasystem, rock plus environment, ΔE_S, ΔV_S and ΔS_S refer to changes in the rock, and Δn_i is the change in the number of moles of *i* in the environment ($= -\Delta n_{is}$).

It can be shown that the chemical potential may also be defined by the relation

$$\mu_{ia} = \left(\frac{\partial E}{\partial n_{ia}}\right)_{S,V,n_{ja},n_{ka},\ldots} \qquad (16b)$$

so that the combined first and second laws for open systems have the form

$$dE_S = TdS_S - PdV_S + \Sigma_i \mu_i dn_{is} \qquad (18)$$

and the differential form of (17) is then

$$d(\Delta G) = 0 = \Delta V_S dP - \Delta S_S dT + \Delta n_i d\mu_i \qquad (19)$$

Equations (17) and (19) are analogous to equations (1) and (2) for completely closed systems. Equation (17) is that of a *surface* of *divariant* equilibrium in a three-dimensional P-T-μ_i diagram. The field of stability of a specific mineral facies in such a diagram is a volume bounded by divariant surfaces (rather than an area on a P-T diagram bounded by univariant lines). The facies-volume is a region of *trivariant* equilibrium, and the maximum number of phases in a facies is equal to the number of *fixed* components. The intersection of two divariant surfaces is a univariant line, and of three an invariant point. At the invariant point the number of phases may exceed by two the *total* number of components.

Equations (17) and (19) may be generalized to

$$\Delta G = 0 = \Delta E_S + P\Delta V_S - T\Delta S_S + \Sigma_i \mu_i \Delta n_i \qquad (17a)$$

and

$$d(\Delta G) = 0 = \Delta V_S dP - \Delta S_S dT + \Sigma_i \Delta n_i d\mu_i \qquad (19a)$$

if two or more mobile components are involved. and they are now equations

of trivariant or multivariant equilibrium. The equations are no longer amenable to simple graphical representation but we may think of the field of stability of a mineral facies as a region in $(m + 2)$-dimensional space limited by equations of $(m + 1)$-variant equilibrium, where m is the number of mobile components. Fortunately, few specific reactions involve more than one mobile component. For a random choice of P, T and all μ_i we are, in general, in a facies-region and the variance is $m + 2$. This means that in open systems of this sort Goldschmidt's "mineralogical" phase rule should be modified to

$$p = c - m \tag{20}$$

where p is the maximum number of phases, c is the total number of components, and m, as above, the number of mobile components. This relationship was first derived by Korzhinsky (1936, 1950). It has, moreover, commonly been assumed or implied in triangular diagrams for mineral assemblages, in that the water or carbon dioxide content of a phase is generally neglected. The fact that this procedure is successful has been taken in some instances as indicating that water or carbon dioxide was present in *excess* (Bowen, 1940; Yoder, 1952) during the metamorphic process. In view of the lack of other geologic or petrographic evidence that water or carbon dioxide was present as a separate phase in such instances, it appears more reasonable to draw the alternative conclusion, specifically, that a petrologic system is open to water and carbon dioxide.

It will be noted that a system in which *all* components are mobile will, for a random choice of P, T and all μ_i, have "no" phases. This appears anomalous but is not, since we have little interest in systems without phases. Better ways of stating the situation might be to say that for a random choice of P, T and all μ_i there is, in general, no actual phase that will have the specified properties, or to say that the variables are not all independent. When a phase exists in which all components are mobile, the equilibrium between this phase and its environment is univariant, that is, for any random choice of P and all μ_i, T is specified, or for a choice of T and all μ_i, P is specified. Clearly no more than two phases containing *only* mobile components can ever coexist stably in an open system and these only at a specific temperature and pressure.

The limiting cases.—The problem, then, is to consider the ways in which the chemical potential of a given mobile component, i, may vary within the crust of the Earth. Two extreme limiting cases have already been mentioned. To repeat, these occur: (1) when the chemical potential of i is allowed to decrease indefinitely ($\mu_i \rightarrow -\infty$) and (2) when the chemical potential of i is allowed to approach its maximum possible value for a given pressure and temperature ($\mu_i \rightarrow \mu_i \max.(P,T)$).

Regarding i as a component in a solution, condition (1) above is fulfilled as the mole-fraction (N_i) of i in the solution approaches zero, or, for our purposes, when i is virtually absent from the immediate environment of the system in question. In this event no phase containing i is stable at any pressure or temperature.

Condition (2) is effectively fulfilled when the stable form of pure i is present ($N_i = 1$), making $\mu_{i\max.}$ equal to the free energy per mole of the most stable form of pure i at the given pressure and temperature. Values of μ_i in excess of this can never represent the most stable state inasmuch as there must then be a decrease in free energy upon separation of the "pure i." Condition (2) thus corresponds, in essence, to the condition of "excess water" (= excess i) discussed by Yoder (1952). As long as condition (2) is fulfilled the equilibrium is univariant and essentially identical to that in a closed system containing excess i as a nearly pure phase. The qualification "essentially identical" enters in that condition (2) is defined with reference to "strictly" pure i, whereas actual closed systems contain at best "nearly" pure i. This means that conditions (1) and (2) also represent the effective limiting values of μ_i in closed systems. In a closed system, however, it is n_i, not μ_i that must be specified to determine the state of the system, and the two variables are by no means equivalent. Specifically, the *amount* of a phase containing i may be changed at P, T without affecting μ_i, but obviously changing n_i. Similarly. the statement that a hydrate and its anhydride are in equilibrium at P, T *fixes* μ_{H_2O}, though n_{H_2O} may be changed by simply varying the amount of either phase, and conversely if component j is removed at P, T from a solution containing i, μ_i will be changed but n_i will not.

Distribution of the mobile components.—There are at least two alternative hypotheses which might be considered to represent the stable vertical distribution of a given mobile component, i, in the crust of the Earth. One is to assume that the distribution of i is such that there is no longer any tendency for vertical diffusion of i. Complexities arise here, however, owing to the difficulty in determining the diffusion potential in non-isothermal systems.

The other hypothesis, which we shall investigate first, is to suppose that the rock is in osmotic equilibrium with an adjacent fissure system containing a dilute aqueous (hydrothermal) solution at the same temperature. Here, we shall consider the closed megasystem (rock plus nearby fluid) rather than the rock alone. It is instructive, however, to review first the general principles of *osmotic equilibrium*.

Osmotic equilibrium.—Perhaps the simplest example of osmotic equilibrium is that in which the system is divided into two parts separated by a partition or membrane, permeable with regard to certain components, impermeable to others. When equilibrium is reached under such conditions, it is found experimentally that the hydrostatic pressure upon the two parts of the system is different, the difference being supported by the semi-permeable partition. Conversely, the *distribution* of the mobile constituents relative to the partition is found to depend on *three* independent variables: the temperature (which at equilibrium must be constant throughout the system), and the pressures on each side of the partition. As an example let us consider an equilibrium of the sort:

$$\text{hydrous solid} = \text{anhydrous solid} + \text{water}$$

and let us suppose that the solid is separated from the fluid by a wall permeable to water, and that the pressures on opposite sides of the wall may be different. We have then, at equilibrium

$$\Delta G = \Delta G_S + \Delta G_F = 0 \qquad (21)$$

If the "fluid" is not pure water such a transition will take place over an interval owing to the changing composition of the fluid. If the fluid is kept at constant composition, possibly through a continuous supply of "fresh" fluid, however, the transition will be abrupt, and if the volume of fluid is large relative to the reacting solids any interval must be narrow, since the mole fraction of water in the fluid cannot then change appreciably in the course of the reaction. In any event we may consider, alternatively, a metastable equilibrium within the actual interval, as outlined in an earlier section of this paper.

