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MIXING PROPERTIES OF SANIDINE CRYSTALLINE SOLUTIONS: III. CALCULATIONS BASED ON TWO-PHASE DATA[1]

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ABSTRACT

Analytic expressions for the binodal curve (solvus) bounding a binary two-phase region may be obtained by two distinct methods using observed pairs of coexisting phases. One method is to plot appropriate functions of composition against reciprocal temperature and to obtain Margules parameters by linear least-squares fits to the values plotted. The other method makes use of near-linear relationships in the critical region between the square of the difference in composition of the two phases, the mean composition, and reciprocal temperature.

Analysis of the two-feldspar data of Orville (1963) and of Luth and Tuttle (1966) shows that the two methods are in good quantitative agreement, although the second method is preferable for some data since it completely separates the mean composition and the composition difference. This is necessary when it seems likely that some experimental runs represent incomplete equilibration. Both methods show that the three sets of two-feldspar data obtained by Luth and Tuttle (1966), using different starting materials, yield binodal curves that are clearly distinct from one another. The binodal curve obtained from runs with excess alkali silicate agrees closely with that obtained from the two-phase data of Orville (1963). The foregoing results are consistent with the hypothesis that feldspars crystallized in the presence of excess alkali show the least amount of substitution of hydronium for alkali in their structures, and should yield phases most nearly resembling naturally occurring feldspars.

INTRODUCTION

In Part I of this series (Thompson and Waldbaum, 1968a) thermodynamic mixing properties of high temperature alkali feldspars were calculated by making use of the data of Orville (1963) on exchange equilibria between feldspars and alkali chloride aqueous solutions. Part II (Waldbaum and Thompson, 1968) was an analysis of the volume data of Donnay and Donnay (1952) and of Orville (1967). In this paper our purpose is to calculate tentative mixing properties from the compositions of coexisting phases as given by Luth and Tuttle (1966). We shall also make use of the two-feldspar runs reported by Orville (1963) in connection with his exchange studies. Although data from these same runs were used in Part I, only the fact that each feldspar was in exchange equilibrium with the aqueous solutions was used in the calculations in that

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paper. The additional equilibrium condition that must hold if the two feldspars coexist with each other was not taken into account, hence the calculations below that are based on Orville's two-phase data are to a large degree independent of those in Part I and make use of relations not there considered.

The following analysis of the two-feldspar data follows in its essential features that employed by Thompson and Waldbaum (1969) in an analysis of the two-phase region halite-sylvite. A first approach will be to calculate Margules parameters for each pair of coexisting phases and smooth the results as functions of pressure and temperature by the method of least squares. A second approach will be to make use of semi-empirical relationships in the critical region in order to calculate the critical temperatures, pressures, and compositions independently of the Margules formulation.

SOURCES OF DATA

Data of Orville (1963). Two distinct feldspar phases were observed by Orville (1963) in the products of many of his exchange experiments. It is clear, however, that some of these represent incomplete equilibration, particularly in certain short term runs where two feldspars were present in the initial materials, and that others must be runs in which only the partial exchange equilibrium was achieved, as discussed in Part I of this series (Thompson and Waldbaum, 1968a, see especially Appendix B). Although runs of the latter type were usable in Part I, where only exchange equilibrium was a requirement for the analysis, we must here select those two-phase runs that are most likely to represent complete feldspar-feldspar equilibrium and thus lie on or near the true feldspar binodal (solvus).

Fortunately Orville has given a full account of the nature of each run so that it is possible to evaluate the necessary factors pertinent to the probable degree of equilibration and to the direction in which the exchange reaction proceeded. From this it is possible to select, for each temperature, the run or runs that appear most likely to yield reactants lying on or near the binodal. The following selection is our own, but from comparison with Figures 4–8, 9, and 11 of Orville it appears that his own estimate as to the most likely location of the binodal is not significantly different from ours.

The preferred values for the several isotherms are selected as follows:

500°*C*, 2 *kbar*: The feldspar products of run no. 883 (720 hr) appear to be the only reasonable choice.

600°*C*, 2*kbar*: Run no. 787 (288 hr) probably gives the best values. Run no. 788 (not plotted by Orville in his Fig. 5) had similar starting materials, but probably represents only a stage passed *en route* to the results of no. 787.

600°*C*, 5*kbar*: Run no. 835 (288 hr) is the only pair obtained at this pressure and temperature, but from the course of the reaction and the nature of the results it is probably reliable. It should be pointed out that this run was not used in the analysis of Part I of this series solely because there were not enough runs at this temperature and pressure to define an exchange isotherm.

650°*C*, 2 *kbar*: No single run is wholly satisfactory for the present purpose except possibly no. 756, but the K-rich phase in this run was stated to have an indistinct $(\bar{2}01)$ peak, suggesting possible inhomogeneity. We have therefore selected the product feldspar of run no. 755 and the K-rich feldspar of run no. 703 as the phases most likely to be near the binodal at this temperature and pressure.

670°C, 2 kbar: No single run appears wholly satisfactory. We have selected the feldspar of run no. 758 and the K-rich feldspar of run no. 738 as being the most likely values.

680 and 700°C, 2 kbar: Neither isotherm shows clear evidence of a miscibility gap. The 700° isotherm is almost certainly supercritical and that at 680° is probably so. No values were selected at these temperatures.

The compositions of the two-phase pairs selected as outlined above are listed in Table 1a, with various parameters calculated from them as indicated.

Data of Luth and Tuttle (1966). Luth and Tuttle (1966) synthesized pairs of alkali feldspars hydrothermally from gels at temperatures between 550 and 700°C at 2 kbar and at 650° at 2, 5, and 10 kbar. Three types of starting material were used: one type containing alkalis, alumina, and silica in the ideal stoichiometric proportions for feldspar; a second type containing alumina in excess; and a third type containing alkali silicate in excess. The three types of material gave reproducibly different results, hence we shall treat them below as three distinct bodies of data. The results of runs with excess alkali silicate are listed in Table 1b, those with ideal proportions in Table 1c, and those with excess alumina in Table 1d. We shall here refer to these three types of *starting materials* as *peralkaline*, *one-to-one*, and *peraluminous*, respectively. However, the nature of the *feldspars* crystallizing from these starting materials will be discussed later.

Luth and Tuttle reran materials of three selected compositions at different temperatures in the hope of locating the binodal reversibly. The results were inconclusive but bracketed the synthesis points in nearly all instances, indicating that the synthesis points are probably fairly close to the true binodal surface. As we shall see below it is probable that exchange equilibrium was achieved in most of their runs, but that *complete* equilibrium was achieved is less certain. This is indicated by the fact that the parameter s in Table 1, related to the composition *difference* (Appendix A) between the feldspars, behaves more systematically than does the parameter r, related to the *mean* composition. A series of different pairs of feldspars that were in exchange equilibrium only, at a given pressure and temperature, would have similar values of s (see Thompson and Waldbaum, 1968a, Fig. 2; Waldbaum and Thompson, 1969, Fig. 4b) but could have widely differing values of r.

Earlier two-phase data. The earlier hydrothermal investigation at 981 bars by Bowen and Tuttle (1950) yielded the three feldspar pairs listed in Table 1e. These show much less regular behavior than the more recent data. They have therefore not been included in the following analysis and are listed only for comparative purposes. Yoder, Stewart, and Smith (1957) synthesized coexisting feldspars from glasses, hydrothermally, at 5 kbar and estimated the critical temperature to be 715 ± 5°C and the critical composition to be 44 mole percent *Or*, however they reported no coexisting compositions.

We have treated five sets of data in the analysis presented below. These are:

1. Orville two-phase data as selected above.
2. Luth-Tuttle *peralkaline* data.
3. A combination of (1) and (2) such that Orville's data points, having been selected from a larger body of data, are given double weight.
4. Luth-Tuttle *one-to-one* data.
5. Luth-Tuttle *peraluminous* data.

Table 1. Alkali Feldspar Two-Phase Data Used in Computations.

