ART. XLIX.—*The Melting Phenomena of the Plagioclase Feldspars*; by N. L. BOWEN.

INTRODUCTION.

THE exact relation which the feldspars, albite and anorthite, bear to each other has for a good many years been a question of much interest to mineralogists and petrologists. The continuous passage from the one to the other in chemical composition, found in the plagioclase feldspars, and the like passage in optical and other physical properties, has been regarded by the great majority as satisfactory evidence of complete solid solution. Since Day and Allen* added thermal properties to this list the evidence has been generally conceded to be conclusive.†

These investigators, working with chemically pure, artificial mixtures, studied the temperature of change of state from solid to liquid of various compositions under precisely similar conditions and were able to establish a perfectly continuous relation between them. The temperatures at which maximum heat absorption was found to occur, when plotted against composition, gave a smooth curve. The method used was not suitable for the determination of the magnitude of the melting interval or, more technically stated, the position of solidus and liquidus. The curve obtained by Day and Allen might, therefore, lie anywhere between the solidus and liquidus, and is not necessarily the liquidus itself, as some appear to have assumed. The attempt of Day and Allen to decide the question of a melting interval by trying to establish a difference of composition between the first crystals and the residue gave only negative results, but this fact, as they recognized,‡ might have been due to the extreme viscosity of the melts. Since the completion of this pioneer work of its kind, the facilities of the Geophysical Laboratory have been greatly increased, and one of the methods introduced (sudden cooling after long exposure to a fixed temperature) is especially useful for the study of melting phenomena in substances which form viscous liquids on melting. It was, therefore, deemed advisable to undertake the study of the plagioclase feldspars by this method of sudden quenching. The time consumed in the work was greatly les-

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* The Isomorphism and Thermal Properties of the Feldspars, Carnegie Institution of Washington, Pub. No. 31.

† Cf., however, Weinschenk-Clark, Petrographic Methods, New York, 1912, p. 331-332.

‡ L. c., p. 72.

sened by the fact that the writer was able to use in the present investigation the same artificial mixtures prepared by Day and Allen.

EXPERIMENTAL PART.

Method of Working.

An idea of the principle involved in quenching may be conveyed by a brief description of the method as practised. A charge of a given composition is held at a measured temperature for a definite period of time and is then quenched by allowing it to fall into a dish of mercury at room temperature. The instantaneous chilling precludes any possibility of physical or chemical readjustment in the charge; any portion that was liquid at the furnace temperature appears as glass, and any crystalline portion remains, in general, unchanged in crystal form. Examination of the quenched charge under the microscope, then, reveals those phases which were present at the furnace temperature. The time of holding the charge at constant temperature may be lengthened at will and equilibrium assured even in extremely viscous materials.

The furnace used in the present work was a platinum resistance furnace, kept at constant temperature by regulating a resistance in series with it. By constant watching, the temperature could be held within one degree of the temperature desired. The furnace thus becomes a high-temperature thermostat. The junction of the thermoelement was within seven or eight millimeters of the charge, which offered abundant accuracy in a thermostat arrangement.

This system (furnace and thermoelement) was calibrated by quenching charges of substances of known melting points, lithium metasilicate, diopside and anorthite, under like conditions. The results of this calibration are tabulated below. In each individual case the initial material was completely crystalline.

TABLE I.

Composition	Temperature microvolts	Time	Result	Date
Li_2SiO_3	11820	1/2 hr.	cryst.	Jan. 10, 1913
Li_2SiO_3	11920	1/2 hr.	cryst.	Jan. 10, 1913
Li_2SiO_3	11950	1/2 hr.	glass	Jan. 10, 1913
Li_2SiO_3	11950	1/4 hr.	glass	Jan. 10, 1913

The melting-point therefore lies between 11920 and 11950 microvolts; value by standard element 11953 microvolts. Correction to be applied to quenching system is therefore, for the present purpose, negligible.

$CaMg(SiO_3)_2$	14160	1/2 hr.	cryst.	Nov. 22, 1912
“ “	14200	1/2 hr.	glass	Nov. 22, 1912
“ “	14150	1/2 hr.	cryst.	Jan. 10, 1913
“ “	14180	1/2 hr.	glass	Jan. 10, 1913

Melting point between 14160 and 14180 M.V.
Value by standard element 14231 M.V. Correction + 60 M.V.

$CaAl_2Si_2O_8$	16100	1/2 hr.	glass	Nov. 22, 1912
“	16050	1/2 hr.	glass	Nov. 22, 1912
“	16010	1/2 hr.	cryst.	Nov. 22, 1913
“	16030	1/2 hr.	cryst. & glass	Jan. 10, 1913
“	16000	1/2 hr.	cryst. only	Jan. 10, 1913

Melting temperature 16030 M.V.
Value by standard element 16150 M.V. Correction + 120 M.V.

It will be noted that after several weeks continuous use (Nov. 22 to Jan. 10) the thermoelement was found unaltered. By interpolating between these values, the correction to be applied to the individual readings, in order to express them in terms of the standard element of Sosman and the nitrogen scale,* is readily found. These corrections have been applied to all readings in changing to degrees.

The application of this method of quenching to the specific problem of the feldspars was directed towards two definite ends; first, the determination of the exact limits of the melting interval for a given composition, and second, the determination of the composition of the solid and liquid phases present at a given temperature within the melting interval.

Determination of the Limits of the Melting Intervals.

The location of the temperature of the lower limit of the melting interval (solidus) was accomplished by starting with completely crystalline material of a certain composition and holding it for one hour at successively higher temperatures until a temperature was reached at which the quenched product showed a trace of glass. For the upper limit (liquidus), a charge wholly or partially crystalline was held at successively higher temperatures, again for periods of one hour each, until the quenched product showed that the last tiny crystals had dissolved in the glass. This temperature was then further checked by holding a clear glass of the same composition at successively lower temperatures until crystals appeared in the quenched product.

The results of these trials may be most concisely presented in tabular form.

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* This Journal, xxx, p. 1, 1910. Day and Sosman, High Temperature Gas Thermometry; Carnegie Institution of Washington, Pub. 157, p. 119.

TABLE II.