From equation (1) we may also write

$$\Delta G = 0 = \Delta E - T\Delta S + P_S\Delta V_S + P_F\Delta V_F \tag{22}$$

and from equation (2)

$$d(\Delta E) = Td(\Delta S) - P_S d(\Delta V_S) - P_F d(\Delta V_F) \tag{23}$$

hence. if equilibrium is to be maintained,

$$d(\Delta G) = 0 = \Delta V_S dP_S + \Delta V_F dP_F - \Delta S dT \tag{24}$$

It must be emphasized here that P_F is the actual pressure on the fluid, and *not* to be identified with its vapor pressure, if liquid, nor with the "partial pressure" or "partial vapor pressure" of *any* of its components. Holding each of our variables P_F. P_S and T constant in turn, and maintaining equilibrium we have

$$\left(\frac{\partial P_S}{\partial T}\right)_{P_F} = \frac{\Delta S}{\Delta V_S} \tag{25}$$

$$\left(\frac{\partial P_F}{\partial T}\right)_{P_S} = \frac{\Delta S}{\Delta V_F} \tag{26}$$

and

$$\left(\frac{\partial P_F}{\partial P_S}\right)_{T} = -\frac{\Delta V_S}{\Delta V_F} \tag{27}$$

A useful relation[2] is

$$\left(\frac{dP_S}{dT}\right)_{\Delta G = 0} = \frac{\Delta S}{\Delta V_S + \Delta V_F \dfrac{dP_F}{dP_S}} \tag{28}$$

The relative fields of stability of rocks A and B in the above example can be represented by a three-dimensional diagram based upon the variables P_F, P_S and T, the surface separating their respective fields of stability being one of *divariant* equilibrium. It is instructive, however, to consider first equations (25), (26) and (27) above.

Equation (25) is the slope of the trace of the equilibrium surface on a section at constant P_F. ΔS is defined as positive and ΔV_S, with few exceptions (table 5), will be negative, hence it may generally be assumed that the curve will have a negative slope. Its curvature will depend chiefly upon variations

[2] With the stipulation $P_F = P_S = P$ equations (22) and (28) become identical with equations (1) and (3) for ordinary, non-osmotic equilibrium.

in ΔS, but will be slight if ΔC_P is small, that is, if the fluid is a liquid or in a liquid-like supercritical state.

Equation (26) is the slope of the corresponding curve on a section at constant P_S. ΔV_F can be negative only if the mobile component in question has a negative partial molar volume in the fluid. This is possible but unlikely. This curve should thus have in general a positive slope, and, particularly if the fluid is a gas, be markedly concave toward the P_F-axis. The curvature will be most pronounced at low P_F where the compressibility of the fluid is high.

Equation (27) is the slope of the corresponding curve on a section at constant temperature. It should, in general, have a positive slope, and if the fluid is a gas, be markedly concave to the P_F-axis in regions of low P_F.

Another section of some interest is that defined by the stipulation that $P_F = P_S$. The curve on this section is essentially that for an ordinary non-osmotic equilibrium and will have the form of the experimental curves discussed earlier, though offset toward lower temperatures if the fluid is not "pure."

TABLE 5

Change of Volume with Dehydration

Reaction	ΔV_S (cc)	$\frac{\Delta V_S}{\Delta n_{H_2O}}$ (cc)
Brucite → Periclase + Water	−13.0	−13.0
Serpentine → Forsterite + 2 Water + Enstatite	−33.5	−16.8
Talc → 3 Enstatite + Quartz + Water	−19.1	−11.1
Phlogopite + 3 Quartz → 3 Enstatite + Orthoclase + Water	−17.7	−17.7
2 Diaspore → Corundum + Water	−9.2	−9.2
2 Gibbsite → Corundum + 3 Water	−38	−12.7
Kaolinite → Kyanite + Quartz + 2 Water	−32.6	−16.3
Pyrophyllite → Kyanite + 3 Quartz + Water	−16.8	−16.8
Pyrophyllite → Andalusite + 3 Quartz + Water	−8.8	−8.8
Pyrophyllite → Sillimanite + 3 Quartz + Water	−11.8	−11.8
Muscovite + Quartz → Kyanite + Orthoclase + Water	−15.4	−15.4
Muscovite + Quartz → Andalusite + Orthoclase + Water	−7.4	−7.4
Muscovite + Quartz → Sillimanite + Orthoclase + Water	−10.4	−10.4
Chlorite + 2 Quartz → Pyrope + 2 Enstatite + 4 Water	−80	−20.0
2 Chlorite + 7 Quartz → Cordierite + 8 Enstatite + 8 Water	−91	−11.4
3 Chlorite + Muscovite + 3 Quartz → 4 Pyrope + Phlogopite + 12 Water	−240	−20.0
3 Staurolite + 2 Quartz → Almandine + 5 Kyanite + 3 Water	−43	−14.3
3 Staurolite + 2 Quartz → Almandine + 5 Andalusite + 3 Water	−3	−1.0
3 Staurolite + 2 Quartz → Almandine + 5 Sillimanite + 3 Water	−18	−6.0
Analcite → Jadeite + Water	−38	−38.0
2 Analcite → Nepheline + Albite + 2 Water	−37.5	−18.8
Lawsonite → Anorthite + 2 Water	−3	−1.5
4 Clinozoisite + Quartz → Grossularite + 5 Anorthite + 2 Water	+44.6	+22.3
2 Clinozoisite + Muscovite + 2 Quartz → 4 Anorthite + Orthoclase + 2 Water	+62.6	+31.3

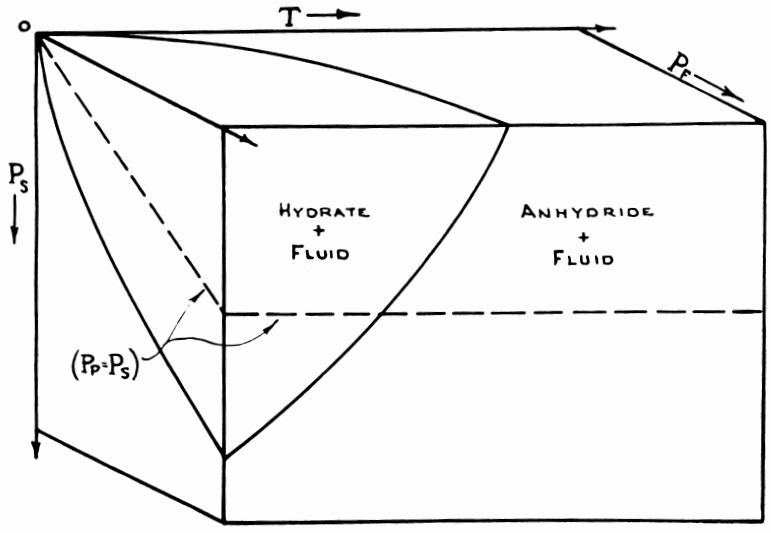

Fig. 1. Probable form of the surface of divariant osmotic equilibrium for reactions of the type: Hydrate + Fluid → Anhydride + Fluid.