T(°C)	P (kbar)	$1/T\times10^3$	$N_{2\alpha}$	$N_{2\beta}$	B_G	C_G	$\frac{(\text{artanh } s)}{s}$	$\ln r^2$
(a) Orville (1963), peralkaline synthesis conditions								
500	2	1.2934	0.0340	0.8030	2.661	0.877	1.3236	−3.6280
600	2	1.1453	0.1240	0.6370	2.045	0.570	1.1049	−2.8626
650	2	1.0832	0.2080	0.5250	1.878	0.485	1.0357	−2.6410
670	2	1.0603	0.2490	0.4500	1.779	0.518	1.0138	−2.4013
600	5	1.1453	0.0660	0.6880	2.150	0.834	1.1708	−2.8048
(b) Luth and Tuttle (1966), peralkaline starting materials.								
550	2	1.2148	0.0662	0.7490	2.372	0.661	1.2219	−3.3770
575	2	1.1790	0.0757	0.6261	1.916	0.923	1.1246	−2.4200
577	2	1.1763	0.0472	0.6567	1.957	1.171	1.1618	−2.4341
600	2	1.1453	0.0757	0.6363	1.960	0.892	1.1304	−2.4896
625	2	1.1134	0.1810	0.5252	1.832	0.575	1.0426	−2.4497
627	2	1.1109	0.1330	0.5352	1.741	0.769	1.0599	−2.2064
635	2	1.1011	0.1234	0.5553	1.784	0.770	1.0702	−2.2708
642	2	1.0927	0.1810	0.4851	1.714	0.669	1.0327	−2.1938
650	2	1.0832	0.2003	0.4651	1.706	0.642	1.0244	−2.1896
658	2	1.0739	0.2584	0.4452	1.786	0.502	1.0119	−2.4321
665	2	1.0659	0.2584	0.4651	1.829	0.462	1.0146	−2.5711
650	5	1.0832	0.0948	0.6059	1.891	0.821	1.1039	−2.4126
650	10	1.0832	0.0378	0.6976	2.146	1.184	1.2011	−2.6591
(c) Luth and Tuttle (1966), one-to-one starting materials.								
550	2	1.2148	0.0948	0.6976	2.199	0.588	1.1572	−3.1443
575	2	1.1790	0.1330	0.6465	2.077	0.508	1.1051	−3.0237
577	2	1.1763	0.1330	0.6567	2.102	0.487	1.1102	−3.1184
600	2	1.1453	0.1330	0.6059	1.970	0.596	1.0865	−2.6857
625	2	1.1134	0.1714	0.6059	2.011	0.444	1.0712	−3.0039
627	2	1.1109	0.2293	0.5352	1.926	0.406	1.0331	−2.8921
635	2	1.1011	0.2099	0.5453	1.924	0.440	1.0403	−2.8146
642	2	1.0927	0.2293	0.4651	1.775	0.544	1.0192	−2.3710
650	2	1.0832	0.2974	0.4452	1.850	0.407	1.0074	−2.7142
650	2	1.0832	0.2681	0.4353	1.783	0.497	1.0095	−2.4307
658	2	1.0739	0.2974	0.4552	1.867	0.388	1.0084	−2.7935
665	2	1.0659	0.3464	0.4452	1.907	0.308	1.0033	−3.1366
650	5	1.0832	0.1521	0.5856	1.942	0.557	1.0708	−2.6765
650	10	1.0832	0.0567	0.6669	2.043	1.001	1.1623	−2.5718
(d) Luth and Tuttle (1966), peraluminous starting materials.								
550	2	1.2148	0.0948	0.6567	2.072	0.688	1.1312	−2.7846
575	2	1.1790	0.1138	0.5856	1.867	0.748	1.0860	−2.4039
577	2	1.1763	0.1234	0.6059	1.954	0.644	1.0906	−2.6135
600	2	1.1453	0.1521	0.5654	1.887	0.602	1.0636	−2.5282
625	2	1.1134	0.2003	0.4851	1.764	0.595	1.0284	−2.3129
627	2	1.1109	0.2293	0.4452	1.723	0.589	1.0160	−2.2448
635	2	1.1011	0.1906	0.4951	1.770	0.607	1.0328	−2.3148
642	2	1.0927	0.2974	0.4254	1.814	0.445	1.0055	−2.5660
650	5	1.0832	0.1330	0.5352	1.741	0.769	1.0599	−2.2064
650	10	1.0832	0.0662	0.6567	2.021	0.925	1.1489	−2.5668
(e) Bowen and Tuttle (1950).								
500	1	1.2934	0.0662	0.7387	2.337	0.690	1.2123	−3.2682
530	1	1.2451	0.2099	0.6873	2.154	0.193	1.0884	−4.5513
600	1	1.1453	0.1906	0.6669	2.129	0.276	1.0879	−3.8971

Combination of (1) or (2) with (4) or (5), or of (4) and (5) with each other did not prove successful, and the following analysis suggests strongly that the feldspars of (4) and (5) are quite distinct from each other and from (1) and (2).

SMOOTHING OF DATA

The procedures followed in the following analysis have been developed elsewhere (Thompson, 1967; Thompson and Waldbaum, 1969). The definitions of the parameters used and the relationships from which the various quantities may be calculated are listed in Appendix A of this paper. Our (1969) analysis of the two-phase region *halite-sylvite* was carried out in the expectation that that system would constitute a simplified analogue of the alkali feldspars. (Readers interested in a more complete theoretical treatment are referred thereto.)

First method. This method employs a simple asymmetric Margules-type equation containing two adjustable parameters at any given pressure and temperature. The dimensionless Margules parameters B_G and C_G have been calculated for each coexisting pair using the relationships given in Appendix A. A linear least-squares fit in terms of $(1/T)$ and (P/T) yields the results shown in Tables 2 and 3. The quantities in Table 2 permit calculation of a complete binodal or solvus, using either graphical methods of locating the coexisting phases or iterative methods most easily handled by computer (Thompson and Waldbaum, 1969). The reresults for the combined Orville and Luth-Tuttle peralkaline data are also shown in 2-kilobar sections in Figure 1 so that they may be compared with the data points at that pressure. It is graphically evident, and has been partially confirmed by using the Gauss criterion (Thompson and Waldbaum, 1969, Appendix A), that higher order fits are not warranted.

It is also apparent in Figure 1 and Table 3 that the least-squares fits for B_G are generally more satisfactory than for C_G (based on the standard deviation of fit), and of interest to note that B_G is largely, but not wholly, dependent upon the quantity s, which is a mesaure of the composition *difference* between the phases, and that C_G is largely, but not wholly, dependent upon the magnitude of r, which is a measure of the *mean* composition of the two phases (Appendix A). Unfortunately the quantities r and s can not be separated in the equations of the Margules type owing to the transcendental terms in which they appear. It is thus desirable to try an alternative approach in which r and s, or functions of them, may be smoothed separately.

Second method. It was found in our analysis of the two-phase region halite-sylvite that the quantities $\ln(r^2)$ and $(\operatorname{artanh} s)/s$ were nearly

TABLE 2. MARGULES PARAMETERS CALCULATED FROM LEAST-SQUARES FITS TO TWO-PHASE DATA

Data	B_S (cal deg^{-1})	C_S (cal deg^{-1})	B_H (kcal)	C_H (kcal)	B_V (cal bar^{-1})	C_V (cal bar^{-1})
Orville peralkaline	2.22	1.30	3.73	1.54	0.0177	0.0645
	.17	.22	.14	.12	.0085	.0110
Luth-Tuttle peralkaline	1.76	2.28	3.14	2.55	0.0465	0.0644
	.24	.36	.21	.32	.0040	.0061
Combined peralkaline	2.32	1.24	3.70	1.57	0.0415	0.0622
	.17	.23	.14	.20	.0048	.0067
Luth-Tuttle one-to-one	0.75	0.97	2.37	1.15	0.0214	0.0644
	.12	.14	.11	.25	.0020	.0024
Luth-Tuttle peraluminous	1.03	0.92	2.35	1.26	0.0336	0.0474
	.21	.22	.18	.19	.0030	.0032

The least-squares *thermochemical uncertainties* (Thompson and Waldbaum, 1969, Appendix A) are shown below the coefficients.

linear functions of reciprocal temperature. The results of linear least-squares fits for these quantities as functions of $1/T$ are given for the five sets of 2-kilobar data in Table 4a, and the results are plotted in Figures 2 and 3. Higher order fits show no improvement according to the Gauss criterion, and inspection of the points in Figures 2 and 3 also indicates that it would be unreasonable to ascribe curvature to the existing data. Similar plots of $\ln(r^2)$ and $(\operatorname{artanh} s)/s$ against P or P/T for data at constant temperature show near-linear relationships. We have, therefore, also carried out polybaric least-squares fits expressing $\ln(r^2)$ and $(\operatorname{artanh} s)/s$ as functions of $1/T$ and P/T. The results are given in Table 4b.

TABLE 3. STANDARD DEVIATION OF LEAST-SQUARES EQUATIONS IN TABLE 2

Data	s_y for $B(P, T)$	s_y for $C(P, T)$
Orville peralkaline	0.04	0.05
Luth-Tuttle peralkaline	0.10	0.16
Combined peralkaline	0.10	0.14
Luth-Tuttle one-to-one	0.06	0.07
Luth-Tuttle peraluminous	0.06	0.06

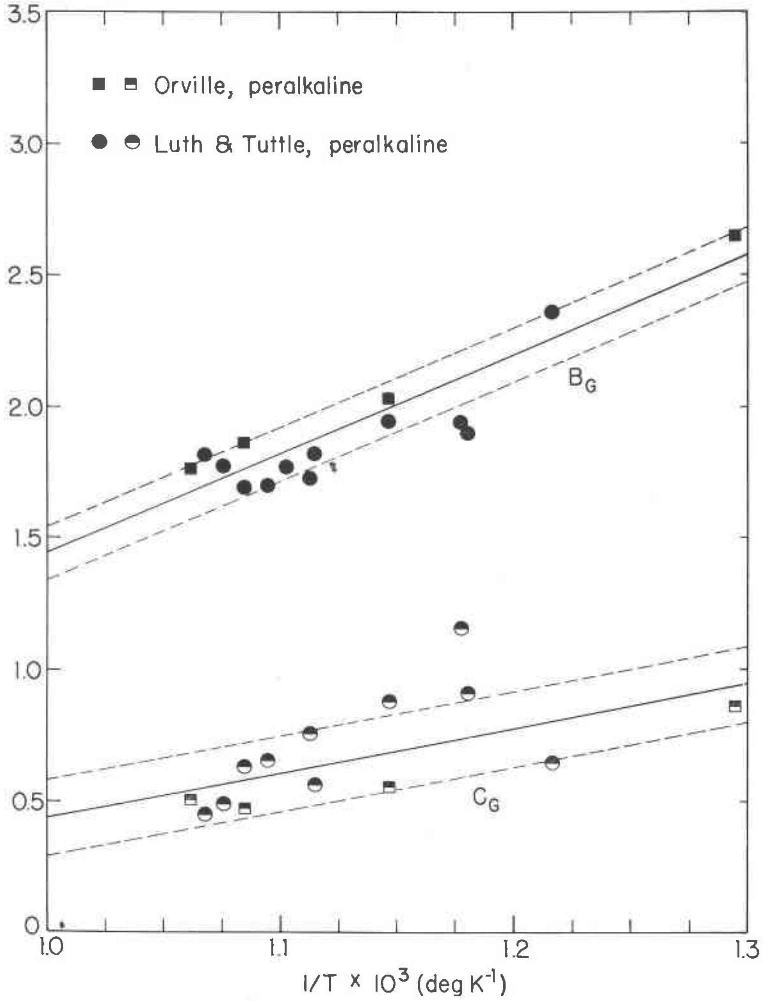

FIG. 1. Margules parameters calculated from two-phase data (first method). Solid lines denote least-squares fits to combined peralkaline data. Dashed lines are least-squares standard deviations.