Date 1912	Initial Condition	Temp. microvolts	Temp. degrees.	Time	Result
		Ab_1An_5			
Nov. 24	Cryst.	15110	1470	1 hr.	Small amount of glass formed.
Nov. 24	Cryst.	15000	1461	1 hr.	No change apparent.
Nov. 24	Cryst.	14900	1453	1 hr.	No change apparent.
		Solidus 1465° ± 4°			
Nov. 26	Cryst.	15800	1530	½ hr.	All glass.
Nov. 26	Cryst.	15750	1526	½ hr.	All glass.
Nov. 26	Cryst.	15720	1522	½ hr.	All glass.
Nov. 27	Cryst.	15700	1520	1 hr.	Glass and a very few crystals.
Nov. 27	Glass	15650	1516	1 hr.	Glass and a very few crystals.
		Liquidus 1521° ± 2°			
		Ab_1An_2			
Nov. 22	Glass	15270	1484	1 hr.	Glass and a few crystals.
Nov. 22	Cryst.	15340	1489	1 hr.	Glass and crystal specks.
Nov. 22	Cryst.	15370	1492	1 hr.	Glass only.
1913					
Jan. 7	Cryst.	15300	1486	1 hr.	Glass and a few crystals.
Jan. 7	Cryst.	15350	1490	1 hr.	Glass only.
		Liquidus 1490° ± 2°			
1912					
Nov. 23	Cryst.	13900	1368	1 hr.	No change.
Nov. 23	Cryst.	14010	1377	1 hr.	A very little glass formed.
Nov. 23	Cryst.	14200	1394	1 hr.	Glass formed.
		Solidus 1372° ± 4°			
		Ab_1An_1			
Dec. 8	Cryst.	13000	1291	1 hr.	Minute quantity glass.
Dec. 8	Cryst.	12900	1283	1 hr.	No change.
Dec. 12	Cryst.	13300	1316	1 hr.	Considerable amount of glass.
		Solidus 1287° ± 4°			
Dec. 17	Cryst.	14650	1430	1 hr.	Glass and crystals.
Dec. 17	Cryst.	14770	1440	1 hr.	Glass and crystals.
Dec. 17	Cryst.	14800	1442	1 hr.	Glass and a few needle crystals.
Dec. 20	Glass	14800	1442	1 hr.	Glass and a few stout crystals.
Dec. 20	Cryst.	14870	1449	1 hr.	Glass and extremely rare crystals.
Dec. 20	Cryst.	14890	1452	1 hr.	Glass only.
		Liquidus 1450° ± 2°			
		Ab_2An_1			
1913					
Jan. 3	Cryst.	12600	1257°	1 hr.	Glass formed.
Jan. 3	Cryst.	12200	1223	1 hr.	Glass formed.
Jan. 8	Cryst.	12000	1209	1 hr.	Minute quantity glass.
Jan. 8	Cryst.	11900	1200	1 hr.	No glass discernible.
		Solidus 1205° ± 5°			

TABLE II (continued).

Date 1912	Initial Condition	Temp. microvolts	Temp. degrees	Time	Result
Ab_2An_1					
1912					
Dec. 19	Cryst.	14100	1386	1 hr.	Glass with a few crystals.
Dec. 24	Cryst. 1st preparation	14200	1394	1 hr.	Glass and crystal specks.
Dec. 24	Part cryst. 3d preparation	14200	1394	1 hr.	Glass and crystal specks.
Dec. 24	Diopside	14200	1394°	1 hr.	Glass only.
Liquidus 1394° ± 2°					
Ab_3An_1					
1913					
Jan. 7	Cryst. with trace glass	11690	1182	1 hr.	Slight increase of glass.
Jan. 7		11550	1169	1 hr.	No change apparent.
Solidus* 1175 ± 8°					
Jan. 9	Cryst.	13680	1349	1 hr.	Glass and a few crystals.
Jan. 9	Glass	13680	1349	1 hr.	Glass and a few crystals.
Jan. 9	Cryst.	13720	1352	1 hr.	Glass and rare crystals.
Jan. 10	Cryst.	13770	1356	1 hr.	Glass and very rare crystals.
Jan. 10	Cryst.	13820	1360	1 hr.	Glass and very rare crystals.
Jan. 10	Cryst.	13840	1363	1 hr.	All glass.
Liquidus 1362° ± 2°					
Ab_4An_1					
1912					
Dec. 17	Crystallized for one week, only partly crystalline.	13500	1332	1 hr.	Glass and extremely rare crystals.
Dec. 17		13410	1325	1 hr.	Glass and a few crystals.
Dec. 17		13530	1335	1 hr.	All glass.
Liquidus 1334° ± 2°, solidus indeterminate.					
Ab_8An_1					
1913					
Jan. 6	Partly cryst.	12580	1255	1 hr.	Glass and a few crystals.
Jan. 6	Partly cryst.	12600	1257	1 hr.	Glass and a few crystals.
Jan. 6	Partly cryst.	12680	1263	1½ hr.	Glass and rare crystals.
Jan. 6	Partly cryst.	12740	1268	½ hr.	Glass only.
Liquidus 1265° ± 3°, solidus indeterminate.					
Amelia County albite, $Ab_{98}An_2$					
Jan. 14	Cryst. coarse grains	10760	1102	1 hr.	No change.
Jan. 14	Cryst. coarse grains	11000	1122	1 hr.	A very little glass.

* Accuracy not quite as great as others on account of trace of glass in original.

TABLE II (continued).

Amelia County albite, $Ab_{98}An_2$.

Date 1913	Initial Condition.	Temp. microvolts	Temp. degrees	Time	Result
Jan. 14	Cryst. coarse grains	11130	1133	1 hr.	A very little glass.
Jan. 15	Cryst. coarse grains	11240	1143	2 hr.	Glass in stringers.
Jan. 15	Cryst. coarse grains	11440	1160	1 hr.	Glass in stringers.
Jan. 17	Cryst. fine powder	11450	1161	1 hr.	Much glass.
Jan. 18	Cryst. fine powder	11200	1140	1 hr.	Much glass.
Jan. 18	Cryst. fine powder	11000	1122	1 hr.	Glass in stringers.
Jan. 18	Cryst. fine powder	10800	1105	1 hr.	Glass in small stringers.
Jan. 18	Cryst. fine powder	10700	1097	2 hrs.	Doubtful slight change from original.
Jan. 18	Cryst. fine powder	10600	1089	2 hrs.	No change.

