Subsolidus phase relations in the nepheline–kalsilite system at 0.5, 2.0, and 5.0 kbar

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Abstract

This paper presents: (1) X-ray diffraction data and refined unit-cell parameters for $(Na,K)_3K(AlSiO_4)_4$ nephelines and kalsilites synthesized at 0.5 kbar; (2) experimental data on the nepheline–kalsilite solvus in the $Na_3K(AlSiO_4)_4$–$K_4(AlSiO_4)_4$ system from 400 to 1000°C at 0.5, 2.0, and 5.0 kbar; (3) thermodynamic mixing-parameter equations for $(Na,K)_3K(AlSiO_4)_4$ crystalline solutions; and (4) calculated nepheline–kalsilite solvi and subsolidus activity–composition relations for the $Na_3K(AlSiO_4)_4$–$K_4(AlSiO_4)_4$ system at pressures in the range 0.5–5.0 kbar.

X-ray diffraction data and refined unit-cell parameters for $(Na,K)_3K(AlSiO_4)_4$ nephelines and kalsilites crystallized at 0.5 kbar indicate that $d_{20,1}$ spacings and unit-cell parameters for the synthetic nephelines, as well as $d_{10,2}$ spacings and unit-cell parameters for the synthetic kalsilites, are a linear function of $XK_4(AlSiO_4)_4$. However, the a unit-cell dimensions and unit-cell volumes for the synthetic nephelines are systematically smaller than those for nephelines crystallized at one atm by Smith and Tuttle (1957) and Donnay *et al.* (1959). The discrepancies are attributed to slightly Na_2O-deficient starting materials and additional Na_2O volatilization during experimentation in these two earlier investigations.

Three different types of solid starting materials were used to delimit the nepheline–kalsilite solvus at ~100°C intervals from 400 to 1000°C at 0.5, 2.0, and 5.0 kbar. At a given pressure and temperature the three starting materials yielded very similar results indicating that equilibrium was closely approached in all experiments. Collectively the experimental data suggest that nepheline–kalsilite solvi are slightly asymmetric toward $Na_3K(AlSiO_4)_4$. Between 400 and 800°C there is good agreement between our solvus data obtained at 0.5 kbar and the solvus data obtained by Tuttle and Smith (1958) at one atm, 480 bars, and 981 bars, but there are significant discrepancies at higher temperatures.

Comparisons between our solvus data and calculated solvi indicate that values of Margules, van Laar, and quasichemical mixing parameters for $(Na,K)_3K(AlSiO_4)_4$ crystalline solutions are a linear function of temperature but not of pressure. Relative activities for the $Na_3K(AlSiO_4)_4$ and $K_4(AlSiO_4)_4$ components of the crystalline solutions calculated from the Margules and van Laar solution models are nearly identical and significantly different from activities calculated from the quasichemical formulation.

Introduction

Bowen and Ellestad (1936), Miyashiro (1951), and Tilley (1954) (among others) established that the composition of natural nepheline is a function of the bulk composition and crystallization history of the host rock, and this gave impetus to subsequent experimental and theoretical investigations of the subsolidus phase relations and thermodynamic properties of nepheline crystalline solutions. The first detailed experimental study of the nepheline–kalsilite solvus was reported by Tuttle and Smith (1958). They

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noted that rates of nepheline–kalsilite exsolution are very rapid in both dry and (particularly) hydrothermal experiments, and this has been verified by Yund *et al.* (1972), who measured the kinetics of this phase separation under dry and hydrothermal conditions between 400 and 700°C at pressures from one atm to 1.0 kbar. Hydrothermal experimental data obtained by Hamilton and MacKenzie (1960) and Hamilton (1961) on the subsolidus phase relations of nepheline crystalline solutions in the $NaAlSiO_4$–$KAlSiO_4$–SiO_2–H_2O system led these investigators to suggest that both the Na/K ratio and excess silica content of nepheline in equilibrium with alkali feldspar are a function of temperature. Subsequently, Debron (1965), Wellman (1970), and Roux (1974) performed ion-exchange experiments to determine Na–K partitioning between $(Na,K)AlSiO_4$ nepheline crystalline solutions and aqueous $(Na,K)Cl$ solutions. Applying fundamental thermodynamic principles of equilibrium, Perchuk and Ryabchikov (1968) and Powell and Powell (1977) derived alkali feldspar–nepheline geothermometers based upon the thermodynamic properties of alkali feldspar and nepheline crystalline solutions. These investigators demonstrated that final equilibration temperatures of natural alkali feldspar–nepheline pairs can be estimated from the Na/K ratios of the two minerals.

In contrast to the attention devoted to nepheline crystalline solutions, there have been few experimental and theoretical studies of the subsolidus phase relations and thermodynamic properties of kalsilite crystalline solutions. Limited experimental data and/ or brief theoretical treatments have been provided by Smith and Tuttle (1957), Tuttle and Smith (1958), Fudali (1963), Debron (1965), Perchuk and Ryabchikov (1968), Wellman (1970), Yund *et al.* (1972), and Powell and Powell (1977).

This paper presents experimental data on the subsolidus phase relations of the $Na_3K(AlSiO_4)_4$–$K_4(AlSiO_4)_4$ system at 0.5, 2.0, and 5.0 kbar. X-ray diffraction data and refined unit-cell parameters are listed for nephelines and kalsilites synthesized in the one-phase regions of the system at 0.5 kbar. Two-phase data delimiting the nepheline–kalsilite solvus at 0.5, 2.0, and 5.0 kbar are also listed, and these data have been used to derive Margules, van Laar, and quasichemical mixing-parameter equations for the crystalline solutions. Nepheline–kalsilite solvi and activity–composition relations for the crystalline solutions calculated from the mixing-parameter equations are discussed in detail.

Crystallographic considerations

Considerable crystallographic evidence indicates that $Na_3K(AlSiO_4)_4$ is not simply a composition in

Table 1. One-phase experimental data and unit-cell parameters for $(Na,K)_3K(AlSiO_4)_4$ crystalline solutions synthesized at 0.5 kbar

T^* (°C)	t (hrs)	Wt. % H_2O	X_2^{**}	$a^{\dagger}$ (Å)	c (Å)	V (Å³)	$d_{10.2}^{\dagger\dagger}$ (Å)	$d_{20.1}$ (Å)
797	141	5.5	0.031	10.0114(13)	8.3932(15)	728.53(20)	–	3.854
800	162	4.6	0.031	10.0122(10)	8.3933(12)	728.66(15)	–	3.852
900	23	–	0.100	10.0321(12)	8.4048(14)	732.57(19)	–	3.859
797	141	5.0	0.152	10.0564(12)	8.4176(13)	737.24(18)	–	3.869
904	24	3.8	0.229	10.0719(13)	8.4280(15)	740.42(20)	–	3.877
897	115	5.1	0.229	10.0760(11)	8.4294(12)	741.14(17)	–	3.874
1004	92	4.5	0.568	5.1167(19)	8.5265(46)	193.32(16)	3.074	–
904	24	3.3	0.708	5.1334(1)	8.6056(4)	196.39(1)	3.089	–
900	26	3.4	0.780	5.1391(6)	8.6155(16)	197.05(5)	3.095	–
800	169	5.0	0.853	5.1500(4)	8.6507(11)	198.70(3)	3.103	–
807	141	5.0	0.927	5.1547(6)	8.6815(15)	199.77(5)	3.112	–
700	432	5.0	1.000	5.1597(3)	8.7024(9)	200.64(3)	3.115	–
800	162	5.0	1.000	5.1608(5)	8.7019(12)	200.72(4)	3.118	–

* Temperatures listed in this table are believed to be accurate within ± 15°C (see text).

** X_2 = mole fraction of component 2, $K_4(AlSiO_4)_4$.

† Numbers in parentheses to the right of each unit-cell parameter value are 2σ (two estimated standard deviations) values at the unit-weight level which refer to the last decimal place quoted. For example, 10.0114(13)Å indicates a 2σ of 0.0013Å, and 728.53(20)Å³ indicates a 2σ of 0.20Å³.

†† Measurement errors are estimated to be ± 0.002Å for $d_{10.2}$ values and ± 0.003Å for $d_{20.1}$ values.

the binary system $NaAlSiO_4$–$KAlSiO_4$, but rather a distinct compound. The system $NaAlSiO_4$–$KAlSiO_4$ is analogous to several other binary systems such as $CaCO_3$–$MgCO_3$, $CaSiO_3$–$MgSiO_3$, and Ca_2SiO_4–Mg_2SiO_4 which: (1) contain an ordered intermediate compound [$CaMg(CO_3)_2$, $CaMgSi_2O_6$, and $CaMgSiO_4$], and (2) exhibit a solvus in at least one of the subsystems [e.g., $CaCO_3$–$CaMg(CO_3)_2$, $CaMgSi_2O_6$–$MgSiO_3$, and $CaMgSiO_4$–Mg_2SiO_4]. Accordingly, depending upon Na/K ratio, $(Na,K)AlSiO_4$ nephelines belong to one of two separate crystalline solution series: $NaAlSiO_4$–$Na_3K(AlSiO_4)_4$ and $Na_3K(AlSiO_4)_4$–$KAlSiO_4$.