The results of the isobaric least-squares equations give direct solutions for T_c and r_c (hence N_{2c}) by simply setting s equal to zero in the series expansion (Eq. A-9, Appendix A), or, in practice, by setting the expression for (artanh s)/$s=1$. The polybaric equations, similarly, give direct solutions for T_c and r_c as functions of P. The least-squares equations also

TABLE 4a. COEFFICIENTS OF ISOBARIC (2 KBAR) LEAST-SQUARES FITS OF (ARTANH s)/s AND ln (r^2) AS FUNCTIONS OF $1/T$

	(artanh s)/s		ln r^2	
	a_0	a_1	b_0	b_1
Orville	−0.4219	1345	2.887	−5037
Luth-Tuttle peralkaline	−0.4556	1368	3.379	−4305
Combined peralkaline	−0.4437	1361	3.176	−5089
Luth-Tuttle one-to-one	−0.1103	1040	0.214	−2730
Luth-Tuttle peraluminous	−0.0456	966	0.742	−2814

TABLE 4b. COEFFICIENTS OF POLYBARIC LEAST-SQUARES FITS TO (ARTANH s)/s AND ln (r^2) AS FUNCTIONS OF $1/T$ AND P/T

	(artanh s)/s			ln r^2		
	a_0	a_1	a_2	b_0	b_1	b_2
Orville	−0.4219	1315	0.0151	2.887	−5082	−0.0224
Luth-Tuttle peralkaline	−0.4432	1317	0.0205	2.392	−4231	−0.0428
Combined peralkaline	−0.4323	1312	0.0193	3.278	−5160	−0.0300
Luth-Tuttle one-to-one	−0.1104	1006	0.0169	0.216	−2772	+0.0199
Luth-Tuttle peraluminous	−0.0364	923	0.0172	1.220	−3168	−0.0275

permit direct calculation of binodal (solvus) points and the Margules parameters B_G and C_G at any appropriate P and T. The Margules parameters so obtained are *not*, however, simple linear functions of $1/T$ and P/T, though they are nearly so (see Thompson and Waldbaum, 1969, Figure 6) in the range of the data points.

A comparison of Figures 2 and 3 shows clearly that s is a much better behaved quantity than r. The three bodies of Luth-Tuttle data are clearly separable in Figure 2, but are not in Figure 3. It is also evident that Orville's two-phase data are not significantly different from the Luth-Tuttle peralkaline data, and that a combination of the two is quite justifiable.

As we have already noted the parameter r should not behave smoothly unless the phases are in complete equilibrium, whereas s should behave fairly smoothly even if only exchange equilibrium were achieved. Both r and s show smoother behavior in the Orville data as should be expected from our method of selecting what appear to be the most completely equilibrated feldspars.

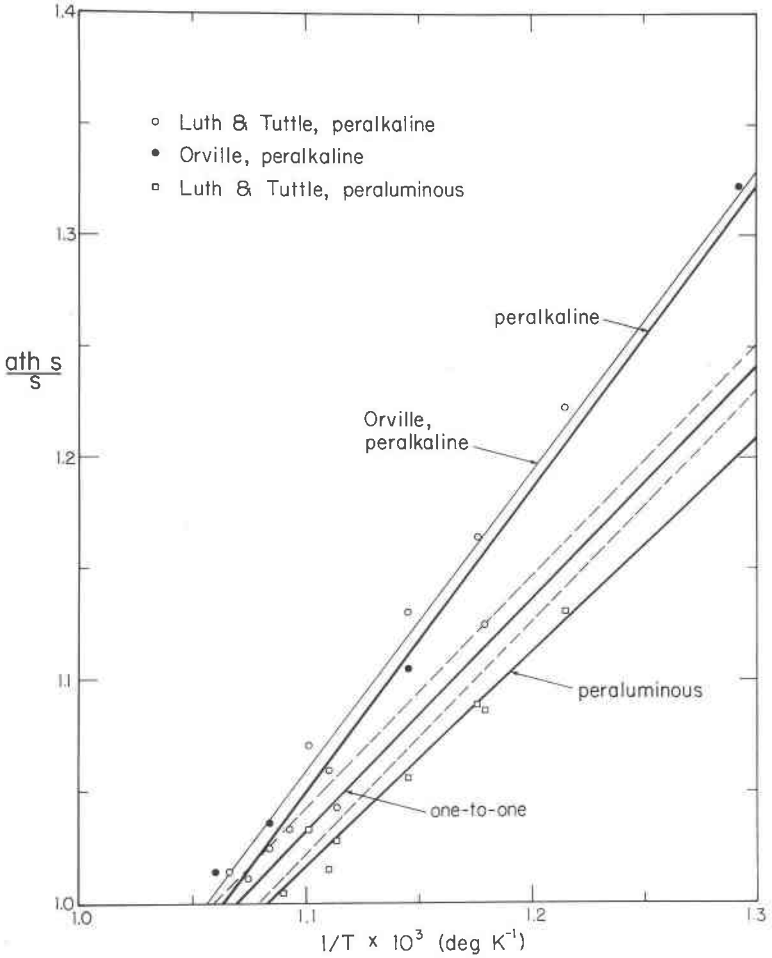

FIG. 2. Results of second method of treating two-phase data. Heavy solid lines denote least-squares fits to Luth-Tuttle data; light solid lines, Orville's data. Dashed lines represent standard deviations to fit to the *one-to-one* data. Ath = $\tanh^{-1}$ = artanh.

Comparison of the methods. The results of both methods permit calculations of a complete binodal for each body of data in *P-T-N* space. We shall confine our attention for the moment to the critical lines. Figures 4 and 5 show the *P-T* projections of these lines as deduced by our first and second methods, respectively. Figures 6 and 7 show the corresponding *P-N* projections of these lines giving the variation of the critical composition with pressure.

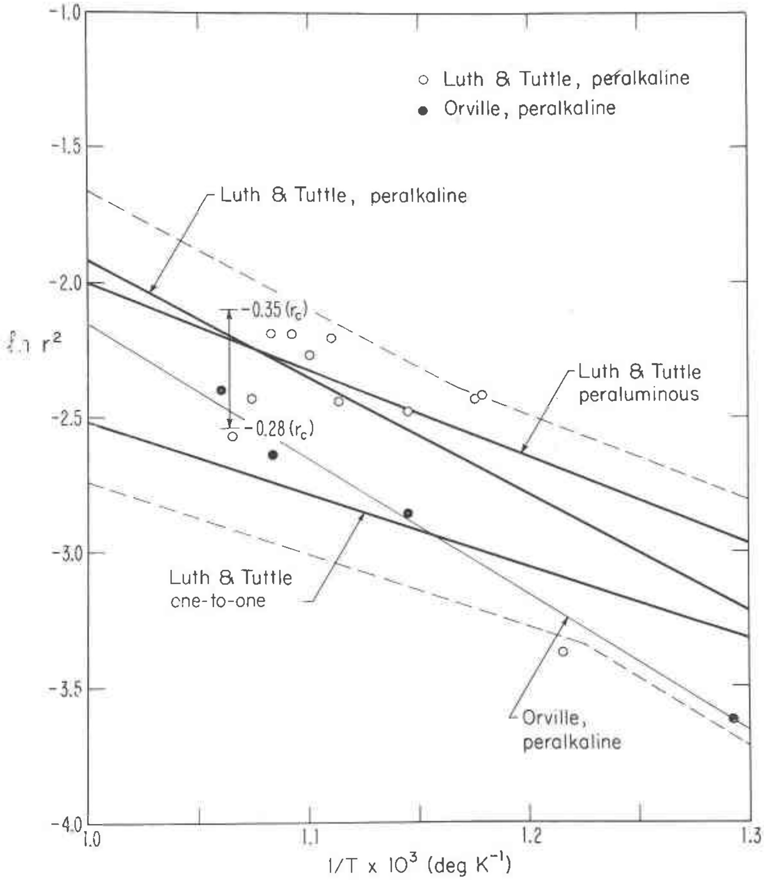

FIG. 3. Results of second method of treating two-phase data. Dashed lines denote maximum limits of standard deviations for all 4 sets of data. Vertical arrow indicates values of $\ln r^2$ for possible critical compositions (r_c) ranging from -0.28 to -0.35, where r is defined by (A-1).