Beginning of melting 1100° ± 10°

Oligoclase from Bakersville, North Carolina.*

$Ab_{77.5}An_{22.5}$

Date 1913	Initial Condition.	Temp. microvolts	Temp. degrees	Time	Result
Jan. 15	Cryst.	11650	1175	1 hr.	Glass in stringers.
Jan. 15	Cryst.	11530	1165	1 hr.	A slight change.
Jan. 15	Cryst.	11420	1154	1 hr.	No change.

solidus 1158° ± 5°

Summary of Melting Intervals,

Composition.	Temperature of Beginning of Melting. Solidus.	Temperature of Completion of Melting. Liquidus.
An	1550° ± 2°	1550° ± 2°
Ab_1An_5	1465° ± 4°	1521° ± 2°
Ab_1An_2	1372° ± 4°	1490° ± 2°
Ab_1An_1	1287° ± 4°	1450° ± 2°
Ab_2An_1	1205° ± 5°	1394° ± 2°
Ab_3An_1	1175° ± 8°	1362° ± 2°
$Ab_{77.5}An_{22.5}$	1158° ± 5°	----------
Ab_4An_1	----------	1334° ± 2°
Ab_8An_1	----------	1265° ± 3°
$Ab_{98}An_2$	1100° ± 10°	----------

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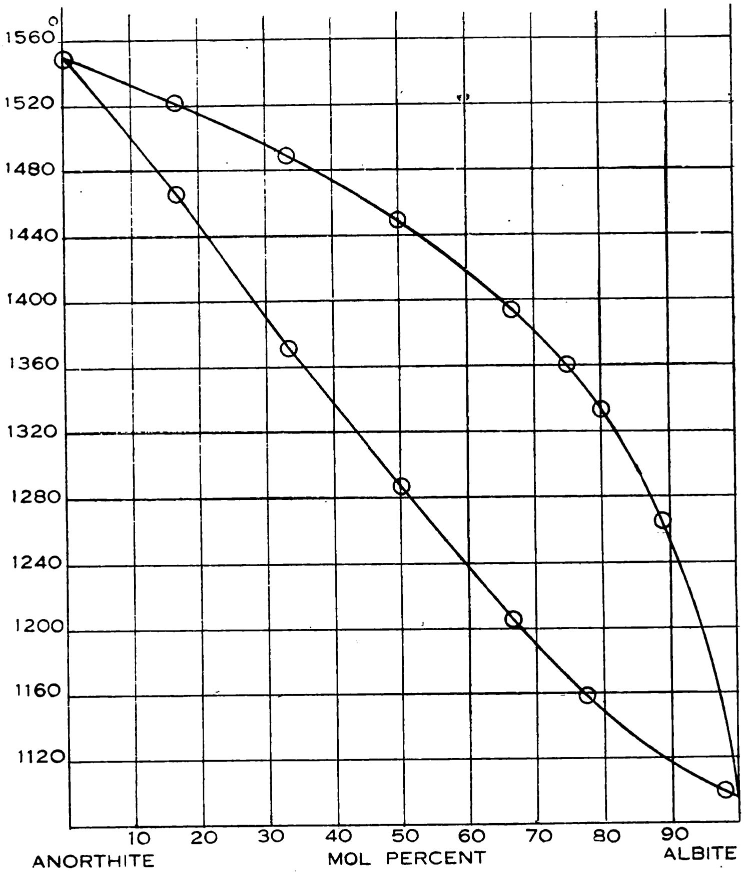
* Penfield and Sperry, this Journal (3), xxxvi, p. 324, 1888.

The data are shown plotted on a temperature-composition diagram in fig. 1. A clear idea of the extent and accuracy of the data on which the diagram rests may be obtained from Table II.

Fig. 1.



Order of Accuracy.

For the reason that it is somewhat easier to detect a few crystals embedded in glass than to find a small amount of glass in a crystalline aggregate, the accuracy of the liquidus is somewhat greater than that of the solidus. No difficulty was found, however, in establishing the solidus within limits of ± 4°.

The limits of error of the figures given for the liquidus (± 2°) are very accurately determined by ascertaining the temperature of the final disappearance of crystals. The check on these values by the reverse method of finding the temperature at which crystals first form in the glass was perfect, within approximately the same limits of error, in all the artificial mixtures except Ab_8An_1. It is possible to hold glass of this composition at a temperature a few degrees below the liquidus for several hours without the formation of crystals. No check on the liquidus point as determined by the reverse method was therefore possible in this case. That the point is sufficiently well established by the former method alone and with an accuracy practically equal to that in the more calcic members, is apparent, however, from the following. Beginning with half-crystalline material and holding it at 1263° for an hour and a half, it was found that a few rare crystals still persisted, whereas the same half-crystalline material held at 1268° (only 5° higher) for only half an hour gave a clear glass. It is obvious from the latter that the persistence of crystals at 1263° for an hour and a half could not have been due to insufficient time of exposure. In spite of the readiness with which undercooling occurs, persistent superheating does not occur with this method of procedure. The importance of fixing the point on the liquidus corresponding to Ab_8An_1 is considerable because it determines the position and slope of the liquidus at a composition fairly close to albite itself.

Use of Natural Feldspars.

It was found impossible to *completely* crystallize pure artificial mixtures richer in albite than Ab_2An_1. The partially crystallized preparations as rich as Ab_8An_1, which were easily obtained, served perfectly well for fixing the liquidus, but, of course, were of no service in locating the solidus. A very pure natural oligoclase from Bakersville, North Carolina, of composition $Ab_{77.5}An_{22.5}$ was therefore used in an effort to fix the corresponding point on the solidus. A small portion of this material, carefully selected under the microscope, was finely ground and subjected to successive quenchings as before. The temperature of the beginning of melting was found to be 1158°±5°. (See Table II.)