The crystal structures of $(Na,K)AlSiO_4$ nepheline and $(K,Na)AlSiO_4$ kalsilite differ slightly (Buerger et al., 1954; Perrotta and Smith, 1965). They belong to the same hexagonal space group ($P6_3$), but they have significantly different a dimensions and unit-cell volumes (Tables 1 and 2, Figs. 1 and 2). Each structure is a "stuffed derivative" of the tridymite structure (Buerger, 1954); one Al atom substitutes for every other tetrahedrally-coordinated Si atom in a distorted tridymite-type framework, and cavities within the framework are occupied by Na and K atoms to preserve charge balance. The unit cell of nepheline, which contains 32 oxygen atoms, has two different types of alkali sites; two of the eight alkali sites have nine-fold oxygen coordination and are larger than the remaining six which have eight-fold oxygen coordination. Crystal structure refinements of nepheline (Buerger et al., 1954; Hahn and Buerger, 1955; Dollase, 1970) indicate a high degree of ordering of Na and K atoms between the two different types of sites; that is, K atoms are located preferentially in the larger sites and Na atoms in the smaller. $Na_3K(AlSiO_4)_4$ is a distinct ordered intermediate compound on the $NaAlSiO_4$–$KAlSiO_4$ join because at this composition, evidently, all small alkali sites are filled with Na atoms only and all large alkali sites are filled with K atoms only. For compositions more K-rich than $Na_3K(AlSiO_4)_4$, the larger alkali sites are completely or nearly completely filled with K atoms. We assume, therefore, that Na–K substitution in $(Na,K)_3K(AlSiO_4)_4$ crystalline solutions occurs only in the smaller of the two types of alkali sites in these feldspathoids. There are three of these sites in the standard formulae for the end-member components that we have selected, $Na_3K(AlSiO_4)_4$ and $K_3K(AlSiO_4)_4$, so we have set $\alpha = 3$ (Thompson, 1967, p. 342) in calculations of mixing-parameter values listed in Table 2. This α term represents the number of sites (per formula unit of designated components) on which atomic substitution occurs.
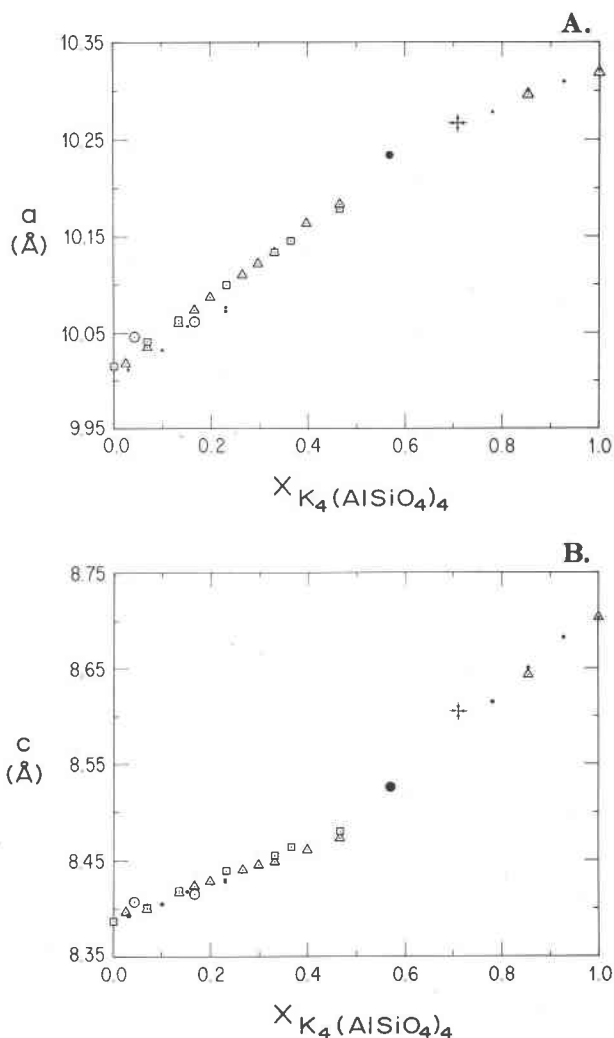

Fig. 1. Unit-cell dimensions (A) a (Fig. 1A) and c (Fig. 1B) for synthetic $(Na,K)_3K(AlSiO_4)_4$ nephelines and kalsilites plotted against mole fraction $K_4(AlSiO_4)_4$ (X_2) in the feldspathoids (the a unit-cell data for kalsilites in Fig. 1A have been multiplied by two). Open circles (Miyashiro and Miyashiro, 1954, Table 2), triangles (Smith and Tuttle, 1957, Tables 2 and 12), and squares (Donnay et al., 1959, Table IV) represent data for $(Na,K)_3K(AlSiO_4)_4$ nephelines and kalsilites synthesized at one atm in previous investigations. Filled circles depict our data for $(Na,K)_3K(AlSiO_4)_4$ nephelines and kalsilites synthesized at 0.5 kbar, and the radius of each circle indicates the 2σ value (A) for the data point (see Table 1). Opposed arrows point to data for the kalsilite synthesized at 0.5 kbar and 904°C in this study.

Experimental methods

Starting materials

$NaAlSiO_4$ and $KAlSiO_4$ gels, prepared by Dr. D. A. Mustart following the method of Luth and Ingamells (1965), were fired at 600°C and one atm for two hours and ground to an average particle size of less than 10 μm. Solid starting materials for nepheline

Table 2. Two-phase experimental data and calculated mixing parameters for $(Na,K)_3K(AlSiO_4)_4$ crystalline solutions synthesized at 0.5, 2.0, and 5.0 kbar