The *P-T* projections based on our second method are necessarily straight lines. The other projections all show some curvature. Those based on our first method all have curvature of like sign, but we hesitate to ascribe any special significance to this. The critical line is, in itself, an *extrapolation* from the two-phase data, and the limited high-pressure data are all at either 650 (Luth and Tuttle) or 600°C (Orville). The critical lines are thus best known at their intersection with the 2-kbar isobar and with the 650° isotherms (Luth and Tuttle) or 600° isotherms (Orville). Figures 6 and 7 show all critical compositions as becoming more

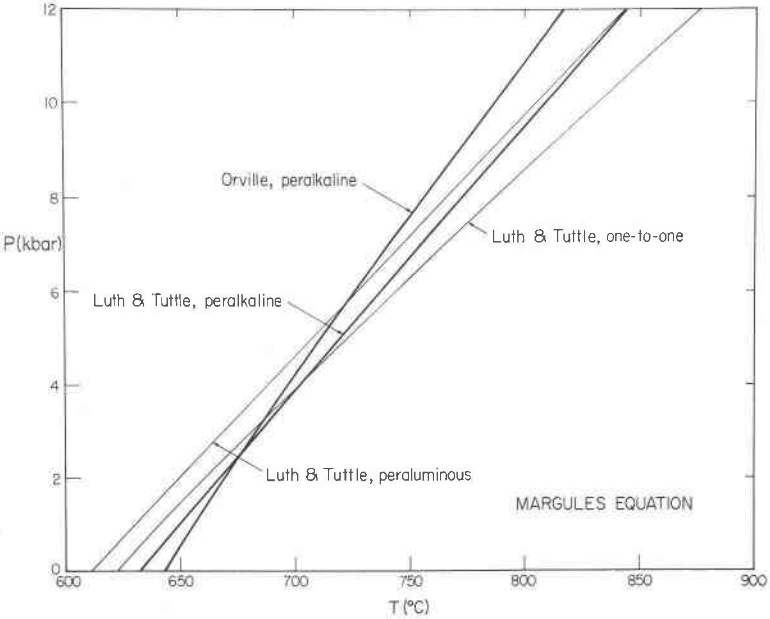

FIG. 4. Critical lines calculated from polybaric equations obtained by first method.

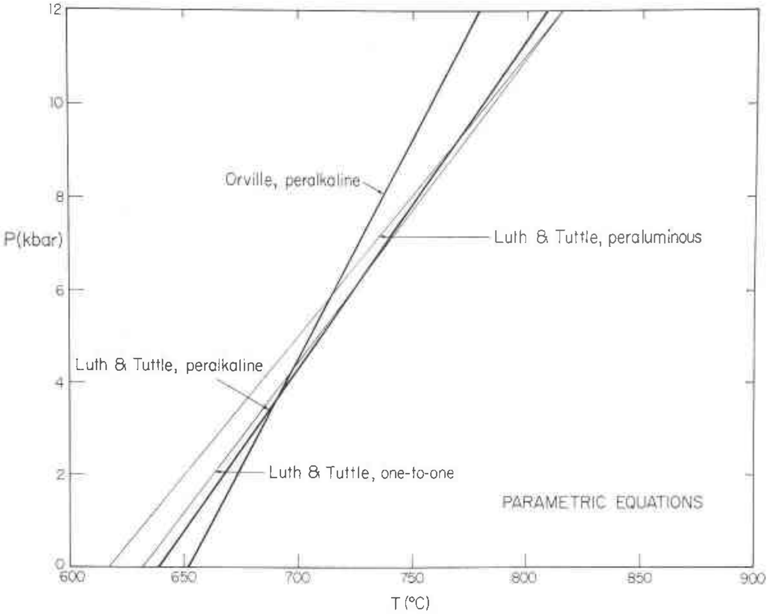

FIG. 5. Critical lines calculated from polybaric equations obtained by second method.

FIG. 6. Critical lines calculated from polybaric equations obtained by first method.

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sodic with rising pressure. This may, as we shall discuss below, be related to the monoclinic-triclinic transformation in the Na-rich feldspars, and might disappear in an analysis based solely on data from monoclinic feldspars rather than mixed monoclinic-monoclinic pairs (high temperatures, low pressures), and triclinic-monoclinic pairs (low temperatures, high pressures) as is the case here.

Despite the scatter and uncertainty, however, the present results are not inconsistent with previous authors' estimates based on these and other data. Bowen and Tuttle (1950), on limited data, estimated the critical temperature and composition at 981 bars to be 660 ± 10°C and about 44 mole percent *Or*. Their data should be comparable to the Luth-Tuttle *one-to-one* data; if so, Bowen and Tuttle's estimated critical temperature seems reasonable, but the critical composition does not. Yoder, Stewart, and Smith (1957) using similar starting materials estimated 715°C and 44 mole percent *Or* for the corresponding values at 5 kbar. Again the temperature is in agreement with the present results but the composition is not (the data upon which they based their estimate were not reported). It is also of interest to compare Orville's estimates, obtained graphically from his own two-phase data, with the results of the two methods used here. Orville estimates T_c and N_c at 2 kbar to be at 680° and 30 mole percent respectively, whereas we obtain 669° and 36 mole percent (first method), and 673° and 35 mole percent (second method). At 5 kbar the corresponding values are 710° and 30 mole percent (Orville); 711° and 33 mole percent (first method), and 705° and 33 mole percent (second method).

Another basis for useful comparison of the data is to calculate the binodal points and Margules parameters for each set of data for 650°C and 2 kbar (Table 5). This temperature and pressure is near the center of gravity for each set of data points, and is also in the temperature range where both coexisting feldspars are very likely to be monoclinic. This is also the approximate center of gravity for Orville's exchange data points, hence we have also included in Table 5 the preferred results of the analysis presented in Part I of this series (Thompson and Waldbaum, 1968a).

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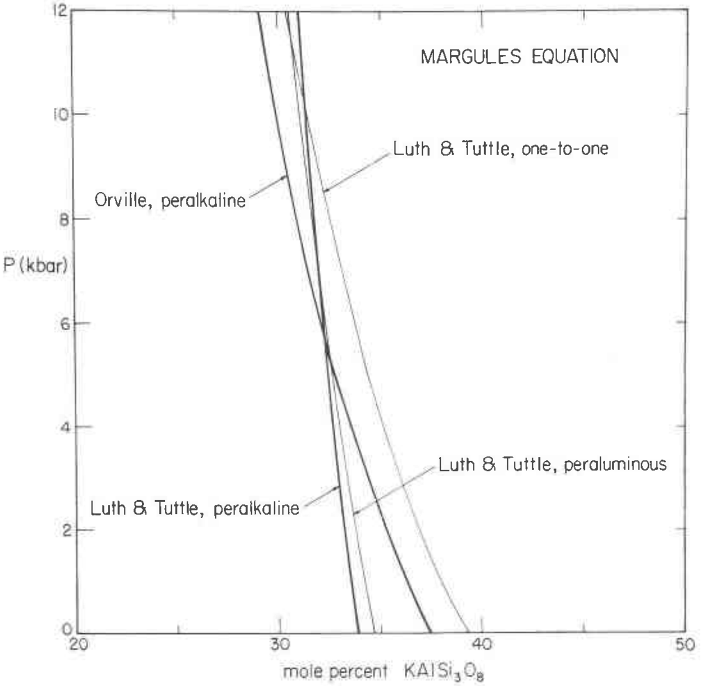
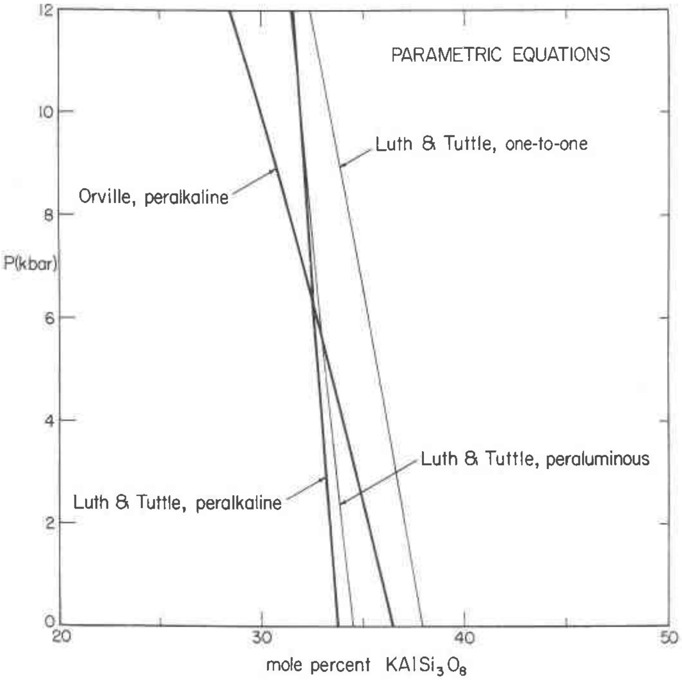
FIG. 7. Critical lines calculated from polybaric equations obtained by second method.