For the same reason pure, natural material was also used to determine the melting point of albite. This Amelia County albite has been carefully analyzed* and found to contain about 2 per cent of anorthite and 1 per cent of orthoclase. What was really determined in this case also was the temperature of

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* Day and Allen, l. c., p. 48.

the beginning of melting of the mix crystals, for the presence of but 2 per cent of anorthite, on account of the steepness of the liquidus, is sufficient to cause a melting interval of about 50°. The temperature found for carefully selected, finely ground material was 1100°±10°. This may be taken as practically the melting temperature of albite itself on account of the flatness of the solidus at this point. In spite of the stubborn nature of albite in the matter of affording complete melting no great difficulty was found in fixing a temperature of beginning of melting of this material. The temperature 1100°, moreover, lies on a rational extrapolation of the liquidus, although extrapolation alone could not fix the point closely on account of the steep slope of the liquidus.

It will be noted that the curve of Day and Allen lies nowhere very far below the liquidus.* At Ab_2An_1 the difference is 20°. Beyond Ab_3An_1 no breaks were obtained by them and extrapolation was correspondingly uncertain.

The Composition of the Liquid Phase.

The composition of the phases present at any temperature could, of course, be predicted from the diagram as determined, but it was desired to obtain independent confirmation of it from actual determinations of optical properties. All hope of success in the case of the solid phase was soon abandoned, for the crystals, embedded in the glass, are always extremely small, sometimes so thin, in fact, that their birefringence is scarcely discernible.

In the case of the liquid phase the outlook was more hopeful, since the determination of a single property, viz., the refractive index of the glass, is sufficient to fix the composition. In most cases it was only when the glass was present in considerable excess over the crystals that its index could be determined, since it was only then that an edge of glass of sufficient size for comparison with the immersion liquid could be obtained. The difficulty was enhanced by the small size of the crystals embedded in the glass, for, on this account, five or six layers of crystals might be contained in the average grain and in the projection viewed under the microscope their apparent proportion was correspondingly multiplied. The difficulty was avoided in part by choosing only the thinnest grains, but this lessened somewhat the accuracy of the comparison with the liquid. In a few favorable instances, however, definite results were obtained.

To determine the refractive index the quenched charge was crushed and the fine powder† immersed in liquids of known

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* See revised temperatures, this Journal (4), xxxi, p. 347, 1911.

† Wright, F. E., The Methods of Petrographic-Microscopic Research, Carnegie Institution of Washington, Pub. No. 158, p. 87.

refractive index. By trying various mixtures one was readily found which exactly matched the glass, the comparison being made by the Becke line method. The index of the liquid was then immediately determined on the refractometer. The indices of the pure, artificial glasses of the albite-anorthite series had previously been determined at this laboratory by Larsen,* so that when the index was known the composition was also known.

The results obtained are tabulated below in such form as to indicate the extent of agreement of the two methods.

TABLE III.

Composition of charge Mol. % An.	Initial Condition.	Temperature.	Measured Index of glass.	Composition from index Mol. % An.	Composition from liquidus Mol. % An.
66·6 (Ab_1An_2)	Glass	1482°	1·542	63	63
	Glass	1462	>1·534<1·538	53·5—58	54·5
	Glass	1454	1·532	51	51·5
50·0 (Ab_1An_1)	Cryst.	1405	1·520	37	36
	Glass	1385	>1·514<1·518	30—35	31
	Glass	1432	1·525	43	44
33·3 (Ab_2An_1)	Cryst.	1324	1·506	20	19

By means of fig. 2 the composition of the liquid phase for each experiment, determined from its refractive index, may be quickly compared with the composition determined by the temperature method of fixing the liquidus. The agreement is excellent.

The temperature method is somewhat more accurate and much more generally applicable than the refractive index method. The latter, however, provides entirely independent confirmation of the former, and serves to demonstrate beyond doubt the great difference in composition between liquid and solid phases at any temperature. For example, a mixture of total composition Ab_1An_1 at 1385° gives a glass nearly 20 per cent richer in albite, and since about one-half of the charge is crystalline, it follows that the crystals must be approximately 20 per cent richer in anorthite. The actual difference between solidus and liquidus at 1385° is seen from fig. 1 to be 38 per cent.

From the zoned feldspars of nature it has long been known to geologists that a very considerable difference of this kind must exist. Vogt† has even ventured an estimate, for which he makes no claim of exactness, of the magnitude of this difference based on a comparison of the composition of the total

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* This Journal, xxviii, p. 283, 1909.

† T.M.P.M., xxiv, p. 514, 1905.

plagioclase of a rock, and that of the "first" plagioclase, but the actual determination of this magnitude has had to wait for the development of appropriate methods of measurement.

Fig. 2.

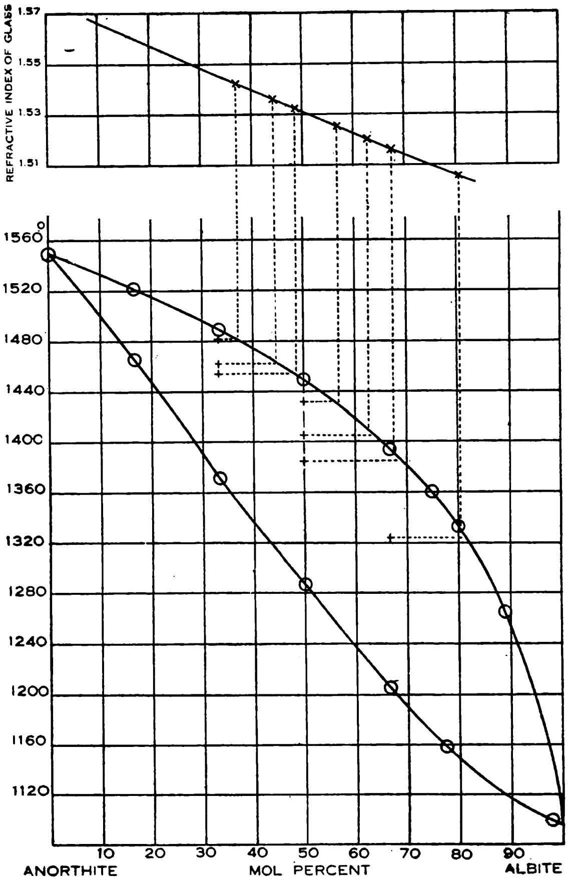

Fig. 2. + Total composition of charge and temperature of experiment.
× Determined refractive index of glass phase.