The probable appearance of such an equilibrium surface is shown in figure 1. Clearly we have, here, no interest in the region where P_F exceeds P_S and may take as our limiting cases the conditions: $P_F = 0$ and $P_F = P_S$.[3]

The special case of equation (25) where P_F is constant has been given by Johnston and Niggli (1913) and later by Harker (1939) as representing the effect of increasing pressure upon a transition temperature when that pressure increase acts only upon the solid phase. For equation (25) to be applicable to equilibria in the Earth's crust, however, a situation must exist wherein the rock pressure is variable but the fluid pressure remains constant. Inasmuch as *both* rock and fluid pressure may be expected to vary there does not seem to be any justification for the use of equation (25).

EQUILIBRIUM BETWEEN A FLUID-FILLED FISSURE AND THE SURROUNDING ROCK

A situation in which the principles of osmotic equilibrium might legitimately be applied is in the chemical equilibrium between a column of rock and a column of fluid in a nearby fissure. Obviously such a model cannot represent a state of hydrostatic equilibrium unless rock and fluid are of the same density, which is highly unlikely. The immediate walls of the fissure in such a model must be under a non-hydrostatic stress, and must also be

[3] The use of P_F rather than μ_i as the extra variable in dealing with osmotic equilibrium is chiefly a matter of convenience, since P_F and μ_i are not independent in a fluid of given temperature and composition. The condition $P_F = P_S$ corresponds, where the fluid is pure i, to $\mu_{i\,max.}$. If P_F were to exceed P_S the free energy of the system would be lowered by the passage of i through the membrane so as to form a phase of composition i on the "solid" side of the membrane. P_F greater than P_S thus does not correspond to an equilibrium state where the membrane is permeable to all fluid components.

subjected to a mean hydrostatic pressure considerably less than that prevailing in the rock as a whole at the same depth. Because of this, the chemical equilibrium between the fluid and the portions of the rock immediately adjacent to it will be different from that between the fluid and those portions of the rock at sufficient distance from the fissure that the mean hydrostatic pressure may be regarded as determined solely by the weight of the overlying column of rock. For the moment, then, we will set aside the problem of the chemical equilibria *within* the fissure walls and regard the "wallrock" simply as the semi-permeable partition supporting the difference in pressure between rock and fluid.

Hydrostatic equilibrium.—Before proceeding with the fissure system we must first consider the vertical variation of pressure in any medium at hydrostatic equilibrium in a gravitational field. Under these conditions

$$dP = \rho g dz \tag{29}$$

where ρ is the density, g the acceleration of gravity and z the depth taken as positive downward. At any point in such a column

$$P - P^a = \int_a^z \rho g dz \tag{30}$$

where P^a is the pressure when $z = a$. Equation (30) can also be written

$$P - P^a = \rho^m g\ (z - a) \tag{30a}$$

where ρ^m is the mean density of the column between z and a. It is generally safe to assume that mean rock density, $\rho_s{}^m$, is about 2.7 gms/cc.

For the fluid column it is difficult to predict the value of $\rho_F{}^m$ between any two points in the column or even the value of ρ_F at any given point. In general, however, we are perhaps safe in assuming that the fluid is a dilute aqueous solution, closely resembling, in its physical properties, pure water at the same pressure and temperature. Fortunately, the density of pure water is known over a wide range of temperatures and pressures (Kennedy, 1950).

It is convenient to make use of the relations

$$\rho_F = \frac{\overline{M}_F}{\overline{V}_F} \tag{31}$$

(where $\overline{M}_F$ and $\overline{V}_F$ are the mean molecular weight and mean molar volume, respectively, of the fluid at the point in question) and

$$\rho_F{}^m = \frac{\overline{M}_F{}^m}{\overline{V}_F{}^m} \tag{32}$$

where the superscript signifies the corresponding mean quantities over the interval from a to z.

We now have:

$$dP_F = \frac{\overline{M}_F}{\overline{V}_F}\, g dz \tag{33}$$

and

$$P_F - P_F{}^a = \frac{\overline{M}_F{}^m}{\overline{V}_F{}^m}\, g(z - a) \tag{34}$$

Eliminating the terms containing z or dz we may now express P_F and dP_F in terms of P_S and dP_S so that

$$dP_F = \frac{\rho_F}{\rho_S} dP_S = \frac{\overline{M}_F}{\rho_S \overline{V}_F} dP_S \tag{35}$$

or, since *local* variations in rock density are of no concern here

$$dP_F = \frac{\overline{M}_F}{\rho_S{}^m \overline{V}_F} dP_S \tag{36}$$

and

$$P_F - P_F{}^a = \frac{\rho_F{}^m}{\rho_S{}^m} (P_S - P_S{}^a) = \frac{\overline{M}_F{}^m}{\rho_S{}^m \overline{V}_F{}^m} (P_S - P_S{}^a) \tag{37}$$

If our fluid column extends to the Earth's surface it is convenient to have a at zero depth so that $P_F{}^a = P_S{}^a =$ atmospheric pressure (1.013 bars). In the event that the fluid column does not extend to the surface, or is obstructed by some relatively impermeable barrier, it is convenient to have a represent the top of the free fluid column. In this case $P_F{}^a$ is equal to or less than $P_S{}^a$.

With the assumption that our fluid is a dilute aqueous solution, we may substitute the molecular weight of water (18 gms) for $\overline{M}_F$ and $\overline{M}_F{}^m$ so that our final equations of hydrostatic equilibrium become

$$dP_F = \frac{V^*}{\overline{V}_F} dP_S \tag{38}$$

and

$$P_F - P_F{}^a = \frac{V^*}{\overline{V}_F{}^m} (P_S - P_S{}^a) \tag{39}$$

where V^* is a constant with the dimensions of volume defined by

$$V^* = \frac{\overline{M}_F}{\rho_S{}^m} = \frac{\overline{M}_F{}^m}{\rho_S{}^m} = 6.7 \text{ cc.} \tag{40}$$

For a column open to the Earth's surface, and at a depth such that $P_F{}^a$ and $P_S{}^a$ are negligible compared with P_F or P_S, we may use the relation

$$P_F = \frac{V^*}{\overline{V}_F{}^m} P_S \tag{41}$$

in place of equation (39).

The quantity leading to the greatest uncertainty in the above relations is $\overline{V}_F{}^m$, the mean molar volume of the overlying fluid column. For some purposes $\overline{V}_F{}^m$ may be assumed constant at about 18 cc/mole, the molar

volume of water at 25°C. and atmospheric pressure. In this case the ratio $\frac{V^*}{\overline{V}_F{}^m}$ is $\frac{1}{2.7}$ and equations (39) and (41) may be simplified accordingly. If the temperatures and pressures over a significant portion of the fluid column are such that this assumption is unreasonable, $\overline{V}_F{}^m$ may be estimated from the tables of Kennedy (1950).