MARGULES EQUATION
Luth & Tuttle, one-to-one
Orville, peralkaline
Luth & Tuttle, peraluminous
Luth & Tuttle, peralkaline
P (kbar)
0
2
4
6
8
10
12
20
30
40
50
mole percent $KAlSi_3O_8$



PARAMETRIC EQUATIONS
Luth & Tuttle, one-to-one
Orville, peralkaline
Luth & Tuttle, peraluminous
Luth & Tuttle, peralkaline
P(kbar)
0
2
4
6
8
10
12
20
30
40
50
mole percent $KAlSi_3O_8$

TABLE 5. MARGULES PARAMETERS AND CALCULATED COEXISTING COMPOSITIONS AT 650°C AND 2 kbar

Data		W_{G1} (kcal)	W_{G2} (kcal)	$N_{2\alpha}$	$N_{2\beta}$
Orville ion-exchange data (peralkaline; Part I, Table 5)		2.95	4.20	.2564	.5347
Orville 2-phase data (peralkaline)	r, s method	2.48	4.35	.2032	.5201
	B, C method	2.47	4.34	.2055	.5172
Luth-Tuttle peralkaline data	r, s	2.10	4.32	.2003	.4806
	B, C	2.06	4.34	.1943	.4827
Combined peralkaline data	r, s	2.236	4.336	.2007	.4946
	B, C	2.17	4.35	.1954	.4936
Luth-Tuttle one-to-one data	r, s	2.67	4.19	.2650	.4813
	B, C	2.65	4.18	.2712	.4720
Luth-Tuttle peraluminous data	r, s	2.17	4.13	.3118	.3669
	B, C	2.13	4.12	($T_c = 648.9$°C)	

It is clear from Table 5 and Figure 8 that the exchange results indicate larger values of $\overline{G}_{ex}$ than do the results obtained from peralkaline two-phase pairs to which they should be comparable. The exchange results might be untrustworthy through an error in our assumptions concerning the activity coefficients in the aqueous phase, or possibly to undetected unmixing or other anomalous behavior in the aqueous phase, but it is more probable that the general magnitudes of $\overline{G}_{ex}$ indicated by the exchange data are more nearly correct than are those calculated from two-phase data. $\overline{G}_{ex}$, at any given composition and at a temperature and pressure corresponding to one of Orville's exchange curves, is related directly to the area under a fairly well-defined curve (Thompson and Waldbaum, 1968a, p. 1976, Fig. 9a), hence its magnitude is quite well known. Knowledge of only the *compositions* of two coexisting phases, however, yields reliable information only on the shape of the $\overline{G}_{ex}$ curve near those compositions for the pressure and temperature in question, and may be rather seriously in error (see Thompson and Waldbaum, 1969; also Sundquist, 1966) with regard to the magnitude of $\overline{G}_{ex}$ and hence of the quantities $(\mu_i - \mu_i^\circ)$. In fact to yield correct values of $(\mu_1 - \mu_1^\circ)$, $(\mu_2 - \mu_2^\circ)$, $N_{2\alpha}$, and $N_{2\beta}$ for a two-phase equilibrium α–β would require a Margules formula with *four*[1] rather than only two adjustable parameters for each pressure

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[1] A Margules formula may be extended to any number of adjustable parameters according to the scheme:

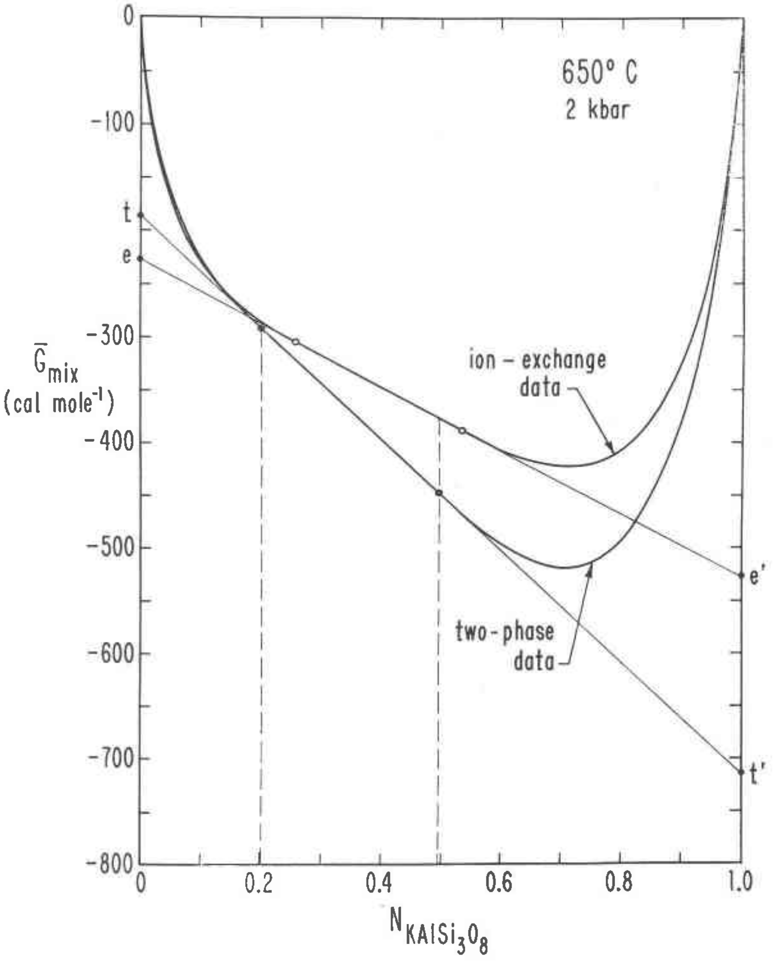

FIG. 8. Gibbs energy of mixing at 650°C and 2 kbar calculated from Margules parameters obtained from ion-exchange data ($W_{G1}=2.95$, $W_{G2}=4.20$) and two-phase data ($W_{G1}=2.236$, $W_{G2}=4.336$). Open circles and e and e' denote compositions and chemical potentials, respectively, of coexisting feldspars calculated from ion-exchange parameters; solid circles and t and t' denote the same for coexisting feldspars calculated from two-phase parameters. Light solid lines, ee' and tt' are tangents to the respective curves at the compositions of the coexisting phases. See Figure 1 of Part IV (Waldbaum and Thompson, 1969) for a plot of the Gibbs energy of mixing of an *ideal* solution at 650°C.

$$\begin{aligned}\overline{X}_{ex} &= N_1N_2(N_2W_{X1} + N_1W_{X2}) + N_1^2N_2^2(N_2W_{X3} + N_1W_{X4}) \\ &\quad + N_1^3N_2^3(N_2W_{X5} - N_1W_{X6}) + \cdots + N_1^aN_2^a(N_2W_{X(2a-1)} + N_1W_{X(2a)})\end{aligned}$$

Terms for which $W_{X(2-1)} = W_{X(a)}$ yield only *symmetrical* contributions to $\overline{X}_{ex}$.

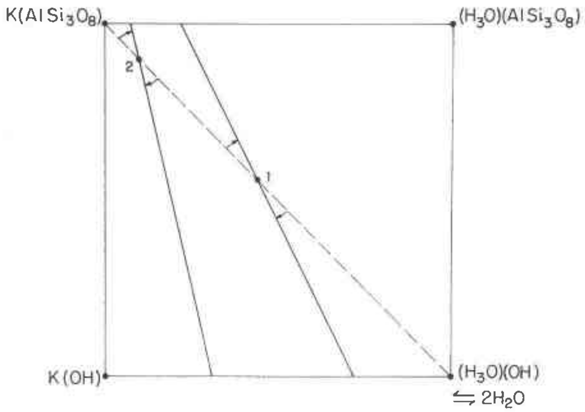

FIG. 9. Isothermal, isobaric, reciprocal ternary section in the system K_2O-Al_2O_3-SiO_2-H_2O. Dashed line represents the $KAlSi_3O_8$-H_2O join (see text). Solid lines represent possible equilibrium tie lines.

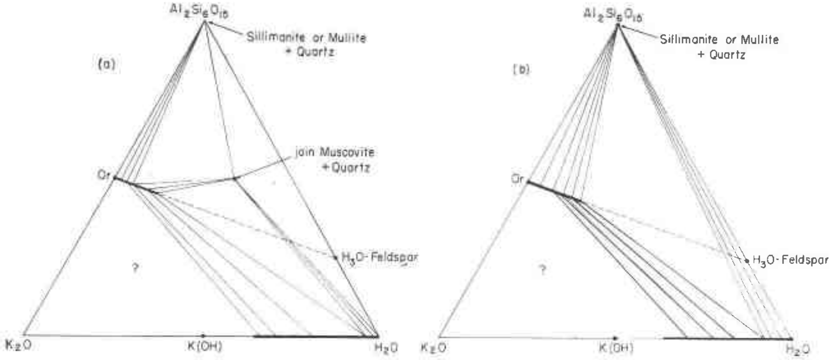

FIG. 10. Isothermal, isobaric section (schematic) through the system K_2O-Al_2O_3-SiO_2-H_2O at low temperatures (Fig. 10a) and at higher temperatures (Fig. 10b). Dashed line represents the alkali feldspar-hydronium feldspar join. The join alkali feldspar-hydrogen feldspar (not shown) is parallel to the join K_2O-H_2O, passing through the piercing point of the quartz-muscovite join.

and temperature. In view of this it is of interest that the agreement in Table 5 is as close as it is.

THE PROBLEM OF THE STARTING MATERIALS

One possible explanation of the distinctly different behavior of the different types of starting material is that anhydrous alkali feldspars are not strictly binary solutions, but vary from their idealized formulas in both alkali-alumina ratio and alkali-silica ratio. We do not regard the evidence for this as convincing, however, owing to analytical uncertainties, even when dealing with well-crystallized natural specimens.