Theoretical Considerations.

Van Laar, in 1906, endeavored by means of a general equation, derived by consideration of the thermodynamic potential, to estimate the magnitude of the melting intervals of the plagioclase feldspars. He made use of the value of Day and

Allen for the melting point of anorthite (1532°) and the extrapolated value, 1220°, for albite, and with reasonable simplifying assumptions concerning the latent heats was able to show* that there should be large melting intervals.

For the case of complete solid solution of the type exhibited by the feldspars, we may derive equations expressing the relations between the composition of the liquid and solid in equilibrium at any temperature in the following manner. If both the liquid solutions and the solid solutions are *perfect physical solutions*, i. e., if there is no heat effect or volume change on mixing, then Raoult's law of vapor pressure lowering, and the Clausius equation for the change of vapor pressure with temperature, should apply to both components in both phases.

Raoult's law may be written in the following manner:

$$p = p_0 \, (1 - x)$$

where p_0 = vapor pressure of the pure solvent at any temperature, and p = partial vapor pressure of the solvent at the same temperature, from a solution in which the mol fraction of solvent is $(1 - x)$.

The Clausius equation in its most general form is written

$$\frac{dp}{dT} = \frac{l}{(v_1 - v_2)T}$$

where dp is the change of vapor pressure of liquid (or solid) corresponding with a change of temperature dT at absolute temperature T, l = latent heat of vaporization of one gram of the liquid (or solid) at T, v_1 = the volume of one gram of the gas at T, and v_2 = the volume of one gram of liquid (or solid) at T.

By assuming that the gas laws apply to the vapor and that the volume of the liquid (or solid) is negligible compared with that of the gas, then the equation may be written in a form easily integrated.

$$\frac{d \log p}{dT} = \frac{L}{RT^2}$$

where L is the latent heat of vaporization of one mol. of the liquid (or solid) and R the gas constant. By assuming that L remains constant over the temperature range under consideration, we may integrate between the temperature limits T_1 and T_2, when the equation becomes

$$ln \, \frac{p_{T_1}}{p_{T_2}} = \frac{L}{R}\left(\frac{1}{T_2} - \frac{1}{T_1}\right).$$

This, written in the exponential form, is the equation used in the present instance. Its complete derivation is given in order that the fundamental assumptions involved may be clear.

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* Zs. phys. Chemie, lv, 4, p. 435.

For component A let

p_o = vapor pressure of pure liquid at its melting point T_1 and therefore also the vapor pressure of pure solid at T_1.
$(p_o)_T$ = vapor pressure of pure liquid at T.
$(P_o)_T$ = vapor pressure of pure solid at T.
L_v = latent heat of vaporization of the liquid per mol at T.
L_s = latent heat of sublimation of the solid per mol at T.

then from the integrated Clausius equation the following relation holds for the liquid:

$$\frac{p_o}{(p_o)_T} = e^{\frac{L_v}{R}\left(\frac{1}{T} - \frac{1}{T_1}\right)}$$

and for the solid

$$\frac{p_o}{(P_o)_T} = e^{\frac{L_s}{R}\left(\frac{1}{T} - \frac{1}{T_1}\right)}$$

For a liquid solution of mol fraction $1 - x$, applying the Raoult's Law equation, we have then,

$$p_T = p_o \,.\, e^{\frac{L_v}{R}\left(\frac{1}{T_1} - \frac{1}{T}\right)} .(1 - x)$$

where p_T is the partial vapor pressure of A over the liquid solution at T.

For a solid solution of mol fraction $(1 - x_1)$ we have similarly

$$P_T = p_o \,.\, e^{\frac{L_s}{R}\left(\frac{1}{T_1} - \frac{1}{T}\right)} .(1 - x_1)$$

where P_T is the partial vapor pressure of A over the solid solution at T.

If T be the temperature at which this liquid solution and solid solution are in equilibrium, then $p_T = P_T$ and

$$p_o \,.\, e^{\frac{L_v}{R}\left(\frac{1}{T_1} - \frac{1}{T}\right)} \,.\, (1 - x) = p_o \,.\, e^{\frac{L_s}{R}\left(\frac{1}{T_1} - \frac{1}{T}\right)} \,.\, (1 - x_1)$$

whence $$\frac{1 - x}{1 - x_1} = e^{\frac{L_s - L_v}{R}\left(\frac{1}{T_1} - \frac{1}{T}\right)}$$

or $$\frac{1 - x}{1 - x_1} = e^{\frac{L_1}{R}\left(\frac{1}{T_1} - \frac{1}{T}\right)}$$

where L_1 = latent heat of melting (molal) of A at T.

By applying similar reasoning to component B we get

$$\frac{x}{x_1} = e^{\frac{L_2}{R}\left(\frac{1}{T_2} - \frac{1}{T}\right)}$$

where L_2 = latent heat of melting (molal) of B at T.

These two equations express the simultaneous concentrations on the liquidus and solidus at any temperature T in terms of the latent heats of melting at T and the temperatures of melting of the two components (T_1 and T_2).

Van Laar derives a more rigid relation which contains factors for the heats of mixing in both phases, but in its application he finds it necessary to neglect these and the equations then reduce substantially to the form given above.

In the present instance T_1 and T_2 and also the values for x and x_1 (the mol-fraction of albite on the liquidus and solidus curves respectively) for various values of T have been experimentally determined. (See fig. 1.) It suffices, then, in order to test the applicability of the equations in the case at hand, to substitute in the general equations and see whether or not L_1 and L_2 remain nearly constant and of appropriate order of magnitude. In the following table the calculated values are given:

TABLE IV.