Osmotic equilibrium in a fissure system.—The equations of osmotic equilibrium for the model fissure system now take the form:

$$\Delta G = 0 = \Delta E + P_S \Delta V_S + (P_F{}^a - P_S{}^a \frac{V^*}{\overline{V}_F{}^m} + P_S \frac{V^*}{\overline{V}_F{}^m}) \Delta V_F - T\Delta S \qquad (42)$$

and

$$\left(\frac{dP}{dT}\right)_{\Delta G = 0} = \frac{\Delta S}{\Delta V_S + \frac{V^*}{\overline{V}_F} \Delta V_F} \qquad (43)$$

The practical use of these equations is hampered by the difficulty in evaluating the quantities $\Delta\overline{V}_F$, $\overline{V}_F{}^m$, ΔS and ΔE. If, however, we restrict our discussion, at first, to reactions where the only volatile component involved is the *solute* itself—in this case, water—we may make simplifications not otherwise possible. It is fortunate in this regard that many of the petrologically important reactions are simple hydrations or dehydrations.

Reactions with water the only mobile component.—In a sufficiently dilute solution the *partial* molar properties of the solute, the corresponding *mean* molar properties of the solution as a whole, and the corresponding molar properties of the pure solute, at the same pressure and temperature, are virtually identical quantities. If the property in question is volume this may be expressed formally by the equation

$$\overline{V}_{iF} = \overline{V}_F = \overline{V}_{iF}{}^\circ \qquad (P,T) \qquad (44)$$

where the subscript, *i*, refers to the solute and the quantities are given in the order mentioned above.

Relations analogous to (44) also hold for other extensive properties such as S, E, H, and G except that conventional notation in the case of the Gibbs free energy leads to

$$\mu_{iF} = \overline{G}_F = \mu_{iF}{}^\circ \qquad (45)$$

Because of (44) we then have, where *i* is the solute,

$$\Delta V_F = \overline{V}_F \Delta n_{iF} \qquad (46)$$

and equation (43) may immediately be simplified to

$$\left(\frac{dP}{dT}\right)_{\Delta G = 0} = \frac{\Delta S}{\Delta V_S + V^* \Delta n_{iF}} \qquad (47)$$

To simplify equation (42), however, a further assumption is necessary, specifically

$$\overline{V}_F = \overline{V}_F{}^m \qquad (48)$$

that the mean molar volume of the fluid at the point in question is nearly equal to its mean value taken over the entire overlying column. This is certainly valid where the column is in a liquid or liquid-like, supercritical state throughout, a condition probably fulfilled in most cases. The range of validity of this approximation, however, is actually somewhat greater than this because the increase of pressure with depth tends to offset the effects of the rise in temperature, and (48) is thus valid wherever the thermal gradient in the column approaches $\left(\frac{\partial T}{\partial P}\right)_V$ for water. With approximation (48) equation (42) simplifies to

$$\Delta G = 0 = \Delta E + P_S \Delta V_S + (P_F{}^a\overline{V}_F - P_S{}^aV^* + P_S V^*)\Delta n_{iF} - T\Delta S \qquad (49)$$

From equation (41) (valid where $P^a{}_S$ and $P^a{}_F$ are negligible), this in turn becomes

$$\Delta G = 0 = \Delta E + P_S(\Delta V_S + V^*\Delta n_{iF}) - T\Delta S \qquad (50)$$

The close analogy between equations (47) and (50) and equations (3) and (1) respectively is interesting. V^* is evidently to be interpreted as the effective molar volume of water under the above conditions of "fissure equilibrium." It is also instructive to compare equation (47) with equation (25).

From the values in table 5 it is evident that ΔV_S per mole of water lost is generally on the order of 8 to 20 cc/mole of water. The values for reactions involving epidote or lawsonite versus plagioclase are exceptional, probably because the dehydration is incidental, here, to major crystal-structural changes analogous to those in the reaction *2 jadeite → nepheline + albite.*

Entropy determinations on hydrated minerals are few, the only data currently available being for the hydroxides of magnesium, aluminum and calcium. The reaction *2 gibbsite → corundum + 3 water* involves an entropy change, at 25°C. and one atmosphere, of 408 ± 18 decijoules/deg/mole of water, and the reaction *brucite → periclase + water* an entropy change of 344 ± 21 decijoules/deg/mole of water. Noting that these dehydrations do not involve a change in the first-order coordination of the aluminum or magnesium atoms, it might be suggested that the mean of these values (375 dj/deg/mole of water) is a fair approximation wherever this condition is fulfilled, and the water is held as hydroxyl. This assumption, though admittedly shaky, has been employed in compiling table 6, for reactions in which there is no major change in the first-order coordination of the metallic elements. Where there is a coordination change, as in the breakdown of pyrophyllite to andalusite or sillimanite, rather than to kyanite; or in the breakdown of analcite to jadeite, rather than to nepheline and albite, the ΔS has been modified in accord with the data in table 3. It will be observed that the values of dP/dT so calculated are *negative* and somewhat steeper than the curves for most solid-solid univariant equilibria. In any region where the fluid is a gas or gas-like supercritical fluid ΔS will certainly be greater than our estimate and the slopes of the curves steeper than in table 6. If the mean density of the overlying fluid column is significantly less than that at the point in question, moreover, $\overline{V}_F{}^m$ and the dehydration temperature at any P_S will be less than predicted by relation (48) Dehydration temperatures under

the conditions of "fissure equilibrium" should thus, in general, vary with depth (P_S) as indicated by curve *c* in figure 2. Curve *a* is the general form of curves, calculated or determined experimentally, where P_F is equal to P_S and the fluid is pure water. Curve *b* is that predicted by the Johnston-Niggli relation (25), and curves *d* and *e* suppose "fissure equilibrium" beneath an impermeable barrier.

Metamorphism of carbonate rocks.—It must be emphasized that the above simplifications cannot safely be made in dealing with reactions involving carbon dioxide. Specifically, we cannot make any simple assumption as to the partial molar volume, or partial molar entropy of carbon dioxide in the fluid, even with the assumption that it is a dilute aqueous solution. The mixing properties of water and carbon dioxide, owing to the formation of carbonate and bicarbonate ions, are complex and are sensitive to the presence of other components in solution. It is clear that curves such as that calculated by Goldschmidt (1912) represent *maximum* decarbonatization temperatures at any depth, but we cannot, at present, evaluate equations (42) and (43) with sufficient confidence to say how much the conditions of fissure equilibrium would lower these temperatures in any specific instance.