T^* (°C)	t (hrs)	Wt. % H_2O	S. M.**	$V_A^\dagger$ (Å³)	V_B (Å³)	$d_{20.1}^{\dagger\dagger}$ (Å)	$d_{10.2}$ (Å)	$X_{2A}^@$	X_{2B}	$W_{G1}^{@@}$	W_{G2}	A_1	A_2	W_G	q_1
												(cal/gfw)			
a) 0.5 Kilobars															
399	480	4.9	XM	728.58(41)	200.70(13)	–	–	0.031	0.989	18443.8	14538.6	18466.2	14589.0	20626.3	1.0609
501	522	3.1	XM	731.72(28)	200.67(21)	–	–	0.081	0.987	20422.0	12363.2	20548.5	12852.8	21843.5	1.1193
600	190	4.7	GL	733.08(47)	199.49(13)	–	–	0.102	0.917	15063.8	14119.3	15073.2	14130.4	21954.9	1.0133
600	190	4.9	GL	734.12(52)	199.62(23)	–	–	0.119	0.925	15502.1	13371.8	15546.6	13435.8	21851.9	1.0303
601	480	5.0	XM	734.84(45)	199.88(16)	–	–	0.130	0.940	16400.6	12771.0	16506.6	12963.3	21967.6	1.0516
694	261	5.0	XM	735.51(36)	198.57(9)	–	–	0.141	0.863	14636.6	14490.4	14636.9	14490.7	23256.9	1.0020
702	141	5.0	GL	735.89(26)	199.20(51)	–	–	0.147	0.900	16121.8	14137.7	16169.0	14201.9	23745.5	1.0262
797	163	4.9	GL	740.46(55)	197.85(6)	–	–	0.219	0.820	15299.0	14162.8	15324.6	14193.0	24838.2	1.0146
805	165	4.3	HX	740.88(38)	197.24(34)	–	–	0.226	0.784	14644.6	14377.6	14646.3	14379.3	24809.3	1.0034
805	165	3.9	XM	738.84(24)	197.64(12)	–	–	0.194	0.808	15006.6	14946.6	15006.7	14946.7	25108.1	1.0008
897	113	5.1	XM	744.75(30)	195.01(18)	–	–	0.288	0.652	13902.0	15237.3	13959.6	15285.1	26170.4	1.0192
950	74	4.2	GL	747.66(27)	193.41(16)	–	–	0.334	0.557	13493.4	15806.5	13688.7	15950.7	27027.3	0.9726
1004	74	4.5	GL	–	193.01(27)	3.895	–	0.387	0.533	14392.9	16082.2	14493.3	16163.0	28168.8	0.9806
1004	74	3.2	XM	750.53(59)	193.40(21)	–	–	0.379	0.556	14632.5	16016.0	14697.9	16070.7	28217.7	0.9841
b) 2.0 Kilobars															
400	522	3.8	HX	731.61(45)	–	–	3.113	0.079	0.955	13532.9	11508.1	13562.3	11553.5	17789.6	1.0353
400	522	3.8	XM	728.35(58)	200.83(10)	–	–	0.027	0.997	23399.4	14836.0	23429.0	15002.8	22657.7	1.1302
498	522	3.9	HX	732.62(56)	–	–	3.114	0.095	0.965	16437.0	12247.4	16526.7	12439.3	20375.5	1.0644
498	522	5.2	XM	731.81(49)	200.26(13)	–	–	0.082	0.963	16238.6	12926.8	16295.9	13032.2	20542.6	1.0503
598	522	3.8	GL	732.79(52)	199.72(12)	–	–	0.098	0.931	15767.3	14155.5	15790.1	14185.5	22176.2	1.0225
598	522	3.9	HX	734.10(38)	–	–	3.110	0.119	0.925	15466.6	13341.2	15511.0	13405.0	21801.8	1.0303
598	522	4.9	XM	734.58(42)	199.69(14)	–	–	0.126	0.929	15687.2	13032.9	15753.6	13136.8	21773.3	1.0380
701	329	4.2	HX	735.80(29)	199.05(14)	–	–	0.146	0.891	15740.4	14241.0	15769.7	14278.0	23638.6	1.0198
701	329	4.9	XM	735.27(32)	199.05(10)	–	–	0.137	0.891	15715.2	14545.4	15732.8	14566.6	23729.8	1.0154
801	168	4.3	HX	739.51(36)	198.05(26)	–	–	0.204	0.832	15598.2	14478.3	15621.3	14505.5	25093.1	1.0142
801	168	4.8	XM	738.66(20)	197.79(11)	–	–	0.191	0.817	15156.3	14910.1	15157.5	14911.4	25087.4	1.0031
901	44	3.1	GL	743.26(68)	194.21(14)	–	–	0.264	0.604	12818.3	15800.9	13135.1	16014.5	26115.2	0.9641
901	44	3.2	XM	744.60(84)	194.85(18)	–	–	0.285	0.642	13752.6	15378.6	13839.7	15448.2	26244.5	0.9801
953	70	3.7	GL	747.39(34)	193.77(16)	–	–	0.329	0.578	13802.8	15798.8	13943.3	15906.7	27157.3	0.9764
953	70	3.2	GL	744.91(246)	193.61(23)	–	–	0.290	0.569	13111.1	16284.3	13474.9	16527.9	27124.1	0.9631
953	70	3.3	XM	744.94(26)	–	–	3.076	0.291	0.585	13422.9	16216.7	13697.7	16408.7	27187.6	0.9674
998	66	3.2	GL	748.66(29)	192.38(34)	–	–	0.350	0.496	13196.6	16553.8	13623.1	16837.0	27903.6	0.9620
998	66	3.7	GL	749.27(48)	192.42(10)	–	–	0.359	0.498	13378.6	16466.4	13737.2	16711.4	27922.9	0.9649
998	66	4.9	XM	748.86(46)	191.74(41)	–	–	0.353	0.458	12521.0	16690.1	13203.0	17107.7	27774.9	0.9532
c) 5.0 Kilobars															
400	478	4.4	GL	–	200.02(35)	3.855	–	0.052	0.949	13069.0	12999.3	13069.1	12999.4	18148.5	1.0012
400	478	3.9	XM	–	200.44(20)	3.855	–	0.052	0.973	15244.7	12844.7	15267.5	12882.8	18856.7	1.0397
501	478	3.8	GL	–	199.73(19)	3.853	–	0.035	0.931	13682.9	16516.6	13747.2	16554.7	20943.6	0.9596
501	478	3.6	HX	731.12(37)	199.57(4)	–	–	0.071	0.922	13474.7	13858.0	13476.3	13859.4	19959.0	0.9941
501	478	3.8	XM	731.51(61)	200.21(17)	–	–	0.078	0.960	16007.2	13230.4	16050.0	13301.9	20609.5	1.0419
599	526	5.3	HX	733.63(39)	199.82(25)	–	–	0.111	0.937	16168.0	13544.4	16224.5	13632.1	22119.1	1.0369
599	526	4.0	XM	732.09(31)	199.76(8)	–	–	0.087	0.933	15882.1	14681.1	15894.1	14695.8	22407.1	1.0165
701	333	3.3	GL	735.01(36)	198.96(15)	–	–	0.133	0.886	15508.3	14720.8	15516.6	14730.2	23718.9	1.0103
701	333	3.3	HX	735.19(23)	198.47(4)	–	–	0.136	0.857	14527.0	14783.9	14528.1	14785.0	23416.5	0.9966
701	333	4.2	XM	734.98(9)	198.97(12)	–	–	0.133	0.886	15508.3	14720.8	15516.6	14730.2	23718.9	1.0103
798	165	5.6	GL	737.47(33)	198.08(4)	–	–	0.172	0.834	15464.8	15252.9	15465.5	15263.7	25258.4	1.0025
798	165	3.4	GL	737.00(21)	198.02(8)	–	–	0.165	0.830	15312.8	15482.4	15313.3	15482.9	25280.3	0.9979
798	165	3.4	XM	737.64(275)	198.10(6)	–	–	0.175	0.835	15508.4	15173.7	15510.4	15175.8	25243.7	1.0042
894	69	3.4	GL	739.38(103)	196.97(20)	–	–	0.202	0.768	15321.5	16205.0	15339.3	16220.8	26893.8	0.9896
894	69	3.4	GL	737.57(55)	196.54(22)	–	–	0.174	0.742	14416.3	16963.7	14576.5	17078.0	26862.0	0.9705
894	69	4.5	XM	739.50(46)	197.08(10)	–	–	0.204	0.774	15476.6	16128.6	15486.1	16137.2	26918.1	0.9923
951	68	5.7	XM	742.77(90)	196.08(8)	–	–	0.256	0.715	15386.2	16136.4	15401.0	16149.8	27715.1	0.9913
999	69	–	GL	–	–	3.887	3.081	0.320	0.635	15152.2	16188.6	15185.0	16217.3	28318.5	0.9822

[*] Temperatures listed in this table are believed to be accurate within ± 10–15°C (see text).

[**] Starting materials: GL = mechanical mixtures of $NaAlSiO_4$ and $KAlSiO_4$ gels with bulk compositions in the range $0.15 \leq X_2 \leq 0.64$, HX = synthetic $(Na,K)_3K(AlSiO_4)_4$ nepheline crystals with a composition $X_2 = 0.15$ or $X_2 = 0.30$, XM = mechanical mixtures of synthetic $NaAlSiO_4$ and $KAlSiO_4$ crystals with a bulk composition $X_2 = 0.43$.

[†] See footnote in Table 1 for explanation of numbers in parentheses. Unit-cell volume subscript notation: A = Na-rich nepheline phase, B = K-rich kalsilite phase.

[††] A $d_{20.1}$ value is listed for the Na-rich nepheline phase of a solvus-pair when this value and equation (1) were used to obtain an X_{2A} value. Similarly, a $d_{10.2}$ value is listed for the K-rich kalsilite phase of a solvus-pair when this value and equation (3) were used to obtain an X_{2B} value. Measurement errors are estimated to be ± 0.002Å for $d_{10.2}$ values and ± 0.003Å for $d_{20.1}$ values.

[@] Mole fraction subscript notation: 2 = component $K_4(AlSiO_4)_4$, A = Na-rich nepheline phase, B = K-rich kalsilite phase.

[@@] Mixing-parameter values for a solvus-pair were calculated from the compositions (X_{2A} and X_{2B}) of the coexisting phases (see Blencoe, 1977). W_{G1} and W_{G2} are Margules mixing parameters, A_1 and A_2 are van Laar mixing parameters, and W_G and q_1 are quasichemical mixing parameters.

and kalsilite one-phase experiments were mechanical mixtures of the gels with bulk compositions listed in Table 1. Solid starting materials for two-phase (solvus) experiments (Table 2) were of three types: (1) mechanical mixtures of the $NaAlSiO_4$ and $KAlSiO_4$ gels with bulk compositions in the range $0.15 \leq X_2 \leq 0.64$;[2] (2) $(Na,K)_3K(AlSiO_4)_4$ nepheline crystals with a composition $X_2 = 0.15$ or $X_2 = 0.30$ synthesized hydrothermally from mechanical mixtures of the gels at 0.5 kbar, 700–1000°C for 24–432 hours; and (3) mechanical mixtures of $NaAlSiO_4$ and $KAlSiO_4$ crystals with a bulk composition $X_2 = 0.43$ (the $NaAlSiO_4$ and $KAlSiO_4$ crystals in these mixtures were synthesized hydrothermally from the gels at 0.5 kbar, 900°C for 24 hours).

Experimental procedure and apparatus

Solid starting materials were dried at 120°C under vacuum for a minimum of 12 hours before being loaded into 2 mm (O.D.) gold or platinum capsules containing weighed amounts (generally 3–6 weight percent) of freshly boiled, distilled and deionized water. After loading, the capsules were sealed using a DC arc welder and reweighed to confirm that water was not lost during welding.

All experiments were performed in either externally-heated cold-seal pressure vessels (Tuttle, 1949; Luth and Tuttle, 1963) or an internally-heated pressure vessel (modified after the design of Yoder, 1950).

Externally-heated low pressure cold-seal pressure vessels (Tuttle, 1949) were used in experiments at 0.5 kbar, $T \leq 900°C$, and at 2.0 kbar, $T \leq 800°C$. The vessels were oriented vertically with the closure-nut assembly up (orientation 1 of Boettcher and Kerrick, 1971, Fig. 2). Temperature in each experiment was maintained within a ± 2–4°C cycle by a Honeywell-Brown Pyr-o-vane controller and measured using a bare-wire chromel–alumel thermocouple. However, filler rods were not used in the pressure vessels, so reported temperatures (Tables 1 and 2) may be accurate only to within $\pm 15°C$. Pressure was generated using a Sprague pump, with water as the pressure medium. Reported pressures, which are believed to be accurate within ± 75 bar, were measured using Bourdon-tube gauges calibrated against a 2.0 kbar Heise gauge.