$(T-273)$:	x observed:*	x_1 observed:	$1-x$ observed:	$1-x_1$ observed:	L_{Ab} calculated:	L_{An} calculated
1500	·277	·098	·723	·902	12670	28600
1450	·500	·192	·500	·808	12750	30000
1400	·651	·282	·349	·718	12790	29200
1350	·772	·376	·228	·624	12790	30400
1300	·846	·475	·154	·525	12470	28300
1250	·905	·575	·095	·425	12920	27700
		Mean			12740	29000
		Average deviation from mean,			0·8%	2·9%

It will be seen from the table that the values for the latent heats vary but little from a mean value, the random variation being what might be expected from the possible errors of the temperature measurements. Any systematic variation with temperature, due to the difference of specific heats of liquid and solid, would, by analogy with other silicates, be still smaller.†

If the calculated mean molal latent heat of melting of anorthite is divided by the formula weight, the result is 29000÷

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*See fig. 1.

†Cf. W. P. White, Specific heats of silicates and platinum, this Journal (4), xxviii, p. 345, 1909.

278 = 104·2. Åkerman and Vogt have found by direct measurement that the latent heat of melting of anorthite is 105 cal. per gram, which agrees well with the calculated value. The extraordinary agreement is, of course, in part pure accident. No direct determinations of the latent heat of melting of albite have been made. The value calculated from the present results is 12740 ÷ 263 = 48·5 cal. per gram, again using the formula weight.

Fig. 3.

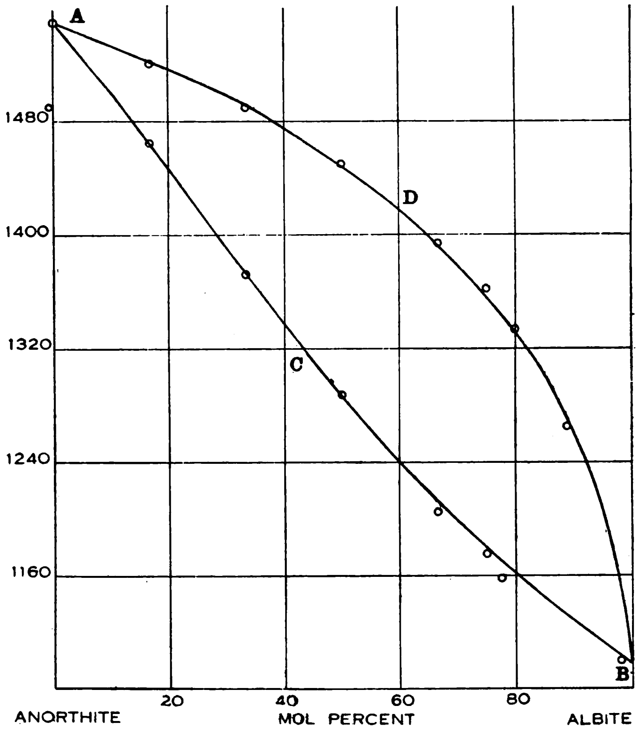

Fig. 3. ACB and ADB calculated curves (see text). o, experimentally determined points.

If the values 29000 and 12740 calories are taken as the molal latent heats of melting of anorthite and albite and the temperatures 1550° C. and 1100° C. as their melting points, complete solidus and liquidus curves can be calculated from these data. Actual calculation gives the curves ADB and ACB of fig. 3. The small circles of this figure indicate the experimentally determined temperatures. None of the determined points lies farther from the calculated curves than the possible limits of experimental error warrant. The greatest deviation occurs where the experimental errors are greatest.

Table V is given in order to show that this agreement is clearly not fortuitous and that no values of the latent heats except those very close to the calculated values will give curves that pass near enough to the experimentally determined points to permit the interpretation that the deviation of the points is due to experimental error.

The table gives the temperatures of some points on liquidus and solidus curves calculated by the use of values of the latent heats differing 10 per cent from the mean values 12740 and 29000 calories. The latent heats are allowed to vary from the mean values both separately and jointly and, in the latter case, both in the same direction and in opposite directions. In each case the differences between the calculated and observed temperatures are well beyond the limits of error of the temperature measurements. The observed temperatures, therefore, fix closely the values of L_{An} and L_{Ab}.

TABLE V.

Case I.

Assuming a value of L_{Ab} 10 per cent lower than above mean value and a value of L_{An} equal to above mean value

Point on Solidus.

Composition	Calculated	Observed	Difference
Ab_1An_5	1475°	1465°	+10°
Ab_1An_2	1390°	1372°	+18°
Ab_1An_1	1305°	1287°	+18°

Point on Liquidus.

Composition	Calculated	Observed	Difference
Ab_1An_2	1493°	1490°	+3°
Ab_1An_1	1454°	1450°	+4°
Ab_2An_1	1400°	1394°	+6°

Case II.

Assuming a value of L_{Ab} equal to above mean value and a value of L_{An} 10 per cent less than mean value

Point on Solidus.

Composition	Calculated	Observed	Difference
Ab_1An_5	1458°	1465°	−7°
Ab_1An_2	1363°	1372°	−9°

Point on Liquidus.

Ab_1An_6	1517°	1521°	− 4°
Ab_1An_2	1480°	1490°	−10°
Ab_1An_1	1436°	1450°	−14°
Ab_2An_1	1380°	1394°	−14°

Case III.

Assuming a value of L_{Ab} 10 per cent lower than above mean value and a value of L_{An} 10 per cent lower than above mean value

Point on Solidus.

Composition	Calculated	Observed	Difference
Ab_1An_2	1382°	1372°	+10°
Ab_1An_1	1299°	1287°	+12°

Point on Liquidus.

Ab_1An_2	1485°	1490°	−5°
Ab_1An_1	1441°	1450°	−9°
Ab_2An_1	1386°	1394°	−8°

Case IV.

Assuming a value of L_{Ab} 10 per cent higher than above mean value and a value of L_{An} 10 per cent lower than above mean value

Point on Solidus.

Composition	Calculated	Observed	Difference
Ab_1An_2	1350°	1372°	−22°

Point on Liquidus.