Goldschmidt's curve for the calcite-wollastonite equilibrium has been recalculated recently by Danielsson (1950). Danielsson also, in the same

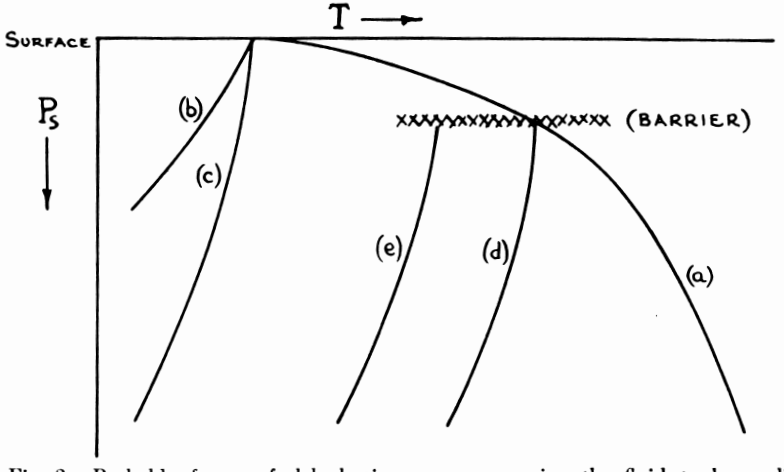

Fig. 2. Probable forms of dehydration curves assuming the fluid to be a dilute aqueous solution:

(a) $P_F = P_S$
(b) P_F = constant (Johnston-Niggli equation)
(c) The fluid occupies a fissure system open to the surface
(d) The fluid occupies a fissure system beneath an impermeable barrier at the base of which $P_F = P_S$
(e) The fluid occupies a fissure system beneath an impermeable (or semi- permeable) barrier at the base of which $P_F < P_S$

Curves (c), (d) and (e) are uniquely determined for a given dehydration only in the event that the mean density of the overlying fluid column is known.

TABLE 6

Dehydration Data (Fissure Equilibrium)

Reaction	$\frac{\Delta S}{\Delta n_{H_2O}}$ (dj/deg)	$\left(\frac{\Delta V_S}{\Delta n_{H_2O}} + V^*\right)$ (cc.)	$\frac{dP}{dT}$ (bars/deg)
Brucite → Periclase + Water	344±21	-6.3	-55
Serpentine → Forsterite + Enstatite + 2 Water	375*	-10.1	-37+
Talc → 3 Enstatite + Quartz + Water	375*	-12.4	-30+
2 Gibbsite → Corundum + 3 Water	408±18	-6.0	-68
Kaolinite → Kyanite + Quartz + 2 Water	375*	-9.6	-39+
Pyrophyllite → Kyanite + 3 Quartz + Water	375*	-10.1	-37+
Pyrophyllite → Andalusite + 3 Quartz + Water	470*	-2.1	-225+
Pyrophyllite → Sillimanite + 3 Quartz + Water	500*	-5.1	-98+
Analcite → Jadeite + Water	65*	-31.3	-2+
2 Analcite → Nepheline + Albite + 2 Water	375*	-12.1	-31

* Entropies of dehydration estimated by method outlined in text.

paper, considered the reaction from the point of view of simple osmotic equilibrium, assuming the fluid to be pure carbon dioxide. He pointed out, however (p. 69), that the presence of water vapor and, implicitly, other components would alter the results.

The walls of the fissure.—The equilibria within the fissure walls, as distinct from those in the main body of the rock, constitute an interesting problem in view of the extensive current literature on "wallrock alteration." The stress in the walls must be non-hydrostatic wherever P_F is less than P_S, the mean hydrostatic pressure on the solids, P_s^m, tending to approach P_F near the fissure. Assuming that the unequal stress distribution affects the equilibrium only by way of P_s^m, it is probable from the equations of osmotic equilibrium that we should anticipate *higher* dehydration temperatures in the immediate vicinity of the fissure than at a distance. In other words we may expect the degree of hydration of a given rock to increase as the fissure is approached, other things being equal. Conversely, we are not justified in concluding from an observed phenomenon of this sort that "other things" were not equal. It does not, for example, necessarily mean that the fluid in the fissure was at a *lower* temperature at the time of alteration, inasmuch as the formation of a fissure filled with fluid could affect the wallrock in this way even if the fluid were slightly hotter. If the degree of hydration *decreases* toward the fissure, vein or dike, however, it is probably safe to assume that the material in the fissure was significantly hotter than the surrounding rock. In short a "contact metamorphism" gives us positive evidence of a thermal gradient whereas a "wallrock alteration" does not.

VERTICAL DIFFUSION OF THE MOBILE COMPONENTS

An alternative hypothesis is to suppose that an equilibrium distribution of the mobile components in the Earth's crust can be effectively maintained by diffusion alone. In this view the chemical potential gradients by which we might define the limits of stability of a mineral facies would be those obtaining when any tendency for net transport of the mobile components by diffusion has ceased to exist.

Isothermal diffusion.—In a system at constant temperature throughout, net horizontal transport of any mobile component, i, will cease when the horizontal components of its chemical potential gradient are zero. That is, if the x- and y-coordinates are in a horizontal plane,

$$\left(\frac{\partial \mu_i}{\mathrm{d}z}\right)_T = \left(\frac{\partial \mu_i}{\partial y}\right)_T = 0 \tag{51}$$

when there is no net horizontal flow. Vertical flow will cease, however, only when the vertical component of the chemical potential gradient is balanced by the force exerted by gravity upon one mole of i, hence, at equilibrium

$$\left(\frac{\partial \mu_i}{\partial z}\right)_T = \overline{M}_i g \tag{52}$$

where z is the depth, positive downward, M_i is the mass of one mole of i, and g the acceleration of gravity.

Making use of equation (29), then, and neglecting any horizontal components, we have at equilibrium:

$$\left(\frac{d\mu_i}{dP_s}\right)_T = \frac{\overline{M_i}}{\rho s^m} \tag{53}$$

The usefulness of the above relations to petrology is impaired by the constant-temperature restriction. Diffusion at igneous contacts is obviously not isothermal, nor is diffusion over any extended vertical range, owing to the geothermal gradient.[4]

Non-isothermal diffusion.—No system in which there is a net flow of matter (diffusion) or of heat may be regarded as in a state of true thermodynamic equilibrium. Since no known substance is a perfect thermal insulator, there can be no true thermodynamic equilibrium in any system in which there is a thermal gradient.