Externally-heated high pressure cold-seal pressure vessels (Luth and Tuttle, 1963) were used in experi-
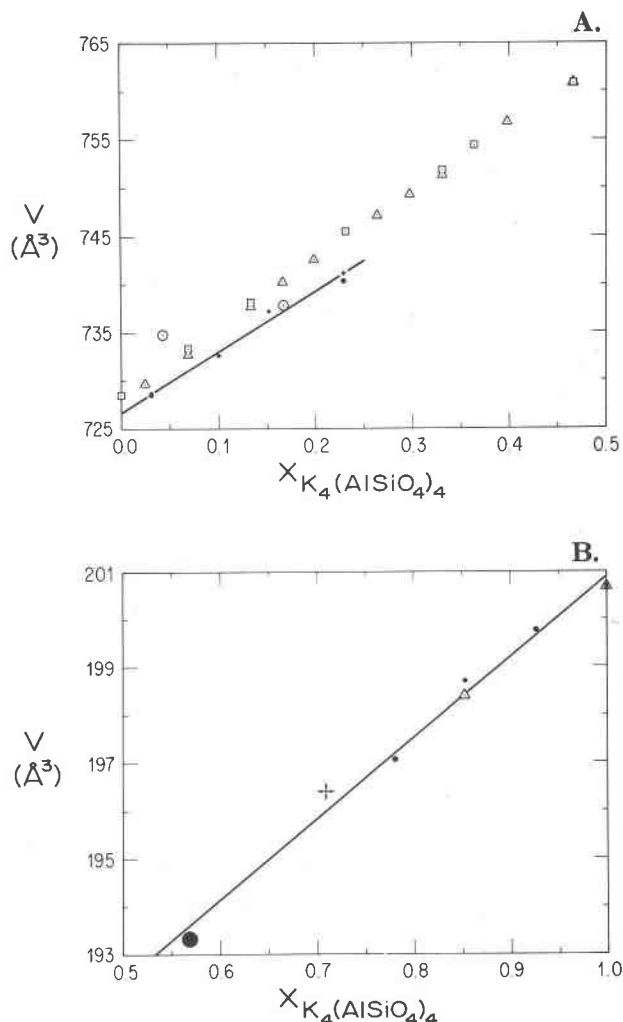

Fig. 2. Unit-cell volumes ($Å^3$) for synthetic $(Na,K)_3K(AlSiO_4)_4$ nephelines (Fig. 2A) and kalsilites (Fig. 2B) plotted against mole fraction $K_4(AlSiO_4)_4$ (X_2) in the feldspathoids. Open circles (Miyashiro and Miyashiro, 1954, Table 2), triangles (Smith and Tuttle, 1957), and squares (Donnay et al., 1959, Table IV) represent data for $(Na,K)_3K(AlSiO_4)_4$ nephelines and kalsilites synthesized at one atm in previous investigations. [Unit-cell volumes for synthetic nephelines described by Smith and Tuttle (1957, Table 2) are given by Donnay et al. (1959, Table IV), and unit-cell volumes for synthetic kalsilites described by Smith and Tuttle (1957, Table 12) were calculated from the relation $V = a^2c(\sin 60°)$.] Filled circles depict our data for $(Na,K)_3K(AlSiO_4)_4$ nephelines and kalsilites synthesized at 0.5 kbar, and the radius of each circle indicates the 2σ value ($Å^3$) for the data point (see Table 1). Opposed arrows point to the unit-cell volume value for the kalsilite synthesized at 0.5 kbar and 904°C. The solid straight lines illustrate the relationship between V and X_2 according to: (A) equation (2), and (B) equation (4) in the text.

ments at 5.0 kbar, $T \leq 700°C$. The vessels were oriented vertically with the closure-nut assembly down (orientation 2 of Boettcher and Kerrick, 1971, Fig. 2). Temperature in each experiment was main-

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[2] X_2 = mole fraction of component 2, $K_4(AlSiO_4)_4$, in binary $Na_3K(AlSiO_4)_4$–$K_4(AlSiO_4)_4$ gels and crystalline phases.

tained within a ±2–4°C cycle by a Honeywell-Brown electronic controller and measured using a sheathed chromel–alumel thermocouple. Filler rods were used in the pressure vessels, and reported temperatures (Tables 1 and 2) are believed to be accurate within ±10°C. Pressure was generated using a two-stage Harwood intensifier, with argon as the pressure medium. Reported pressures, which are believed to be accurate within ±150 bars, were measured using manganin cells and a modified Carey-Foster bridge.

The internally-heated pressure vessel was used in experiments at 0.5 kbar, $T > 900°C$, at 2.0 kbar, $T > 800°C$, and at 5.0 kbar, $T > 700°C$. Temperature in each experiment was maintained within a ±5°C cycle by a Honeywell-Brown electronic controller and measured using a sheathed Pt/Pt-10%Rh thermocouple calibrated against the melting points of NaCl (800.4±0.5°C at one atm according to Roberts, 1924) and gold (1062.5±0.5°C at one atm according to Akella and Kennedy, 1971). Reported temperatures (Tables 1 and 2) are believed to be accurate within ±10°C. Pressure was generated and measured as described for the externally-heated high pressure cold-seal pressure vessels, and reported pressures are believed to be accurate within ±3 percent.

Experiment durations (Tables 1 and 2) were 23–526 hours. In view of the data of Tuttle and Smith (1958) and Yund *et al.* (1972) which indicate very rapid rates of kalsilite exsolution from nepheline in hydrothermal experiments, durations of our hydrothermal exsolution experiments were probably far longer than required to achieve equilibrium. Moreover, since very similar results were obtained in two-phase (solvus) experiments at a given P and T (Table 2) using the three different types of starting materials described previously, we believe that durations of all experiments were sufficient to achieve equilibrium.

Examination of experimental products

After the conclusion of an experiment each capsule was weighed to check for leakage, and leaked capsules were discarded.

Experimental samples were examined by X-ray powder diffractometry using a Norelco high-angle diffractometer and CuKα radiation. Values of 2θ, recorded by a strip chart recorder and measured against a spinel internal standard (U.S. Bureau of Mines, Norris, Tennessee; $a = 8.0833A$ at 25°C), are believed to be accurate generally within ±0.02° 2θ.

Experimental results

One-phase data

Experimental data and unit-cell parameters for $(Na,K)_3K(AlSiO_4)_4$ nephelines and kalsilites synthe-

sized in the one-phase regions of the $Na_3K(AlSiO_4)_4$–$K_4(AlSiO_4)_4$ system at 0.5 kbar are given in Table 1. X-ray diffraction data indicate the presence of only a single, homogeneous $(Na,K)_3K(AlSiO_4)_4$ crystalline phase in each of the experimental samples described in this table, and for each sample we have assumed that this phase possesses an Na/K ratio identical to that of the mixture of $NaAlSiO_4$ and $KAlSiO_4$ gels from which it was synthesized. This assumption ignores the possibility of incongruent solution of alkalis in the coexisting H_2O-rich fluid phase.

Unit-cell dimensions of the crystalline phases were determined from X-ray data using the least-squares unit-cell refinement routine of Burnham (1962). Nephelines in the composition range $0.031 \leq X_2 \leq 0.229$ were refined using 15 reflections and initial estimates of $a = 9.98A$ and $c = 8.32A$, the unit-cell dimensions of $NaAlSiO_4$ nepheline (Smith and Tuttle, 1957, Table 2). Kalsilites in the composition range $0.568 \leq X_2 \leq 1.000$ were refined using 4–14 (an average of 11) reflections and initial estimates of $a = 5.16A$ and $c = 8.70A$, the unit-cell dimensions of $KAlSiO_4$ kalsilite (Smith and Tuttle, 1957, Table 5). In addition, $d_{20.1}$ spacings for the nephelines and $d_{10.2}$ spacings for the kalsilites were measured and are listed in Table 1.

Because a nepheline–kalsilite two-phase region exists in the $Na_3K(AlSiO_4)_4$–$K_4(AlSiO_4)_4$ system at the highest temperature achieved ($\approx 1000°C$ at 0.5, 2.0, and 5.0 kbar), a complete series of $(Na,K)_3K(AlSiO_4)_4$ crystalline phases could not be synthesized. However, $d_{20.1}$ spacings and unit-cell parameters of the $(Na,K)_3K(AlSiO_4)_4$ nephelines show an approximately linear variation with composition in the range $0.031 \leq X_2 \leq 0.229$ (Table 1, Figures 1 and 2A), and the $d_{20.1}$ and unit-cell volume (V) data were used to calculate the following least-squares fit equations for determining compositions of $(Na,K)_3K(AlSiO_4)_4$ nephelines:

$$X_2 = -32.2516 + 8.37963 d_{20.1}(A) \qquad (1)$$
$$(2.6468) \quad (0.68495)$$

$$(esd = 0.0162, fev = 0.974)$$

and

$$X_2 = -11.5242 + 0.01586 V(A^3) \qquad (2)$$
$$(0.5867) \quad (0.00080)$$

$$(esd = 0.0101, fev = 0.990)$$

[esd is the estimated standard deviation of the dependent variable (Deming, 1943), fev is "fraction of explained variance" (Draper and Smith, 1966, p. 26), and numbers in parentheses are coefficient esd's.] Furthermore, $d_{10.2}$ spacings and unit-cell parameters

of the synthetic kalsilites show an approximately linear variation with composition in the range $0.568 \leq X_2 \leq 1.000$ (Table 1, Figures 1 and 2B), and the $d_{10.2}$ and V data were used to calculate the following least-squares fit determinative equations for $(Na,K)_3 K(AlSiO_4)_4$ kalsilites:

$$X_2 = -30.2487 + 10.02380 d_{10.2}(A) \qquad (3)$$
$$(1.1585) \qquad (0.37360)$$

$$(esd = 0.0146, fev = 0.993)$$

and

$$X_2 = -10.8986 + 0.05923 V(A^3) \qquad (4)$$
$$(0.5443) \qquad (0.00275)$$

$$(esd = 0.0181, fev = 0.989)$$

Two-phase data

$T–X$ limits of the nepheline–kalsilite solvus in the $Na_3K(AlSiO_4)_4–K_4(AlSiO_4)_4$ system have been determined at ~100° intervals from 400 to 1000°C at 0.5, 2.0, and 5.0 kbar. Unit-cell dimensions of nephelines in two-phase (solvus-pair) nepheline–kalsilite assemblages were refined using 4–17 (an average of 11) reflections, and unit-cell dimensions of kalsilites in these assemblages were refined using 4–13 (an average of 8) reflections. Compositions of the crystalline solutions were determined from their unit-cell volumes using equations (2) and (4) [or, when X-ray diffraction patterns were of poor quality, from $d_{20.1}$ and $d_{10.2}$ data using equations (1) and (3)]. Results are presented in Table 2 and Figures 3–5.[3] The solvus data obtained from the three types of solid starting materials described previously are very similar, and this suggests that equilibrium was closely approached in all experiments. However, equilibrium at a given P and T has been demonstrated rigorously only where essentially identical results were obtained using the two types of crystalline starting materials.