Ab_1An_1	1430°	1450°	−20°

The marked accord between theory and the measurements here offered is, on first thought, rather surprising. We are not dealing simply with dilute solutions, nor is the solid which separates the pure solvent, and it is commonly only in such cases that measurements of freezing point lowering are found amenable to simple laws. It should be noted, however, that the equations applied have the general form applicable to all solutions and not merely to the limiting case of the dilute solution. Moreover, the fundamental assumption in the derivation was that both the liquid solutions and the solid solutions followed Raoult's law of vapor pressure lowering. This law is well known to be applicable to many pairs of liquids, for all concentrations, when these liquids are miscible in all proportions and when there is neither volume change nor heat effect on mixing. The feldspar liquids fulfill the first two requirements. The density of the feldspar glasses at room temperature is nearly linear with respect to composition and at higher temperatures this relation probably does not change to any great extent.* Of the heat effect on mixing, nothing is known, but it seems that two such similar substances might prove analogous to members of the same homologous series among organic liquids, and that no great effect need be expected.

Turning to the solids, we find the same facts true. They are miscible in all proportions and again the change of density with composition is linear. It would seem, then, on more mature thought, that we are dealing with an especially favorable case, and that Raoult's law might be expected to apply to both phases. This is indeed what has been found.

In the case of solids not completely miscible, it is easy to prove that *both* saturated solid solutions can not obey Raoult's law, i. e., if one does the other can not. In the case, therefore, of two series of mix-crystals with an hiatus, and especially when this hiatus is so large that the two components separate in the pure state, it does not appear possible that any rule of freezing-point lowering, derived from the considerations set forth in the present derivation, would be found to apply.†

The close agreement found between observation and theory points to other important conclusions relative to these components. One is that albite and anorthite, both in the liquid and solid state, consist of simple molecules, or else that they are equally associated and that the degree of association is not affected by mixing them. This follows from the fact that, in plotting mol fractions (mol. percentages), molecular weights were assumed equal to formula weights. If they had been assumed to be equal multiples of the formula weights, the plot would have been, of course, exactly the same. It might be assumed that since L (calculated) for anorthite is found to be equal to the experimentally determined latent heat per gram multiplied by the formula weight, that the molecule is necessarily simple, but L is merely the difference between the heats of vaporization and of sublimation of a mol and refers therefore only to the gas mol. It is a constant characteristic of the substance and in the present instance it is easy to see that, whether simple or equally associated molecules are assumed in its calculation, its value remains the same. The experimental results do not, therefore, throw any light on the actual degree of association of albite and anorthite. They indicate, as pointed out, that each is equally associated in the solid state and also in the liquid state, though the association may be, and probably is, different in the different states.

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* Day and Allen, l. c., p. 71.

† Cf. E. W. Washburn, J. Am. Chem. Soc., xxxii, No. 5, May, 1910, p. 670, for liquids.

The Question of Küster's Rule.

Both the equations derived and the decisive nature of the experimental results demonstrate that Küster's rule* can apply only in a certain limiting case. This rule states that the melting points of isomorphous mixtures should lie on the straight line joining the melting points of the pure components. It can be seen from inspection of the equations for the liquidus and solidus that the two curves may lie close together if either L_1 or L_2 is very small, and that both may approach straight lines if both L_1 and L_2 are small, but that they can not become a single straight line unless $T_1 = T_2$, i. e., the difference between the melting points of the components, is zero.† That vapor pressures, densities and like properties, when measured *at a definite temperature*, should be linear with respect to composition for solid solutions which are perfect physical solutions, is a necessity. That such a rule should apply to melting points, themselves *variable temperatures*, does not follow.

Isomorphism.

The establishment of complete solid solution between the feldspars raises the whole question of the use of the terms "solid solution" and "isomorphism." The latter has been avoided hitherto in this paper on account of the variety of meanings which have at different times been attached to it. Some authors use "isomorphism" to designate complete solid solution, others speak freely of "limited isomorphism," and still others use the term in its original significance of simple crystallographic similarity, without regard to the question of miscibility in the solid state. In view of the recent very complete review of the subject by Hlawatsch,‡ nothing more need be said of this matter except that, for the conception of miscibility in the solid state, the term, solid solution, seems to be much more useful, both in avoiding ambiguity, and because of a certain connotation of similarity with liquid solutions which has been amply justified in the present instance.

It has hitherto proved impossible to agree upon a deciding factor which shall determine whether or not two substances shall form a complete series of solid solutions. The facts indicate rather that no *single* criterion may be safely used alone. Similarity of chemical composition, for example, is known to be favorable. Except that both are alumino-silicates, no great similarity of composition between albite and anorthite, as their formulæ are ordinarily written, can be claimed. For this

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* F. W. Küster, Zs. phys. Chem., viii, p. 577, 1891.

† Cf. Van Laar, loc. cit., p. 439, and Day and Allen, loc. cit., p. 68.

‡ Zs. Kryst., li, p. 417, 1912.

reason a rearrangement of the formulæ has been proposed by Washington* to enable both to be written as salts of the same acid, with, as far as present knowledge goes, extremely dissimilar basic radicles.

It is not, however, clear that a common acid radicle is more favorable to complete miscibility than a common basic radicle, for the pair $CdBr_2-CdI_2$, and also the pair $K_2CrO_4-K_2SO_4$, form complete series of solid solutions. These facts, of course, prove nothing relative to the feldspars, but they indicate that, until more is known of the laws of miscibility in the solid state, there is no compelling need to assume that albite and anorthite are salts of the same acid.

It has been shown in some cases that crystalline similarity alone, even when very marked,† may not be sufficient to determine miscibility in the solid state, but that the molecular volumes of the two substances must also be nearly equal, or, stated in another form, the fundamental structural parallelopipeda must be alike not only in shape but also in size. It happens in the present case that the molecular volumes are nearly identical and it may, therefore, be in part due to this fact that complete miscibility is possible. The molecular volume is equal to the molecular weight divided by the density, but since in general nothing is known of the molecular weight of the solid, the molecular volume is equally indefinite. The melting phenomena have shown, however, in the present case, that in the solid state albite and anorthite consist either of simple or of equally associated molecules. The molecular volumes, calculated on the assumption that the molecules are simple, will therefore give figures which represent the actual ratio of these quantities. The molecular volume of anorthite, so calculated, is $\frac{278{\cdot}9}{2{\cdot}765} = 100{\cdot}8$ and of albite $\frac{263{\cdot}0}{2{\cdot}605} = 100{\cdot}9$, practically identical values.