There has, however, been an extension of thermodynamic methods to the point where such problems may be handled at least qualitatively, provided such a flow of heat or matter has reached a *steady state* (does not change with time). Recent summaries of this work are those by de Groot (1951) and Denbigh (1951). These researches are pertinent in the present instance because we are interested in just such a steady state,—that in which there is no flow of matter and a constant flow of heat. The flow of heat may be held constant by some external agency, the nature of which need not concern us. The phenomenon of a compositional or chemical potential gradient resulting from a steady thermal gradient is known as the *Soret effect.*

Following the method outlined in Denbigh (1951, p. 14-21 and 63-75) we arrive at the relation

$$\text{grad } \mu_i = F_i - \left(\overline{S}_i + \frac{Q_i^*}{T}\right) \text{grad } T \tag{54}$$

for the condition that there be no flow of matter in a system with a steady thermal gradient. F_i is any external force acting on i (in this case gravity) and Q_i^* is a quantity known as the molar "heat of transport" of component i. Q_i^* may be defined by the relation

$$Q_i^* = Q_i - \overline{H}_i \tag{55}$$

where H_i is the partial molar enthalpy of i, and Q_i is the energy transported. per mole of i, in isothermal diffusion at P, T. This suggests correlation of Q_i^* with the extra energy possessed by the moving atoms as compared to the "average" atoms, and suggests, further, a close relationship between Q_i^* and the activation energy of diffusion. Q_i^* will presumably vary with temperature, pressure and composition, but there is virtually no quantitative informa-

[4] What is roughly equation (52) above has been derived by Ramberg (1944) and has appeared more recently in the book by Barth (1952). The necessary stipulation of constant temperature, however, is missing in Ramberg's relation, as is also the acceleration of gravity. This last omission is valid only if it be understood that z is the negative of the geopotential rather than the depth, or, alternatively, if the forces and energies are understood to be in gravitational rather than absolute units. Neither condition is conventional usage, nor was either specified by Ramberg. The constant temperature stipulation has also been neglected in the discussion by Turner and Verhoogen (1951, p. 40-42).

tion available. From the probable relationship to activation energy, however, it appears reasonable to predict that Q_i^* will be a positive quantity at least in the case of solid or liquid diffusion.

Neglecting any horizontal components of the geothermal gradient, and assuming hydrostatic equilibrium in the crust, equation (54) becomes

$$\frac{d\mu_i}{dz} = M_i g - \left(S_i + \frac{Q_i^*}{T}\right)\frac{dT}{dz} \tag{56}$$

or

$$d\mu_i = \frac{\overline{M_i}}{\rho_S^m}\, dP - \left(S_i + \frac{Q_i^*}{T}\right) dT \tag{56a}$$

The integrated form of equation (56a) is

$$\mu_i = \mu_i^a + \frac{\overline{M_i}}{\rho_S^m}(P_S - P_S^a) - \int_{T^a}^{T} \left(\overline{S_i} + \frac{Q_i^*}{T}\right) dT \tag{57}$$

where the superscript a refers to values at the surface of the Earth or at the base of any impermeable barrier. Where a is at the Earth's surface P_S^a may be neglected and we have

$$\mu_i = \mu_i^a + \frac{\overline{M_i}}{\rho_S^m} - \int_{T^a}^{T} \left(\overline{S_i} + \frac{Q_i^*}{T}\right) dT \tag{57a}$$

Multivariant equilibrium.—For simplicity we may define V_i^* and S_i^* by the relations

$$V_i^* = \left(\frac{\partial \mu_i}{\partial P}\right)_T = \frac{\overline{M_i}}{\rho_S^m} \tag{58}$$

and

$$S_i^* = -\left(\frac{\partial \mu_i}{\partial T}\right)_P = \left(\overline{S_i} + \frac{Q_i^*}{T}\right) \tag{59}$$

for steady state conditions with no net flow of i. It is apparent that these quantities are the *effective* molar volume and entropy, respectively, of component i in the immediate environment of a given open system under the above conditions.

By substituting for μ_i and $d\mu_i$ in equations (17a) and (19a) we have then

$$\Delta G = 0 = \Delta E_S + P_S \Delta V_S - T\Delta S_S + \Sigma_i \Delta n_i [\mu_i^a + V_i^*(P_S - P_S^a) - \int_{T_a}^{T} S_i^* dT] \tag{60}$$

and

$$\left(\frac{dP_S}{dT}\right)_{\Delta G = 0} = \frac{\Delta S_S + \Sigma_i S_i^* \Delta n_i}{\Delta V_S + \Sigma_i V_i^* \Delta n_i} \tag{61}$$

In the absence of impermeable barriers equation (60) becomes

$$\Delta G = 0 = \Delta E_S + P_S \Delta V_S - T\Delta S_S + \Sigma_i \Delta n_i (\mu_i^a + V_i^* P_S - \int_{T_a}^{T} S_i^* dT) \tag{60a}$$

Where water is the only mobile component we have then

$$\Delta G = 0 = \Delta E_S + P_S\Delta V_S - T\Delta S_S + \Delta n_{H2O}(\mu^*_{H2O} + V^*_{H2O}P_S - \int_{Ta}{}^{T}S^*_{H2O}dT) \quad (62)$$

and

$$\left(\frac{dP_S}{dT}\right)_{\Delta G=0} = \frac{\Delta S_S + S^*_{H2O}\Delta n_{H2O}}{\Delta V_S + V^*_{H2O}\Delta n_{H2O}} \quad (63)$$

These may be compared with equations (50) and (47) for fissure equilibrium.

It is likely that the partial molar entropy of "interstitial water" ($\overline{S}_{H2O}$) would be significantly greater than the effective molar entropy of the combined water in a given reaction $\left(\frac{-\Delta S_S}{\Delta n_{H2O}}\right)$ owing to its less ordered state of aggregation. It is also probable that Q_{H2O}* is a positive quantity if we are correct in relating it to the activation energy for diffusion. These considerations *suggest* that equation (63), like equation (47), would indicate steep negative slopes for most dehydration curves, and consequently that "diffusion equilibrium" and "fissure equilibrium" do not yield greatly different results.

Diffusion versus flow through fissures.—The merit of "diffusion-equilibrium relative to "fissure equilibrium" depends to a considerable extent upon the nature of the geologic situation to which applied. Where a fissure system exists the water in the fissure would presumably exercise the dominant control over the chemical potential gradient of water, at least, in the immediately adjacent rocks.

For other mobile components the situation is less clear. It is possible, if the fluid in the fissure were not in active circulation, that the chemical potential gradients of the various solute species might reach equilibrium within the fluid column. These gradients would probably differ somewhat from those in the adjacent rock column owing to the dependence of $\overline{S}_i$ and Q_i* upon the environment of *i*, even where rock and fluid are in thermal equilibrium with each other at all depths. In this event the gradients established in the fluid column, when such is present, would probably dominate owing to the faster diffusion in the fluid.

An opening where P_F is less than P_S is thermodynamically metastable, if not unstable, and may be expected to close in time, either through filling by solution and recrystallization or by mechanical collapse of the walls. The *continued* existence of a fissure system at any depth thus depends on its being maintained by some outside agency such as diastrophic or orogenic movements, or explosive igneous activity. It would appear, then, that no definite statement can be made as to the depth at which a fissure system *open to the surface* can exist, the answer depending upon such imponderables as the rate of closure of a fissure, once formed, versus the rate at which it is reopened by tectonic or igneous activity. A fluid-filled opening *not* open to the surface can exist at any depth as long as P_F is not too much less than P_S, owing to support

of the walls of the fluid. In general, then, we might expect the *relative* importance of vertical solid diffusion to be greater for "deep" rather than "shallow" processes, partly because of the relative scarcity of openings at "depth" and partly because of the greater effectiveness of diffusion at high temperatures.