Thermodynamic applications of the two-phase data

Thermodynamic mixing-parameter equations for $(Na,K)_3K(AlSiO_4)_4$ crystalline solutions

Previous investigators (*e.g.*, Thompson, 1967; Green, 1970; Powell, 1974; Blencoe, 1976b and 1977) have shown that two-parameter thermodynamic formulations based upon solvus experimental data can
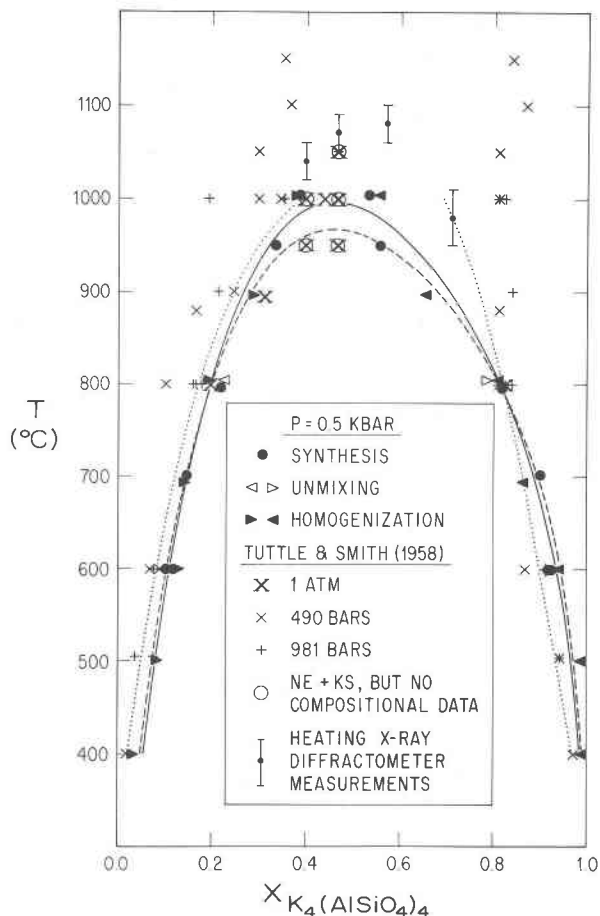
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[3] In this paper nepheline–kalsilite solvus data are usually presented as X_{2A} and X_{2B} values where the subscript 2 designates component 2, $K_4(AlSiO_4)_4$, and the subscripts A and B denote the nepheline and kalsilite, respectively, in each nepheline–kalsilite solvus-pair.

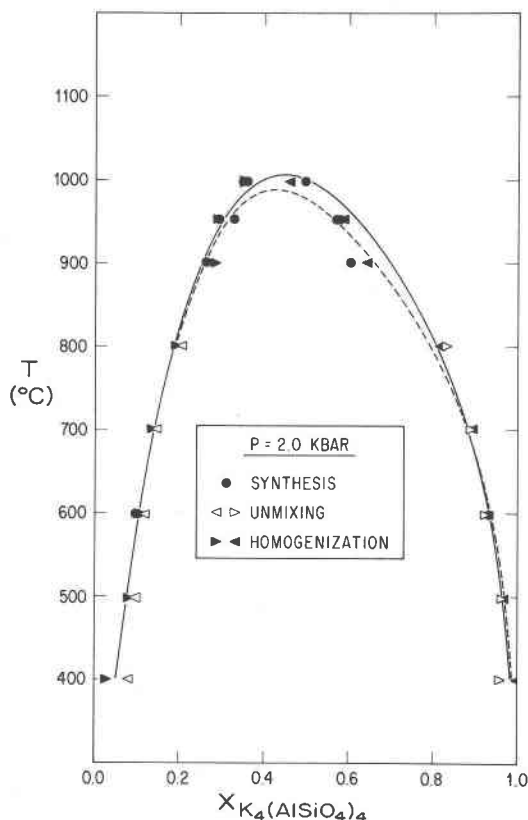Fig. 3. Solvus data and solvi for the $Na_3K(AlSiO_4)_4–K_4(AlSiO_4)_4$ system from one atm to 981 bars. The three starting materials used in our solvus experiments were (see text and Table 2): (1) mechanical mixtures of $NaAlSiO_4$ and $KAlSiO_4$ gels (synthesis experiments), (2) synthetic $(Na,K)_3K(AlSiO_4)_4$ nepheline crystals (unmixing experiments), and (3) mechanical mixtures of synthetic $NaAlSiO_4$ and $KAlSiO_4$ crystals (homogenization experiments). The dashed-line solvus was calculated using the isobaric Margules equations (5)–(6), and the solid-line solvus was obtained using the polybaric Margules equations (23)–(24). However, owing to the different crystal structures of $P6_3$ nepheline ($a \approx 10A$) and $P6_3$ kalsilite ($a \approx 5A$), the critical points of the calculated solvi in this figure and Figs. 4–7 are unstable (see Discussion). Solvus data of Tuttle and Smith (1958, Table 1) were obtained from dry-quenching experiments at one atm and hydrothermal experiments at 490 and 981 bars. As discussed in the text, it is likely that solvus-pairs crystallized by Tuttle and Smith in hydrothermal experiments above 800°C either formed or partially reequilibrated during quenching. This is probably also true for two nepheline + kalsilite samples that they crystallized in dry-quenching experiments at 1200° and another crystallized at 1400°C, so data from these samples are not illustrated in this figure. Recognizing these difficulties with quench reactions, Tuttle and Smith used data obtained from: (1) dry-quenching experiments at temperatures below 1100°C, and (2) high-temperature X-ray diffraction studies to determine the one atm $T–X$ limits of the nepheline–kalsilite solvus (dotted-line solvus in this figure). Inferred phase relations at the high-temperature (≈ 1050°C) termination of this solvus (Tuttle and Smith, 1958, Figure 2) are not illustrated.

Fig. 4. Solvus data (see Table 2) and calculated solvi for the Na$_3$K(AlSiO$_4$)$_4$–K$_4$(AlSiO$_4$)$_4$ system at 2.0 kbar. The dashed-line solvus was calculated from the isobaric Margules equations (11)–(12), and the solid-line solvus was obtained from the polybaric Margules equations (23)–(24).

be used to derive equations of state for nonideal, isostructural binary crystalline solutions. Such equations of state, which can be used to estimate activities and excess properties for binary crystalline solutions, have been employed in phase-equilibrium calculations (e.g., Waldbaum and Thompson, 1969) and geothermometry (e.g., Saxena, 1973; Stormer, 1975; Blencoe and Ferry, 1977).

As noted previously, the crystal structures of (Na,K)AlSiO$_4$ nepheline and (K,Na)AlSiO$_4$ kalsilite differ slightly. Na-rich crystalline solutions on the Na$_3$K(AlSiO$_4$)$_4$ side of the nepheline–kalsilite solvus are $P6_3$ nephelines with $a \approx 10$A, while K-rich crystalline solutions on the K$_4$(AlSiO$_4$)$_4$ side of the solvus are $P6_3$ kalsilites with $a \approx 5$A. Therefore, in deriving equations of state for (Na,K)$_3$K(AlSiO$_4$)$_4$ crystalline solutions, it is technically incorrect to treat nepheline–kalsilite solvus-pairs as phases of a single isostructural crystalline solution series, and this means that "activity-equivalence conditions" (Blencoe, 1977) do not prevail for nepheline–kalsilite solvus-