A more likely interpretation, to us, is that alkali feldspars placed in contact with an aqueous phase will undergo hydrolysis involving substitution of either protons or—more likely—hydronium ions, H_3O^+, (Volmer, 1924; Hamilton and Ibers, 1968, p. 116) for the alkalis (Luth and Tuttle, 1966, p. 1372). This would be in essence an alkali-hydronium exchange reaction between a feldspar and an aqueous phase. A consequence of such an exchange reaction would be that the aqueous phase should contain excess alkali at the completion of a run. Results obtained by Morey (1957), by Garrels and Howard (1959), and by Wyllie and Tuttle (1964) indicate that this may be so in fact. Hydronium substitution for alkalis, particularly for K^+ to which it is comparable in size, is structurally reasonable and may well be anticipated in view of the recent discovery and synthesis of ammonium-bearing feldspar (Erd, White, Fahey, and Lee, 1964; Barker, 1964).[1]

Let us consider this possibility with respect to possible hydronium exchange in a potassium feldspar. The apparent distribution constant for such a reaction would be[2]

$$K_D' = \frac{N_{\mathrm{Or,fsp}} m_{\mathrm{H_3O^+,fluid}}}{N_{\mathrm{Hf,fsp}}\, m_{\mathrm{K^+,fluid}}}$$

It is evident that increasing $m_{\mathrm{K^+,fluid}}/m_{\mathrm{H_3O^+,fluid}}$ will minimize $N_{\mathrm{Hf,fsp}}$, hence it is likely that runs with excess alkali, either as alkali silicate or as alkali chloride, should be buffered against extensive hydronium substitution and should then yield feldspars that are more nearly simple *alkali* feldspars. It is also evident from the geometry, distribution of joins, and

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[1] Alkali-hydronium-ammonium cation substitution in crystals has been reasonably well established (Havighurst, Mack, and Blake, 1925; Hendricks, 1937; Ross and Evans, 1965; Pezerat, Mantin, Kovacevic, 1966; and others). Bondam (1967) reports experimental data which he states verifies potassium-hydronium exchange in adularia. The data presented, however, are somewhat equivocal and probably cannot be regarded confirming hydronium substitution in feldspars. The infrared spectral data of Erd, *et al.* (1964, Table 6), on the other hand, suggests that some of the water in buddingtonite may in fact be hydronium (see Taylor and Vidale, 1956). C. Frondel, W. K. Sabine, and R. W. T. Wilkins (in preparation) recently obtained water analyses and infrared spectra of adularia that indicate the presence of structural water with properties which are also fully consistent with at least some of the water being hydronium ion.

[2] The subscript "HF" identifies the component $H_3O(AlSi_3O_8)$ and fsp refers to a feldspar phase as distinct from a fluid or other crystalline phase.

known solubility relations in a system such as K_2O-Al_2O_3-SiO_2-H_2O, that aqueous phases coexisting with assemblages containing alkali in excess of alumina (peralkaline) will have higher values of $m_{K^+,\text{fluid}}/m_{H_3O^+,\text{fluid}}$ than those coexisting with assemblages having an excess of alumina over alkali (peraluminous). We may thus anticipate that runs using peraluminous starting materials should yield feldspars showing maximum hydronium substitution, hence showing greatest departure from simple alkali feldspar.

Some possible exchange reactions are shown schematically in Figure 9. The dashed line represents compositions of starting mixtures in which the feldspar or glass of feldspar composition has the ideal formula: $K(AlSi_3O_8)$. Point 1 represents a high ratio of fluid to glass or crystal and point 2, a low ratio. The arrows show the expected course of reaction in each case. Hence, where the ratio of fluid to other phases is high, as in most hydrothermal experiments, compared with a natural igneous or metamorphic environment, the possibility of extensive hydronium substitution is enhanced—other things being equal.

The maximum stable hydronium substitution should be as indicated (schematically) in Figure 10. (Figure 10 is a section through the system K_2O-Al_2O_3-SiO_2-H_2O that includes the plane of Figure 9.) Figure 10a shows that the saturation value at low temperatures should occur with muscovite, quartz, and fluid. Figure 10b shows that the saturating assemblage at high temperatures should be sillimanite (or mullite), quartz, and fluid. If the fluid were diluted by extraneous components, the saturation value of $N_{\text{Hf},\text{fsp}}$, whatever it may be, should decrease (move toward the *Or* composition). It is probably also lowered by a decrease in temperature. All considered, we feel that extensive hydrolysis of this kind is, if real at all, far less likely in a natural petrogenetic environment than in standard hydrothermal experiments. We are of the opinion, therefore, that the alkali-buffered (peralkaline) hydrothermal systems should yield feldspars resembling most closely those occurring naturally and conforming more nearly to the classical feldspar formula.

THE PROBLEM OF POLYMORPHISM

It is quite certain that the feldspar pairs obtained in both the Orville and Luth-Tuttle experiments are monoclinic at high temperatures (above about 620°C at 2 kbar), and that at lower temperatures the Na-rich phase is triclinic, coexisting with a monoclinic K-feldspar. The exact nature of the transition is debatable but three possibilities are shown in Figure 11. We believe that Figure 11b is more nearly correct, but the following argument applies to all three possibilities.

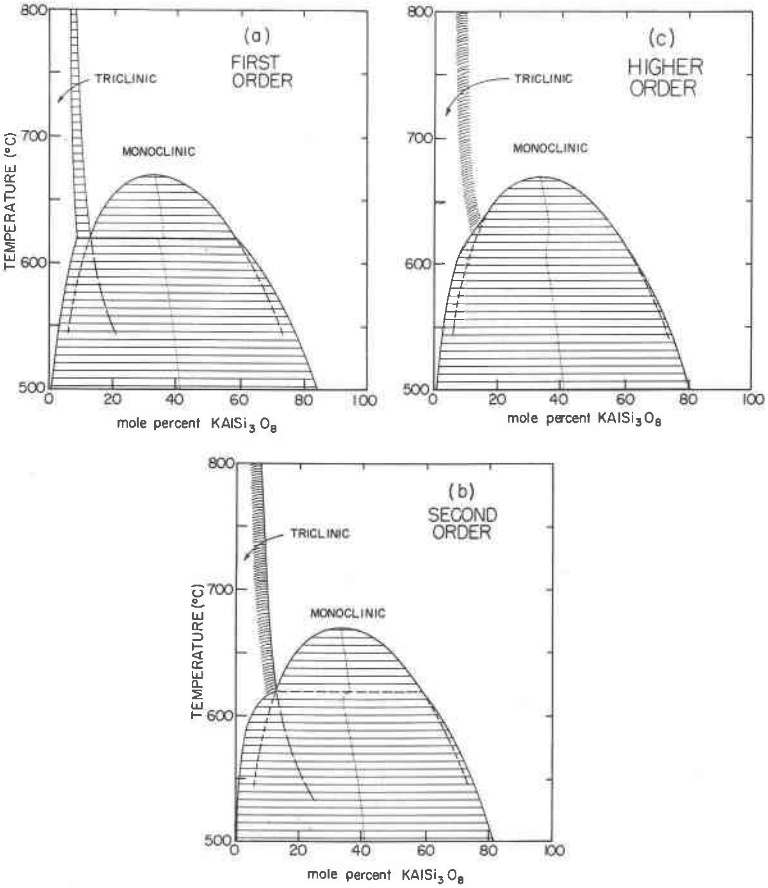

FIG. 11. Possible relations between the equilibrium alkali feldspar binodal and the *equilibrium* symmetry change (corresponding to curve E in Figure 6 of Waldbaum and Thompson, 1968). Phase boundaries are shown as solid lines where they are stable and dashed lines where metastable. Rectilinear diameters are shown as dotted lines. Phase relations are schematic, but the monoclinic binodal is approximately that shown in Figure 13.

We have not allowed for polymorphism (as shown by symmetry changes) in either method of analysis, hence the rectilinear diameters calculated from the parameters in Tables 2 and 4 will not correspond to the true rectilinear diameters shown as dotted lines in Figure 11. The difference in the calculated and true rectilinear diameters for Figure 11b is shown on an expanded scale in terms of $\ln(r^2)$ in Figure 12, where the

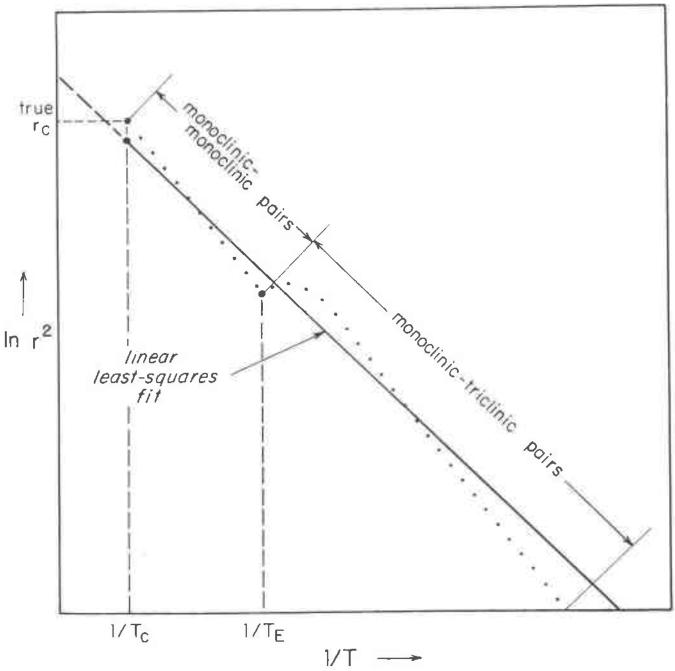

FIG. 12. Critical region of Figure 11b showing (schematically) the form of the rectilinear diameter curve (solid line) obtained by least-squares fit to data which include monoclinic-monoclinic pairs *and* triclinic-monoclinic pairs. Dotted line is same as in Figure 11b for the position of the true rectilinear diameter curve when the symmetry change is taken into account. T_E is the temperature at which the equilibrium symmetry-change curve intersects the Na-rich portion of the two-phase region. (Note: Dotted line refers to *true* coexisting compositions. A similar curve for coexisting feldspars obtained from compositions determined by physical property measurements at room temperature will show an additional discontinuity resulting from a *displacive* symmetry change, as discussed in Part II.)

solid line corresponds to the calculated curve and the dotted line again corresponds to the true relations. It is thus probable that our analysis has given values of r_c that are slightly less negative than the correct values for monoclinic alkali feldspars. If, as seems likely, the Na-rich feldspars in the 5 and 10 kbar runs were all triclinic, the relations in Figures 11b and 12 may also account for the shift to more sodic critical compositions indicated by our analysis (Fig. 7). By the same reasoning our calculated values of s will tend to converge more rapidly with rising temperature than they should, thus yielding slightly too low a critical temperature. We shall therefore attempt, below, to adjust our parameters without doing violence to the data, and in such a way that we may take these factors into account.