GEOLOGIC APPLICATIONS

We have considered several limiting cases with regard to reactions in which mobile components are directly involved. In each of these cases, we have, in effect, treated the chemical potential of a mobile component as a function of pressure and temperature in a way consistent with certain assumptions. In summary, these are:

Case 1. The mobile component in question is present as a pure phase at the same temperature and pressure as the surrounding rock. This is the assumption implicit in current hydrothermal experimental work and in calculated equilibria such as that of Goldschmidt for calcite-wollastonite. It yields a *maximum* equilibrium temperature at any given pressure (depth).

Case 2. The rock is in chemical equilibrium with a fissure system containing a dilute aqueous solution. This method is applicable only when the mobile component in question is water itself. It indicates a decrease in most dehydration temperatures with depth.

Case 3. The vertical gradient of chemical potential of the mobile component has reached a value such that there is no longer any tendency for vertical diffusion of this component. This method also suggests (not without reservations) a slight decrease of most devolatilization temperatures with depth.

Case 4. The chemical potential of the mobile component is sufficiently low that no phases containing it are stable.

For simplicity, we will refer to these limiting cases as cases 1, 2, 3, and 4, respectively. It now remains for us to consider the extent to which these may be applicable to some specific geological problems.

Crystallization of igneous rocks.—It is a point of general agreement among petrologists that the crystallization of a magma will be accompanied by a tendency toward supersaturation of the magma with regard to its "volatile" components. It is also a fairly safe assumption that an unaltered igneous rock contains less of any "volatile" component than the magma from which it is crystallized. This means that magma during crystallization is a "source" of volatiles and should tend to maintain the chemical potential of the volatile components at relatively high values if the "escape" of these components is in any way hindered. That is, we should expect relatively high temperatures for "devolatilization" equilibria, possibly approaching case 1 in some instances. There is, in fact, some evidence to suggest that in certain instances the chemical potentials of the volatiles have reached a value such that a "vapor" phase has separated and boiled off, and there is certainly no doubt that vapor phases have formed when the pressure on a magma has suddenly been lowered in a volcanic eruption, as many vesicular lavas bear witness. To the extent that a "vapor" formed in this way may be regarded as a one-component phase (most likely in the case of water), we have a fair ap-

proximation to case 1. The field of stability of biotite or hornblende, then, under the conditions of case 1, should not greatly exceed its field of stability in igneous rocks.

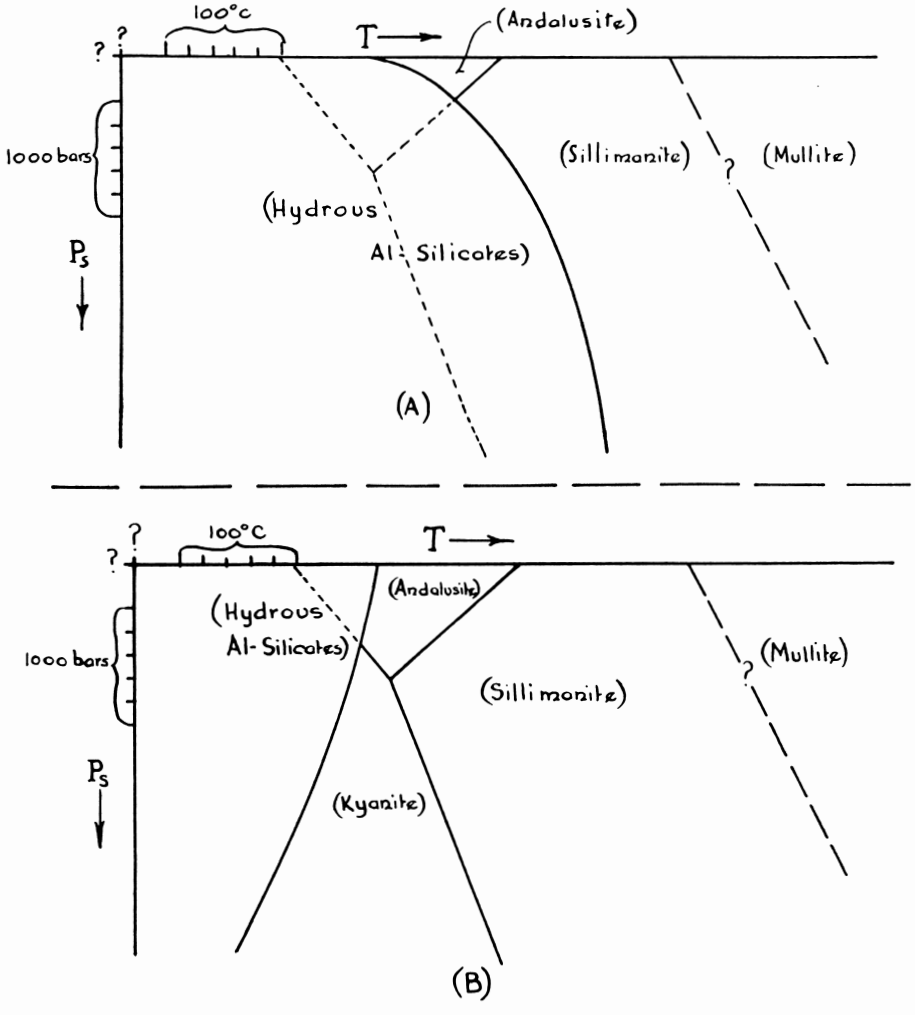

Fig. 3. (A) Possible stability relations among Al-silicates for metamorphism at igneous contacts (intermediate between case 1 and case 2). The field of kyanite is shown as masked by that of hydrous Al-silicates (pyrophyllite, kaolinite). In hydrothermal experiments (case 1) the fields of andalusite and sillimanite appear to be masked as well. Position of kyanite-andalusite-sillimanite triple point is not known, and nature of sillimanite-mullite transition is uncertain.

(B) Possible stability relations among Al-silicates for regional metamorphism (approaching case 2).

A similar relationship among the aluminum silicate polymorphs has been proposed by Miyashiro (1949b).

Metamorphism at igneous contacts.—The conditions prevailing in a contact aureole should not differ greatly in this regard from those in the magma itself, inasmuch as the country rock on heating would also be a source of volatiles. In a limestone, furthermore, a relatively high chemical potential of carbon dioxide might well be obtained, though unlikely to approach case 1, owing to the presence of magmatic water.

Regional metamorphism.—A shale or limestone undergoing regional metamorphism would also constitute a source of volatiles. It would appear, however, that here the chances of building up or maintaining a high chemical potential of any given volatile would be relatively less than in the preceding examples. The rocks are likely to be kept "open" by orogenic movements, and the time involved is presumably greater. In a relatively slow metamorphic process, then, the mobile components have more opportunity to escape, and we may expect an approach to the conditions of case 2 or case 3.

Both fissure equilibrium and free vertical diffusion indicate, in general, little variation of devolatization temperatures with depth. It is probably safe, therefore, to assume that a given devolatilization will take place at a lower temperature for a given depth in typical regional metamorphism than in a typical contact aureole, though the two may overlap inasmuch as there appear to be all gradations between "regional" and "contact" metamorphism.