pairs [Warner and Luth (1974) have described an analogous situation in the CaMgSi$_2$O$_6$–Mg$_2$Si$_2$O$_6$ system]. This is unfortunate, because additional information is required for a rigorous thermodynamic treatment under these circumstances; that is, it is necessary to know the standard-state free energies of the components in the two structures (μ_{1A}^0, μ_{1B}^0, μ_{2A}^0 and μ_{2B}^0) as a function of P and T, and these data are not available. However, since the two structures are very similar, it is probably a good approximation to simply ignore the structural difference and assume activity-equivalence conditions (that is, $\mu_{1A}^0 = \mu_{1B}^0$ and $\mu_{2A}^0 = \mu_{2B}^0$) for nepheline–kalsilite solvus-pairs, and we have adopted this approach in our thermodynamic calculations. This assumption is inconsequential in deriving equations of state for (Na,K)$_3$ K(AlSiO$_4$)$_4$ crystalline solutions that are suitable for calculating nepheline–kalsilite solvi, but there will be some minor effects on calculated activity–composition relations and calculated excess properties for the crystalline solutions.
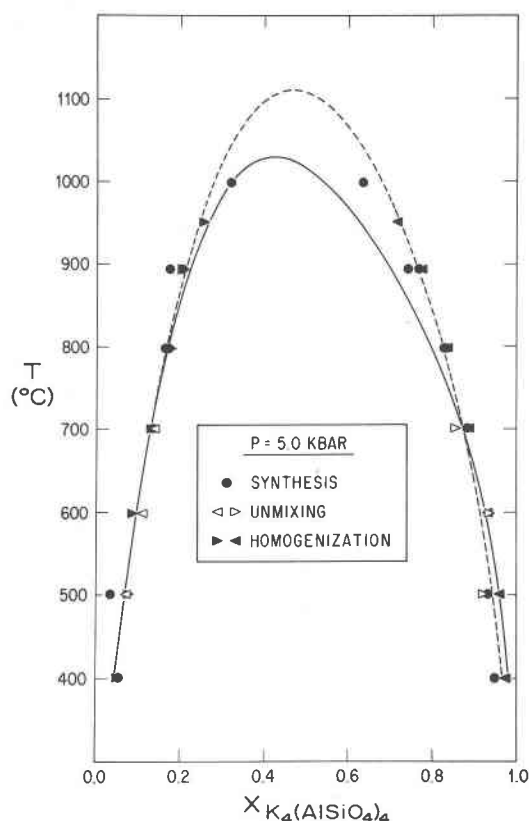

Fig. 5. Solvus data (see Table 2) and calculated solvi for the Na$_3$K(AlSiO$_4$)$_4$–K$_4$(AlSiO$_4$)$_4$ system at 5.0 kbar. The dashed-line solvus was calculated from the isobaric Margules equations (17)–(18), and the solid-line solvus was obtained from the polybaric Margules equations (23)–(24).

Therefore, to obtain thermodynamic equations of state for $(Na,K)_3K(AlSiO_4)_4$ crystalline solutions, we have: (1) assumed activity-equivalence conditions for the $Na_3K(AlSiO_4)_4$ and $K_4(AlSiO_4)_4$ components in nepheline–kalsilite solvus-pairs; and (2) used the compositions of the two phases in nepheline–kalsilite solvus-pairs synthesized in this study to calculate Margules, van Laar, and quasichemical mixing parameters (Table 2) and mixing-parameter equations (Table 3). [Some of the computer methods employed in these calculations and the thermodynamic bases of the two-parameter Margules, van Laar, and quasichemical solution models have been described by Blencoe (1975, 1976a, 1977).] The Margules parameters W_{G1} and W_{G2}, the van Laar parameters A_1 and A_2, and the quasichemical parameters W_G and q_1 calculated from the solvus data were fitted by least-squares methods at 0.5, 2.0, and 5.0 kbar as a linear function of T, and the resulting isobaric equations [equations (5)–(22)] are listed in Table 3, section a.[4] In addition, Margules, van Laar, and quasichemical mixing parameters calculated from all of the solvus data were fitted as a linear function of P and T, and the resulting polybaric equations [equations (23)–(28)] are listed in Table 3, section b.[5]

Calculated nepheline–kalsilite solvi

Nepheline–kalsilite solvi at 0.5, 2.0, and 5.0 kbar have been calculated using both the isobaric mixing-

[4] As noted previously, we assume that Na–K substitution in $(Na,K)_3K(AlSiO_4)_4$ crystalline solutions occurs only on the smaller of the two types of cation intraframework sites, and these sites have eight-fold oxygen coordination. Hence, the "Z" parameter in the quasichemical formulation (Green, 1970; Blencoe, 1977) was assigned the value 8.0 in calculations of values for the quasichemical mixing parameters W_G and q_1 listed in Table 2. For NaCl–KCl crystalline solutions, Green demonstrated that q_1 ($= 1/q_2$) values are essentially independent of temperature at one atm, and he assigned a constant value to this parameter in his thermodynamic and phase-equilibrium calculations. However, the solvus data of the present study (Table 2) indicate that q_1 values for $(Na,K)_3K(AlSiO_4)_4$ crystalline solutions decrease with increasing temperature at 0.5, 2.0, and 5.0 kbar. This inference is supported by the negative coefficients for the temperature terms in equations (10), (16), (22) and (28) (Table 3), and by the esd's for these coefficients, which are significantly smaller than the values of the coefficients themselves. Therefore, unlike previous investigators, we list equations for q_1 as a function of temperature [and pressure in the polybaric equation (28)], because this appears to be justified from regression and statistical analyses.

[5] Polybaric mixing-parameter equations for $(Na,K)_3K(AlSiO_4)_4$ crystalline solutions presented by Ferry and Blencoe (1977) were tentative and are superseded by the equations listed in Table 3, section b. The small differences between the two sets of equations are attributable to recent minor modifications of determinative equations (1) and (2).

parameter equations (5)–(22) and the polybaric mixing-parameter equations (23)–(28) listed in Table 3. These equations were substituted into equations (28)–(30) of Blencoe (1977) to obtain activities of the $Na_3K(AlSiO_4)_4$ and $K_4(AlSiO_4)_4$ components as a function of P, T, and X_2, and nepheline–kalsilite solvi were calculated from the activities using an iterative computer method modified from Luth and Fenn (1973). Solvi calculated from the Margules-parameter equations (5)–(6), (11)–(12), (17)–(18), and (23)–(24) are presented in Figures 3–5 for comparison with our solvus experimental data. Solvi calculated from the van Laar and quasichemical formulations are very similar to these Margules solvi; consequently, the analysis of calculated Margules solvi that follows also applies by analogy to calculated van Laar and quasichemical solvi.

Figures 3 and 4 illustrate that 0.5 and 2.0 kbar solvi calculated from the polybaric Margules-parameter equations (23)–(24) are reasonably accurate representations of our solvus data obtained at these pressures. Furthermore, the 2.0 kbar solvus calculated from the isobaric Margules equations (11)–(12) adequately represents the solvus data obtained at this pressure. However, Figure 3 shows that the 0.5 kbar solvus calculated from the isobaric Margules equations (5)–(6) does not adequately represent the solvus data obtained at 1004°C at this pressure, and Figure 5 illustrates that at 5.0 kbar and high temperatures there are significant discrepancies between the solvus data and both of the calculated solvi.

The discrepancies at 0.5 kbar are attributable to inconsistencies between the X_{2B} (potassic limb) solvus data obtained at 897, 950, and 1004°C. The 897 and 950°C X_{2B} data suggest a comparatively flat slope for the potassic limb of the solvus between these two temperatures, but the 1004°C X_{2B} data indicate a much steeper slope. Crystallization of solvus-pairs at 1004°C suggests that the X_{2B} values obtained at 897 and 950°C are erroneous (too small), but additional experimental data are required to verify this. In any case, from Figure 3 it is evident that the 0.5 kbar isobaric solvus is biased toward the X_{2B} data obtained at 897 and 950°C.

The discrepancies at 5.0 kbar revealed by Figure 5 are: (1) at 999°C the solvus data (one X_{2A} value and one X_{2B} value) indicate that the nepheline–kalsilite two-phase region is less extensive than the isobaric equations (17)–(18) predict, and (2) above 700°C the potassic limb of the polybaric solvus does not accurately represent the X_{2B} solvus data. Discrepancies between the solvus data and isobaric solvus at 999°C

Table 3. Polynomial mixing-parameter equations for synthetic $(Na,K)_3K(AlSiO_4)_4$ crystalline solutions