Of the still more fundamental question as to the factor which determines the crystallographic similarity and therefore, ultimately, the complete miscibility there is very little positive knowledge. It may be noted, however, that the valency-volume theory of Barlow and Pope‡ is applicable to the present pair, inasmuch as they have the same valency volume (32) and could be derived from related, closely-packed assemblages of spheres of atomic influence.

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* This Journal, xxxiv, p. 555, 1912.

† Tutton, A. E. H., Crystalline Structure and Chemical Constitution, p. 128, London, 1910.

‡ Jour. Chem. Soc., lxxxix, p. 1727, 1906.

Geological Significance.

A study of fig. 1 brings out certain facts concerning the plagioclases which seem worthy of some attention. If we start with a mixture of composition Ab_1An_1 at 1500° and cool quickly, crystallization may not begin until some such temperature as 1250° is reached, when the whole will solidify as homogeneous crystals of Ab_1An_1.

If we cool gradually, on the other hand, crystals of composition $Ab_{19}An_{81}$ begin to separate at 1450° and, theoretically, the composition of the crystals will change continuously toward Ab_1An_1 and their amount will increase down to 1287°, when the whole mass will consist of crystals of composition Ab_1An_1. This continuous complete change in the composition of the solid implies, however, free diffusion in the solid phase, whereas diffusion is in general quite slow in solids and in the feldspars is certainly extremely slow. Only excessively slow cooling could therefore be expected to give the result outlined. With moderately slow cooling the process consists in the formation of successive layers of crystalline material of gradually changing composition, the early layers being effectively separated from the liquid by the later. When the temperature 1287° is reached, there will still be some liquid left. Crystallization will therefore continue below this temperature, the process of gradual change of composition in the solid deposited and the liquid residue continuing as before. *If the cooling is at the proper rate, there appears to be no limit to this process ; the final crystals may be nearly pure albite.*

This may be illustrated by a precise numerical example. Start with 100 grams Ab_1An_1 at 1500° and cool it instantaneously to 1386°. At this temperature 50 g. of crystals, $Ab_{31}An_{69}$, will separate and 50 g. of liquid, $Ab_{69}An_{31}$, will remain. (See fig. 1.) Cool again instantaneously to 1282°, 25 g. of crystals, $Ab_{51}An_{49}$, separate and 25 g. of liquid, $Ab_{87}An_{13}$, remain. Again, repeat the cooling and at 1164° 12·5 g. of crystals, $Ab_{76}An_{24}$, form and 12·5 g. of liquid, $Ab_{98.5}An_{1.5}$, remain. It is easy to see how by continuous slow cooling, instead of cooling in steps, the same result might be obtained and that the final crystals might approach pure albite. Absolutely pure albite, however, could not be obtained in finite amount. Moreover, the temperature may fall to 1100° before crystallization is complete.

It is believed that this very large range of temperature through which the crystallization of plagioclase may take place, with moderately slow cooling, is of great importance in igneous geology. Such a behavior may sometimes be favored in the natural rocks, even when cooled exceedingly slowly, on account of the possibility that the liquid may be separated from the crystals, say by the sinking of the latter or by reintrusion of the former to a higher level. The actual temperatures concerned will, of course, be much lower in the natural rocks.

The reversal* of the order of zoning sometimes noted in natural plagioclase may perhaps result from various causes. That undercooling might bring about a reversal may be seen from inspection of fig. 1. If liquid of composition Ab_1An_1 were cooled quickly to 1280°, rapid formation of crystals (Ab_1An_1) might take place at this temperature, and the heat (latent) released might quickly raise the temperature of the whole mixture to 1300°, at which temperature a zone of crystalline material of composition $Ab_{45}An_{55}$ would form around the earlier less calcic crystals. Similar undercooling might bring about a like result in a natural magma.

The secret of reversal may at times be found in the presence of other lime-bearing minerals in the natural rock. Movement of the magma during crystallization might bring about the same result by exposing the crystals to liquid of composition different from that out of which they had been crystallizing. To such movements also, and perhaps, at times, to sudden lowering of temperature, may be attributed the sharp boundaries that various zones often exhibit.

In view of the very great quantitative importance of the plagioclases in igneous rocks, it is a matter of some satisfaction to find them obeying the laws of physical chemistry to the extent here found.

SUMMARY.

The method of quenching was applied to the determination of the melting intervals of pure, artificial plagioclase feldspars. It was found possible to determine accurately the temperatures of beginning of melting (solidus) for compositions ranging from pure An to Ab_3An_1, and of completion of melting (liquidus) for the range $An-Ab_8An_1$. Very pure natural material, Bakersville oligoclase, was used to determine the point on the solidus corresponding to its composition. Similar material, Amelia County albite, served to fix the melting point of albite. The results of this work are summarized at the end of Table II and diagrammatically expressed in fig. 1.

It was also found possible in several instances to determine the composition of the liquid phase, present at temperatures within the melting interval, by measuring the refractive index of the quenched glass. Thus points on the liquidus were determined by an independent method and were found to be

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* N. L. Bowen, J. Geol., xviii, p. 662, 1910.

in excellent agreement with the results of the temperature method. In Table III and fig. 2 the results are shown.

In the theoretical discussion equations are developed which express the concentrations on the liquidus and solidus at any temperature in terms of the melting temperatures and latent heats of melting of the two components. The experimental results therefore make possible the calculation of the latent heat of melting of anorthite and of albite. The calculated values are 104·2 cal. per gm. for anorthite and 48·5 cal. per gm. for albite and these values remain practically constant for all ranges of composition (see Table IV). The calculated latent heat of anorthite is in excellent agreement with the figure found by direct measurement, 105 cal. per gm. No direct determinations of the latent heat of albite have been made.

It is shown that if these values of the latent heats are taken and liquidus and solidus curves calculated, the resulting curves (see fig. 3) pass very close to the experimentally determined temperatures (within the limits of error of the temperature measurements). It is also shown that values of the latent heats differing from these by as little as 10 per cent will not give a like result. (Table V.)

This extreme agreement with the requirements of theory and its bearing on certain theoretical questions is discussed.

The geological significance of the complete solid solution of the feldspars is considered, as well as the extent to which zoning may occur under favorable conditions and the consequent very great range of temperature through which plagioclase may crystallize.

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Washington, D. C., March, 1913.