It is of interest here, however, to speculate that $(H_3O)^+$, a large ion, would probably favor monoclinic symmetry, other things being equal. Thus the proportion of monoclinic-monoclinic pairs should be greatest in the *peraluminous* data, smaller in the *one-to-one* data, and least in the *peralkaline* data. A consequence of this should be a slower convergence of s with rising temperature. That this is in fact so, whatever the correct explanation, may be seen by comparing the slopes for the peralkaline, one-to-one, and peraluminous data, respectively, as plotted in Figure 2. Figure 2 is thus consistent, at least, with our hydronium-feldspar hypothesis. This would also suggest that investigations of equilibrium ordering in alkali feldspars, particularly Na-rich feldspars, should be done under conditions that would minimize hydronium substitution.

ADJUSTMENT OF PARAMETERS FOR HIGH-TEMPERATURE, MONOCLINIC ALKALI FELDSPARS

In view of the interpretations discussed above, we shall now confine our attention to the feldspars formed from peralkaline starting materials as best representing natural alkali feldspars. We shall use the combined peralkaline data of Orville and of Luth and Tuttle, rather than attempt to choose between them, and assume that the critical line calculated by our second method (a straight line) has the correct P-T slope (Fig. 5), but that it lies at slightly too low temperatures. We shall also assume that the calculated critical compositions at 2 kbar are slightly too K-rich, but that the calculated W_G's and N's at 650°C and 2 kbar as given in Table 5 are correct. The last assumption is fairly safe in that the temperature and pressure are near the center of gravity of the data and well within the monoclinic-monoclinic range.

Two points on the critical line and one pair of coexisting phases (at 650°C and 2 kbar) on the binodal surface are sufficient to calculate an equation having the simple asymmetric Margules form (Thompson, 1967), with the quantities W_{V1}, W_{V2}, W_{E1}, W_{E2}, W_{S1}, and W_{S2} assumed constant. Under these restrictions, the hypothesis that the critical line is straight in P-T projection (and we really do not know which way it curves, if at all) is special and requires that the critical composition be constant (Appendix B). As we have discussed above, the apparent shift to more sodic critical compositions at high pressures may be due only to the preponderance of triclinic-monoclinic pairs in the high-pressure data.

In Table 6 we show the effects, using the above assumptions, of minor readjustments of the critical temperature and composition at 2 kbar upon

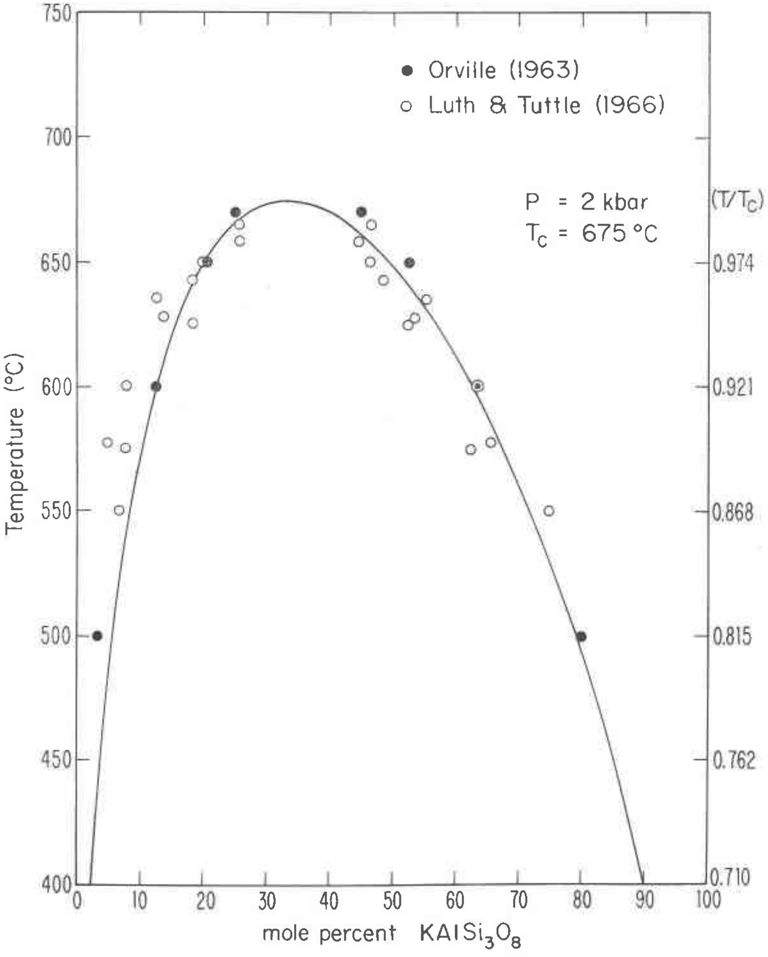

FIG. 13. Comparison of calculated binodal and observed *peralkaline* two-phase data at 2 kbar. Critical temperature is 675°C, critical r is exactly $-\frac{1}{3}$ (Table 6). The ordinate on the right side reduces this figure to a diagram of corresponding states for all pressures, provided the critical line is linear in P–T–N space. Numerical values for this smoothed binodal curve are to be tabulated in Part IV of this series.

the calculated Margules parameters. We also show for comparative purposes values of some tentative excess parameters obtained by other means for different alkali feldspar series and from our analysis of the two-phase region *halite-sylvite* (Thompson and Waldbaum, 1969). It is clear that variations in T_c and N_c that are well within the uncertainty of the data produce significant variations in the Margules parameters. Selecting

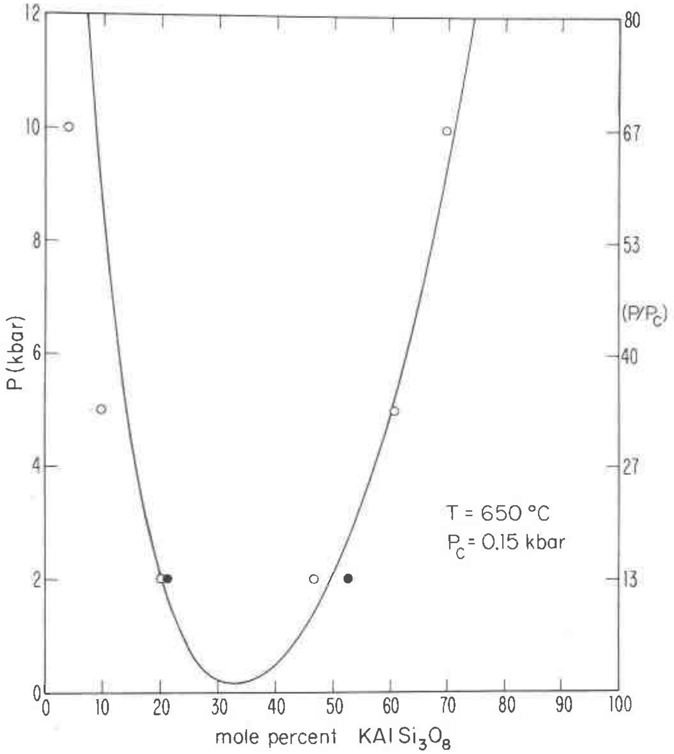

FIG. 14. Calculated isothermal binodal at 650°C compared with observed *peralkaline* two-phase data. The binodal was calcalulated from the same Margules parameters used for Figure 13.

a critical temperature of 675°C (at 2 kbar) and a critical composition of precisely 1/3, however, yields values quite consistent with those obtained by other means—note particularly the comparison of the W_V's with those from cell-volume measurements at room temperature. The calorimetric data of Kracek and Neuvonen (1952) for natural sanidine—high albite solutions also are in excellent agreement with the W_E's.