Eqn. No.[*]	Form.[**]	P (kbar)	M. P.[†]	A[††]	B	C	e.s.d.[@] (cal/gfw)	f.e.v.[@@]
			a) Isobaric equations of the form					
			Y(mixing parameter) $= A + BT(K)$					
(5)	MG	0.5	W_{G1}	23403.1(1831.2)	−7.7333(1.7796)	−	1200.8	0.611
(6)	MG	0.5	W_{G2}	9623.4(1086.3)	4.7728(1.0557)	−	712.4	0.630
(7)	VL	0.5	A_1	23385.9(1870.4)	−7.6597(1.8177)	−	1226.5	0.597
(8)	VL	0.5	A_2	9930.3(1005.6)	4.5567(0.9773)	−	659.4	0.644
(9)	QC	0.5	W_G	11034.5(727.6)	13.0510(0.7071)	−	477.1	0.966
(10)	QC	0.5	q_1	1.1859(0.0357)	−0.1638(0.0347)[††]	−	0.0234	0.649
(11)	MG	2.0	W_{G1}	23061.3(2086.4)	−7.8925(1.9992)	−	1793.8	0.478
(12)	MG	2.0	W_{G2}	8073.1(845.6)	6.4830(0.8103)	−	727.1	0.790
(13)	VL	2.0	A_1	22581.8(2070.7)	−7.2664(1.9842)	−	1780.3	0.441
(14)	VL	2.0	A_2	7945.0(892.5)	6.7403(0.8552)	−	767.3	0.785
(15)	QC	2.0	W_G	10369.7(1047.3)	13.6362(1.0035)	−	900.4	0.916
(16)	QC	2.0	q_1	1.2096(0.0212)	−0.1969(0.0203)[††]	−	0.0182	0.847
(17)	MG	5.0	W_{G1}	13515.5(1076.5)	1.5862(1.0850)	−	849.7	0.118
(18)	MG	5.0	W_{G2}	9774.2(1001.2)	5.3290(1.0091)	−	790.2	0.635
(19)	VL	5.0	A_1	13518.5(1070.6)	1.6091(1.0791)	−	845.0	0.122
(20)	VL	5.0	A_2	9808.1(1007.7)	5.3201(1.0157)	−	795.4	0.632
(21)	QC	5.0	W_G	7758.5(349.6)	16.3412(0.3524)	−	276.0	0.993
(22)	QC	5.0	q_1	1.0547(0.0254)	−0.0540(0.0256)[††]	−	0.0201	0.217
			b) Polybaric equations of the form					
			Y(mixing parameter) $= A + BT(K) + CP(bars)$					
(23)	MG	0.5–5.0	W_{G1}	20329.4(1256.2)	−4.7921(1.1591)	−0.1317(0.1217)	1589.1	0.268
(24)	MG	0.5–5.0	W_{G2}	8591.4(582.6)	5.6827(0.5376)	0.1655(0.0564)	736.9	0.706
(25)	VL	0.5–5.0	A_1	20136.4(1236.2)	−4.4833(1.1407)	−0.1438(0.1197)	1563.8	0.252
(26)	VL	0.5–5.0	A_2	8658.5(591.8)	5.7467(0.5461)	0.1473(0.0573)	748.7	0.702
(27)	QC	0.5–5.0	W_G	9659.6(527.9)	14.3696(0.4871)	0.0012(0.0511)	667.7	0.948
(28)	QC	0.5–5.0	q_1	1.1654(0.0185)	−0.1424(0.0170)[††]	−0.0050(0.0018)[††]	0.0233	0.606

[*] These equation numbers are used in various places in the text to refer to a particular equation or group of equations in this table.

[**] Abbreviations: MG = Margules formulation, VL = van Laar formulation, QC = quasichemical formulation.

[†] M. P. = mixing parameter. Mixing-parameter values calculated from the equations in this table are in cal/gfw with the exception of q_1 values which are dimensionless.

[††] Enough significant figures are provided to prevent serious round-off errors in calculations. The number of figures is not related to the precision or accuracy of the two-phase data listed in Table 2. Numbers in parentheses are estimated standard deviations of the coefficients. The B coefficients in equations (10), (16), (22), (28) and the C coefficient in equation (28), as well as the estimated standard deviations for these coefficients, have been multiplied by 1000.0 to eliminate three zeros to the right of the decimal point.

[@] Estimated standard deviation (Deming, 1943). Units are cal/gfw except e.s.d.'s of q_1 which are dimensionless.

[@@] Fraction of explained variance, or R^2 (Draper and Smith, 1966, p. 26). These values are dimensionless and they vary between 0.0 and 1.0.

are attributable to clustering in the solvus data. Since only two solvus-pairs were crystallized at temperatures above 900°C, that is, one solvus-pair at 951°C and another at 999°C, the isobaric mixing-parameter equations are evidently biased toward the significantly larger quantity of solvus data (nine solvus-pairs) obtained at temperatures between 701 and 894°C. On the other hand, discrepancies between the polybaric solvus and the X_{2B} solvus data at temperatures above 700°C are attributable to an apparent change in symmetry of the solvus between 2.0 and 5.0 kbar. Solvus data obtained at 0.5 and 2.0 kbar (Figs. 3 and 4) indicate that the solvus is appreciably asymmetric toward $Na_3K(AlSiO_4)_4$ at these pressures, but solvus data obtained at 5.0 kbar (Fig. 5) suggest that the solvus is nearly symmetric at this pressure. This change in symmetry is caused by an apparent shift of the potassic limb of the solvus toward $K_4(AlSiO_4)_4$ with increasing pressure above 2.0 kbar, but we cannot explain this phenomenon from either a crystallographic or thermodynamic standpoint. Nevertheless, one consequence of the shift is that the polybaric equation (23) does not accurately represent the values of W_{G1} Margules parameters at 5.0 kbar and temperatures above 700°C. As a result of the shift, W_{G1} values at a given temperature above 700°C (Table 2) are a nonlinear function of pressure, but the form of equation (23) is adequate only in representing linear variations of W_{G1} values with pressure at constant temperature. This is the source of the discrepancies between the X_{2B} data and the position of the potassic limb of the polybaric solvus at temperatures above 700°C, and one remedy would be to introduce additional P terms (e.g., PT and/or P^2) into equation (23). However, since the T–X limits of the nepheline–kalsilite solvus have been determined at only three different pressures in this study, we believe that our solvus data are too clustered to justify more complex polybaric equations for the mixing-parameter values given in Table 2. Consequently, the polybaric equations listed in Table 3, section b should be used only when P is in the range one atm to 2.0 kbar.

Discussion

In general, the unit-cell and phase-equilibrium data for $(Na,K)_3K(AlSiO_4)_4$ nephelines and kalsilites synthesized in this study are in good agreement with the data of previous investigators. The principal discrepancies occur between: (1) the $(Na,K)_3K(AlSiO_4)_4$ nepheline a and V unit-cell data presented in this paper (Table 1) and those listed by Smith and Tuttle (1957, Table 2) and Donnay et al. (1959, Table IV), and (2) the solvus data of the present study and those of Tuttle and Smith (1958) pertaining to the position of the potassic limb of the nepheline–kalsilite solvus at temperatures above 800°C at low pressures (less than 1.0 kbar).

Unit-cell parameter data for $(Na,K)_3K(AlSiO_4)_4$ nephelines and kalsilites

Discrepancies between the $(Na,K)_3K(AlSiO_4)_4$ nepheline a and V unit-cell data of the present study and those of Smith and Tuttle and Donnay et al. are illustrated in Figures 1A and 2A.[6] These figures show that the differences are much larger than the estimated measurement errors (2σ) for the nepheline a and V unit-cell data of the present investigation (Table 1) (Smith and Tuttle and Donnay et al. do not list estimated measurement errors for their unit-cell data). The most likely explanation for these discrepancies is that the a and V values obtained by Smith and Tuttle and Donnay et al. are systematically too large because of slightly Na_2O-deficient starting materials and additional minor Na_2O volatilization during experimentation. This is a logical explanation because: (1) in both of these investigations the starting materials and resulting experimental samples were unsealed during preparation at high temperatures at one atm pressure; (2) Donnay et al. (1959, p. 101) detected small amounts of beta-alumina and corundum in their experimental samples; and (3) Na_2O loss would shift unit-cell data for

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[6] Unit-cell parameters for synthetic nephelines described by Smith and Tuttle and Donnay et al. are listed by Donnay et al. (1959, Table IV) with compositions of the nephelines given in weight percent $KAlSiO_4$. For comparison with the unit-cell data of this study (Table 1), the compositions of these nephelines have been converted from weight percent $KAlSiO_4$ to $XK_4(AlSiO_4)_4$ using the equation

$$XK_4(AlSiO_4)_4 = \cfrac{\left[\cfrac{100(\text{wt.\% } KAlSiO_4/158.167)}{\text{wt.\% } KAlSiO_4/158.167 + \text{wt.\% } NaAlSiO_4/142.055} \right] - 25}{75}$$

where the expression in brackets is equal to mole percent $KAlSiO_4$, and 142.055 and 158.167 are the gram-formula weights of $NaAlSiO_4$ and $KAlSiO_4$ respectively. In both of these previous investigations, experiments were conducted at one atm using $(Na,K)AlSiO_4$ starting materials (usually glasses, or glass-rich materials) prepared by N. L. Bowen and J. F. Schairer. Thus, owing to the essentially identical experimental conditions and good agreement between the unit-cell data for synthetic nephelines (Donnay et al., 1959, Table IV), the unit-cell data of the two studies will be referred to and treated as a single set of internally consistent data.

$(Na,K)_3K(AlSiO_4)_4$ nephelines toward $Na_3K(AlSiO_4)_4$ on plots such as Figures 1A and 2A (thereby yielding erroneously large a and V values for the nephelines), and the unit-cell data of the present study illustrated in these figures indicate such displacement of the corresponding data of Smith and Tuttle and Donnay et al.[7] Extending this line of reasoning, compositional $[XK_4(AlSiO_4)_4]$ changes induced by Na_2O loss can be estimated quantitatively from the differences between the $(Na,K)_3K(AlSiO_4)_4$ nepheline a and V data of this study and those of Smith and Tuttle and Donnay et al. Discrepancies between the two sets of data in Figures 1A and 2A are approximately three mole percent $K_4(AlSiO_4)_4$ near $X_2 = 0.0$, increasing to approximately five mole percent $K_4(AlSiO_4)_4$ at $X_2 = 0.2$. These differences imply that: (1) Na_2O losses from the $(Na,K)_3K(AlSiO_4)_4$ nepheline samples of Smith and Tuttle and Donnay et al. were at least of sufficient magnitude to induce compositional changes (increases) of 3–5 mole percent $K_4(AlSiO_4)_4$ (greater Na_2O volatilization would be required to produce these changes if some K_2O also was lost from each of the samples); and therefore (2) these Na_2O losses were much greater than would be required to produce changes in $KAlSiO_4$ composition of "less than one weight percent" [less than 1.3–1.4 mole percent $K_4(AlSiO_4)_4$ in the range $0.0 \leq X_2 \leq 0.5$], which is the estimate of departure from composition due to alkali loss suggested by Donnay et al. (1959, p. 101).