Stress and antistress minerals.—The generalization that a given "devolatilization" will occur at a lower temperature, other things being equal, in regional metamorphism than in contact metamorphism suggests that certain of the "stress" minerals of Harker may be merely low temperature anhydrous, or nearly anhydrous phases, and that their fields of stability in "thermal" metamorphism may be "submerged" by those of the corresponding hydrous phases; that is, that the breakdown of hydrous Al-silicates to yield Al_2SiO_5 may occur in the field of kyanite (fig. 3) in most regional metamorphism, but may be delayed until andalusite, sillimanite or mullite is stable in contact metamorphism.

A similar comment might be made with regard to the non-appearance of pyrope garnet in the hydrothermal experimental work of Yoder (1952); or to the observed relations between jadeite, analcite, nepheline and albite (Yoder, 1952; Adams, 1953); and possibly to the absence of an anthophyllite field in the work of Bowen and Tuttle (1949). In each of these instances the experimental work has been done under the condition P_S equals P_{H_2O} and should thus yield *maximum* dehydration temperatures.

Metamorphism of igneous rocks.—The metamorphism of pre-existing igneous rocks offers an interesting problem in that the initial material is devoid of volatiles, or nearly so, and should, if the metamorphism is at a sufficiently low temperature, tend to acquire them. Thus an igneous body such as a dunite might constitute a local "sink" for volatiles in a later metamorphism. The observed peripheral alterations to serpentine and thence to talc-carbonate indicate that this is so, at least in some instances. Under such conditions, then, we may expect abnormally *low* temperatures in or near such bodies for equilibria involving volatiles. An igneous mass, in other words,

may be expected to behave as a local desiccator during subsequent low-temperature metamorphism.

Polymetamorphism.—Polymetamorphism, at least where it involves a low temperature metamorphism following one at high temperature, offers a parallel situation to the low-temperature alteration of igneous rocks in that the initial material is dehydrated or partially so. Thus, in the low-grade metamorphism of an older high-grade terrane, as in the regional metamorphism of pre-existing hornfels (Tilley, 1935), or in the Paleozoic metamorphism of Precambrian gneiss in the Green Mountains of Vermont, we should expect anhydrous mineral facies to be stable at relatively low temperatures. Noting that most solid-solid equilibrium curves have positive slopes, this suggests the possibility of the formation at abnormally low temperatures and pressures of facies that under the conditions of case 2 or 3 would be limited to high temperatures and pressures. It is tempting, in this regard, to speculate that some occurrences of eclogite and glaucophane schist may be of polymetamorphic origin (recrystallized pyroxene hornfels) in the regions where, were volatiles more readily available, greenstone schists might otherwise have formed. Another possibility is that these are products of low temperature desiccation of greenstone schists inasmuch as they commonly occur in association with serpentinized or partly serpentinized ultramafics.

Hydrothermal veins.—Fissure equilibrium or, in a more restricted sense, fissure equilibrium beneath an "impermeable barrier" may be regarded as an attempt to establish a model for the thermodynamic treatment of hydrothermal veins and their relations to the surrounding rock. There are at least two restrictions, however, that might well be emphasized. One is that the method is most successful in dealing with reactions involving the *solvent*, in other words, to hydrations and dehydrations. To apply it to metasomatic processes involving other components we need more data than now available on the properties of their aqueous solutions. The other restriction is that the temperatures of rock and adjacent fluid must not be greatly different, the problem otherwise being one of "steady state" conditions rather than a true thermodynamic equilibrium.

Interpretation of experimental results.—In a recent discussion of his hydrothermal investigations Yoder (1952) distinguishes between conditions of "excess" and "deficient" water, analogous to "oversaturation" or "undersaturation" with respect to silica or some other fixed component. Since Yoder did not consider the effect of other components in the aqueous phase, nor the effect of a pressure upon it less than that on the surrounding crystals, "excess water" would thus correspond to our case 1, and a *total* "deficiency" of water to our case 4. In a sense, case 2 and case 3 are special instances of water "deficiency," but the analogy breaks down here in that we have treated rocks as open systems with regard to water and certain other components, whereas Yoder's treatment is applicable, strictly, only to a closed system.

Yoder, in other words, considers equilibria with regard to a given *water-content* or *percent* water, whereas we have done so with regard to a given *chemical potential* of water. Yoder's variables might be given as P, T and

n_{H_2O} or % H_2O and ours as P, T and μ_{H_2O}. The two, furthermore, are not equivalent. If a given phase containing water is present at a given temperature and pressure, the amount of this phase and hence the percent of water in the system may be increased indefinitely without altering in any way the chemical potential of water in the system. In another example we may have present, at a given pressure and temperature, a hydrate and its corresponding anhydride in equilibrium. These stipulations, alone, are sufficient to determine the *chemical potential* of water in the system, but to determine *percent* water we must know the relative amounts of hydrate and anhydride. Thus knowledge of P, T and number of moles of water or percent water does not define the chemical potential of water nor is knowledge of P, T and μ_{H_2O} sufficient to specify the water content.

Clearly it is an advantage to use percent water as a variable in certain types of experimental work, inasmuch as reactions in a "bomb" are in a closed system and must run at a given P (or V), T and "percent" water. In the Earth's crust, however, it appears more reasonable to assume that "percent water" is not fixed, and that reactions will proceed at a given P, T and chemical potential of water rather than at a given P, T and percent water.

Experimental apparatus in which the chemical potential of water may be "controlled" is a possibility. One approach is to apply the hydrostatic pressure to the solids by means of some fluid phase other than pure or virtually pure water, thus making possible values of μ_{H_2O} less than the molar free energy of pure water at the same pressure and temperature. This will lower the equilibrium temperature at a given pressure for *any* dehydration. If the "other" fluid component is an inert gas, incapable of reacting with the solids, its role in the experiment may be regarded as analogous to that of the walls of the bomb—that is, as a necessary part of the apparatus. Although real gases at high pressures are not "ideal" in the sense of obeying the ideal gas law, they are, in certain instances *ideal mixtures*. For water as a component of an ideal mixture, we have

$$\mu_{H_2O} = \mu_{H_2O}^{\circ} + RT\ln N_{H_2O} \tag{64}$$

where $\mu_{H_2O}^{\circ}$ is the chemical potential of *pure* water at the same P and T, and N_{H_2O} the mole-fraction of water in the gas. If the mixture is not ideal we must use the relation

$$\mu_{H_2O} = \mu_{H_2O}^{\circ} + RT\ln N_{H_2O} f_{H_2O} \tag{65}$$

where f_{H_2O} is the activity coefficient of water in the mixture. If the activity coefficients are known, or the system is ideal, we can thus determine μ_{H_2O} from the mole-fraction of water in the fluid phase and the P-V-T data for pure water (Kennedy, 1950). In this regard it would be advantageous to have the volume of fluid large relative to that of the reacting solids so that N_{H_2O} may be regarded as nearly constant. Alternatively, the equilibrium relations for any values of μ_{H_2O} may be calculated from the experimental results with "excess" water if the entropies, volumes and heat capacities of the condensed phases are known. It is perhaps not out of place to emphasize here the definite

need for more thermochemical data on rock-forming minerals, and for additional P-V-T data on such geologically important gases as water and carbon dioxide.

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