Although the excess mixing properties are tentative, a binodal curve consistent with two-phase data in the monoclinic region may be constructed using the formula

$$\begin{aligned}\overline{G}_{ex} &= (6327 + 0.093P - 4.632T)N_1N_2^2 \\ &\quad + (7672 + 0.112P - 3.857T)N_2N_1^2\end{aligned}$$

where $\overline{G}$ is in cal mole^{-1} and P is in bars. A 2-kilobar binodal calculated from the above is shown in Figure 13 and a 650°C isothermal binodal

TABLE 6. CRITICAL CONSTANTS AND MARGULES PARAMETERS FROM COMBINED PERALKALINE DATA AND FROM RELATED STUDIES ON ALKALI FELDSPARS AND THE SYSTEM NaCl-KCl

	r_c	T_c (°C)	W_{E1}	W_{E2}	W_{V1}	W_{V2}	W_{S1}	W_{S2}
			(kcal)		(cal bar^{-1})		(cal deg^{-1})	
Combined Peralkaline Data								
Critical line (r, s) and 650°C r, s values.	−.32	669.6	3.72	9.77	.055	.144	1.73	6.19
r_c adjusted	−.33	669.6	8.03	9.73	.118	.143	6.53	6.16
T_c adjusted	−.32	680.0	2.47	6.45	.036	.094	0.33	2.49
T_c, r_c adjusted	−.33	680.0	5.30	6.43	.077	.093	3.49	2.47
Preferred peralkaline parameters based on available experimental data.	−1/3	675.0	6.33	7.67	.093	.112	4.63	3.86
Related Studies								
Sanidine molar volumes at 25°C (Part II)	—	—	—	—	.090	.090	—	—
Microcline—low albite enthalpies of solution in HF and 25°C volumes (Waldbaum, 1966)	—	—	6.24	8.43	.110	.110	—	—
Halite-sylvite 2-phase data (Thompson and Waldbaum, 1969)	−.30	492.1	5.79	8.99	—	—	5.05	7.28

curve in Figure 14. The data points in Figure 13 have the expected distribution relative to the calculated binodal curve, and the distribution compares favorably with Figure 11b. A useful property of the simplified equation yielding a straight critical line is that one isobaric section through the binodal surface is identical to all others if the temperature is expressed as T/T_c (Fig. 13).

ACKNOWLEDGMENTS

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APPENDIX A. THERMODYNAMIC RELATIONS

The equations for two-phase equilibria (Thompson, 1967, p. 354) may be condensed by recombination and by introducing the following notation:

$$\left.\begin{aligned} s &\equiv N_{2\beta} - N_{2\alpha} \\ r &\equiv N_{2\beta} + N_{2\alpha} - 1 \end{aligned}\right\} \tag{A-1}$$

and

$$\left.\begin{aligned} B_G &\equiv \frac{W_{G2} + W_{G1}}{2RT} \\ C_G &\equiv \frac{W_{G2} - W_{G1}}{2RT} \end{aligned}\right\} \tag{A-2}$$

where N is mole fraction, T is absolute temperature, R is the gas constant, and β identifies the K-rich phase and α the Na-rich phase, and components 1 and 2 are $NaAlSi_3O_8$ (*Ab*) and $KAlSi_3O_8$ (*Or*), respectively. The equations for the two-phase equilibrium may now be written

$$\left.\begin{aligned} (B_G - 3rC_G)s &= \theta_1 \\ C_G s^3 - (B_G - 3rC_G)rs &= \theta_2 \end{aligned}\right\} \tag{A-3}$$

where

$$\left.\begin{aligned} \theta_1 &\equiv \frac{1}{2}\ln\left(\frac{N_{2\beta}N_{1\alpha}}{N_{1\beta}N_{2\alpha}}\right) = \operatorname{artanh}\left(\frac{2s}{1 + s^2 - r^2}\right) \\ {}_2 &\equiv \frac{1}{2}\ln\left(\frac{N_{2\beta}N_{1\beta}}{N_{2\alpha}N_{1\alpha}}\right) = -\operatorname{artanh}\left(\frac{2sr}{1 - s^2 - r^2}\right) \end{aligned}\right\} \tag{A-4}$$

We then have

$$B_G = 3r\left(\frac{r\theta_1 + \theta_2}{s^3}\right) + \frac{\theta_1}{s} \tag{A-5a}$$

$$C_G = \left(\frac{r\theta_1 + \theta_2}{s^3}\right) \tag{A-5b}$$

The right hand side of either (A-5a) or (A-5b) is a function of composition alone and may be readily evaluated for the observed two-phase pairs obtained at each temperature. We shall further define

$$B_X \equiv \frac{W_{X2} + W_{X1}}{2R}; \qquad C_X \equiv \frac{W_{X2} - W_{X1}}{2R} \tag{A-6}$$

where X may be internal energy, E; enthalpy, H; volume, V; or entropy, S. Then, as with the W's (Thompson, 1967, p. 349), we may write

$$\left.\begin{aligned} B_G &= -B_S + B_V\left(\frac{P}{T}\right) + B_E\left(\frac{1}{T}\right) \\ C_G &= -C_S + C_V\left(\frac{P}{T}\right) + C_E\left(\frac{1}{T}\right) \end{aligned}\right\} \tag{A-7}$$

where P is pressure.

Of several functions investigated by Thompson and Waldbaum (1969) the plots that proved to be most nearly linear were $\ln(r^2)$ against $1/T$ and $(\operatorname{artanh} s)/s$ against $1/T$ which can be expressed analytically as

$$\ln r^2 = b_0 + b_1\left(\frac{1}{T}\right) + b_2\left(\frac{P}{T}\right) \tag{A-8}$$

$$\frac{\operatorname{artanh} s}{s} = \sum_{n=0}^{n=\infty} \frac{s^{2n}}{(2n+1)} = a_0 + a_1\left(\frac{1}{T}\right) + a_2\left(\frac{P}{T}\right) \tag{A-9}$$

for polybaric data.

Appendix B. The Critical Line of a Simple Asymmetric Solution

Certain of the desired relationships have been derived elsewhere (Thompson, 1967, p. 357–358), but we shall present them here in a slightly more convenient form for our present purposes, and with different notation. We shall use Γ ($\equiv \bar{G}/RT$) as our thermodynamic potential; ρ ($\equiv 2N_2 - 1$) as our composition variable; and the quantities B_X, C_X (Thompson and Waldbaum, 1969) as Margules parameters, supposing that B_E, C_E, B_V, C_V, B_S, and C_S are constants.

Γ, like $\bar{G}$, must be minimized at equilibrium at a given P and T, hence for a critical phase (the subscript identifies the n-th derivative of Γ with respect to ρ at constant P and T):

$$0 = \Gamma_2 = \frac{1}{(1-\rho_c^2)} - \frac{1}{2}(B_{Gc} - 3\rho_c C_{Gc}) \tag{B-1}$$

$$0 = \Gamma_3 = \frac{2\rho_c}{(1-\rho_c^2)^2} + \frac{3}{2}C_{Gc} \tag{B-2}$$

$$0 < \Gamma_4 = 2\frac{(1+3\rho_c^2)}{(1-\rho_c^2)^3} \tag{B-3}$$

(B-1) and (B-2) are the equations of the critical line along which, therefore:

$$0 = d\Gamma_2 = \left(\frac{\bar{E}}{R}\right)_2 d\left(\frac{1}{T}\right) + \left(\frac{\bar{V}}{R}\right)_2 d\left(\frac{P}{T}\right) \tag{B-4}$$

$$0 = d\Gamma_3 = \left(\frac{\bar{E}}{R}\right)_3 d\left(\frac{1}{T}\right) + \left(\frac{\bar{V}}{R}\right)_3 d\left(\frac{P}{T}\right) + \Gamma_4 d\rho \tag{B-5}$$

Also:

$$\left.\begin{aligned} \left(\frac{\bar{E}}{R}\right)_2 &= -\frac{1}{2}(B_E - 3\rho C_E); & \left(\frac{\bar{V}}{R}\right)_2 &= -\frac{1}{2}(B_V - 3\rho C_V) \\ \left(\frac{\bar{E}}{R}\right)_3 &= \frac{3}{2}C_E; & \left(\frac{\bar{V}}{R}\right)_3 &= \frac{3}{2}C_V \end{aligned}\right\} \tag{B-6}$$

We therefore obtain (noting that $\rho_c = r_c$):

$$\frac{d\left(\dfrac{P_c}{T_c}\right)}{d\left(\dfrac{1}{T_c}\right)} = -\frac{(B_E - 3C_E r_c)}{(B_V - 3C_V r_c)} \tag{B-7}$$

$$\Gamma_4\left[\frac{dr_c}{d\left(\dfrac{1}{T_c}\right)}\right] = -\frac{3}{2} C_V \frac{d\left(\dfrac{P_c}{T_c}\right)}{d\left(\dfrac{1}{T_c}\right)} - \frac{3}{2} C_E$$

$$= \frac{3}{2}\frac{(B_E C_V - B_V C_E)}{(B_V - 3C_V r_c)} \tag{B-8}$$

and from (B-7) and (B-8)

$$\frac{d^2\left(\dfrac{P_c}{T_c}\right)}{d\left(\dfrac{1}{T_c}\right)^2} = \frac{-3(B_E C_V - B_V C_E)\left[\dfrac{dr_c}{d(1/T_c)}\right]}{(B_V - 3C_V r_c)^2}$$

$$= \frac{-2\Gamma_4}{(B_V - 3C_V r_c)}\left[\frac{dr_c}{d(1/T_c)}\right]^2 \tag{B-9}$$

A straight line in (P/T) and $(1/T)$ must be straight in P and T and *vice versa*. The quantity $(B_V - 3C_V r_c)$ is finite, hence if (d^2P_c/dT_c^2) is zero then the critical composition is constant and *vice versa*; and also (from B-8) we must have $(B_E C_V - B_V C_E) = 0$, whence

$$\frac{d\left(\dfrac{P_c}{T_c}\right)}{d\left(\dfrac{1}{T_c}\right)} = -\frac{B_E}{B_V} = -\frac{C_E}{C_V} = -\frac{W_{E1}}{W_{V1}} = -\frac{W_{E2}}{W_{V2}} \tag{B-10}$$