Figure 1 also illustrates a and c unit-cell data for two kalsilites described by Smith and Tuttle (1957, Table 12), and unit-cell volumes for these kalsilites calculated from the relation $V = a^2c(\sin 60°)$ are shown in Figure 2B. Bulk compositions of the kalsilite samples are reported as $X_2 = 1.0$ (100 weight percent $KAlSiO_4$) and $X_2 = 0.853$ (90 weight percent $KAlSiO_4$, 10 weight percent $NaAlSiO_4$), but a small amount of leucite was detected in both of these samples (Smith and Tuttle, 1957, p. 288). The unit-cell data for the Na-free kalsilite are essentially identical to those obtained in the present study (Table 1), and this suggests that this kalsilite is stoichiometric despite the presence of leucite, which implies minor K_2O loss from the sample. The values of a, c, and V for the synthetic kalsilite crystalline solution ($X_2 = 0.853$) are slightly smaller than corresponding values reported in the present study (Table 1), and this (as well as the presence of leucite) is consistent with minor K_2O loss from this sample, or minor alkali loss with K_2O loss greater than Na_2O loss.

Nepheline–kalsilite solvus data

The 0.5 and 2.0 kbar solvus data of this study (Table 2, Figs. 3 and 4) are generally consistent with nepheline–kalsilite solvus data obtained at similar pressures in previous investigations.[8] Between 400 and 800°C our 0.5 and 2.0 kbar solvus data are very similar to those of Tuttle and Smith (1958), who obtained their data at pressures from one atm to 981 bars (Fig. 3). Wellman (1970, Table 2) obtained the following data for two solvus-pairs crystallized at 604 bars pressure: at 502°C, $X_{2A} = 0.027$ and $X_{2B} = 0.915$; and at 503°C, $X_{2A} = 0.036$ and $X_{2B} = 0.920$. He also crystallized a solvus-pair with $X_{2A} = 0.059$ and $X_{2B} = 0.907$ at 2020 bars and 596°C. Yund et al. (1972) conducted exsolution experiments at one atm pressure, which indicate that $X_2 = 0.083$ and $X_2 = 0.115$ at the sodic limb of the solvus at 600 and 700°C, respectively. Furthermore, their hydrothermal experiments at 1.0 kbar suggest that the potassic limb of the solvus is at $X_2 = 0.947$ at 600°C. Figures 3 and 4 show that the solvus data of Wellman and Yund et al. are in fairly good agreement with our data.

The principal discrepancies in the available nepheline–kalsilite solvus data are between our data and those of Tuttle and Smith (1958) obtained at temperatures above 800°C (Fig. 3). Differences between the hydrothermal solvus data of the two studies are most readily explained by quench reactions in the hydrothermal experiments of Tuttle and Smith at 490

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[7] Donnay et al. (1959, p. 101) state that minor "alkali loss" would explain the small amounts of beta-alumina and corundum accompanying their synthetic nephelines. Presumably they meant that both Na_2O and K_2O may have been lost from their experimental samples, but this was not stated explicitly. Differences between the $(Na,K)_3K(AlSiO_4)_4$ nepheline a and V data of the present study and those of Smith and Tuttle and Donnay et al. are not inconsistent with loss of both Na_2O and K_2O from the samples in these two earlier investigations, but if this is the case, these differences indicate that Na_2O loss must have been greater than K_2O loss. Values of the a and V unit-cell parameters for nepheline are distinctive criteria for minor Na_2O loss because the length of the a unit-cell dimension is fairly sensitive to Na/K ratio (Figure 1A), and unit-cell volume is related to the a unit-cell dimension by $V = a^2c(\sin 60°)$. On the other hand, the c unit-cell dimension of nepheline is comparatively insensitive to Na/K ratio, and this explains the negligible differences between the c unit-cell data of the present study and those of Smith and Tuttle and Donnay et al. (Fig. 1B).

[8] Solvus data of the present study obtained at 0.5 and 2.0 kbar are very similar, and this indicates that nepheline–kalsilite solvi from one atm to 2.0 kbar are identical within experimental error. Consequently, in the present discussion, differences in pressure will be ignored in comparing nepheline–kalsilite solvus data obtained between one atm and (approximately) 2.0 kbar.

and 981 bars. These investigators, and later Yund *et al.* (1972), have shown that exsolution rates of $(Na,K)_3K(AlSiO_4)_4$ crystalline solutions are very rapid in hydrothermal experiments, and this suggests that $(Na,K)_3K(AlSiO_4)_4$ phases crystallized at high temperatures may react and partially reequilibrate at lower temperatures if quench rates are too slow. Therefore, assuming that the solvus data of the present study are at least approximately correct, it is likely that solvus-pairs crystallized by Tuttle and Smith in hydrothermal experiments above 800°C either formed or partially reequilibrated during quenching.

Recognizing this experimental difficulty with their hydrothermal experiments, Tuttle and Smith used data obtained from dry-quenching experiments and high-temperature X-ray diffraction studies to determine $T–X$ limits of the nepheline–kalsilite solvus at one atm (dotted-line solvus in Fig. 3). The position of the sodic limb of this solvus is consistent with the 0.5 kbar X_{2A} solvus data of the present study up to 1000°C, and the position of the potassic limb of the solvus is consistent with our 0.5 kbar X_{2B} solvus data up to 800°C. However, Tuttle and Smith's solvus indicates that X_{2B} values decrease from approximately 0.8 at 800° to 0.7 at 1000°C, while our solvus data indicate that these values decrease from approximately 0.8 at 800° to 0.55 at 1000°C.

Examination of Tuttle and Smith's solvus data (Fig. 3) indicates that these investigators located the position of the potassic limb of their solvus above 800°C using only those data obtained from high-temperature X-ray diffraction experiments (Tuttle and Smith, 1958, Table 2). These experiments involved: (1) unmixing a homogeneous $(Na,K)_3$ $K(AlSiO_4)_4$ crystalline solution of "known" composition at 650°C for two hours to produce a nepheline-kalsilite mixture (ostensibly a nepheline–kalsilite solvus-pair), and subsequently (2) heating this mixture at a rate of 150°C/hr and noting (by X-ray diffraction methods) the temperature at which the mixture homogenized.

We believe that there are two principal reasons to question the accuracy of the data obtained from these experiments. First, equilibrium (reversibility) was not demonstrated for the heating experiments pertaining to the position of the potassic limb of the solvus (that is, the temperature at which hypersolvus kalsilite unmixed upon cooling could not be determined accurately). Therefore, and in view of the rapid heating rates in the experiments, it is possible that homogenization temperatures for K-rich samples were overstepped by as much as 50–100°C. Second, alkali loss may have affected the results. As noted previously, Smith and Tuttle (1957) detected small amounts of leucite in kalsilite samples crystallized in one atm dry-quenching experiments, and this suggests minor K_2O loss from these samples. Tuttle and Smith's K-rich samples also contained small amounts of leucite (Tuttle and Smith, 1958, p. 572), so in their X-ray diffraction experiments it is likely that K-rich samples lost some K_2O prior to (and perhaps during) the experiments, particularly since these samples were prepared and crystallized at high temperatures (980–1080°C). K_2O loss would shift the bulk composition of a K-rich sample slightly off the $Na_3K(AlSiO_4)_4$– $K_4(AlSiO_4)_4$ join but toward $Na_3K(AlSiO_4)_4$, and this would increase the temperature at which this sample would pass from the nepheline–kalsilite two-phase region into the kalsilite one-phase region with increasing temperature. Consequently, K_2O loss would shift the apparent (experimentally-determined) position of the potassic limb of the solvus toward $K_4(AlSiO_4)_4$, and this also could explain, at least in part, why the potassic limb of Tuttle and Smith's solvus is on the $K_4(AlSiO_4)_4$ side of our 0.5 kbar X_{2B} solvus data at high temperatures. In view of these uncertainties regarding the accuracy of the data that Tuttle and Smith obtained from their X-ray diffraction experiments, we believe that our 0.5 kbar solvus data more accurately represent the position of the nepheline–kalsilite solvus at low pressures.

Finally, it should be noted that, owing to the different structures of the coexisting phases, a solvus between $P6_3$ nepheline ($a \approx 10A$) and $P6_3$ kalsilite ($a \approx 5A$) cannot have a stable critical point at any pressure. Tuttle and Smith (1958, p. 578) recognized this, and they hypothesized that at one atm the solvus is truncated at approximately 1050°C by the reaction Na-rich nepheline ($a \approx 10A$) + kalsilite ($a \approx 5A$) $\rightleftarrows$ K-rich nepheline ($a \approx 10A$) which produces two high-temperature phase assemblages: Na-rich nepheline ($a \approx 10A$) + K-rich nepheline ($a \approx 10A$), and K-rich nepheline ($a \approx 10A$) + kalsilite ($a \approx 5A$). Furthermore, at temperatures above 1050°C, Tuttle and Smith (1958, Fig. 2) depict the two-nepheline region as a small, isostructural solvus with a critical temperature at approximately 1070°C, and the high-temperature nepheline–kalsilite region is illustrated schematically as a transition loop trending slightly toward $Na_3K(AlSiO_4)_4$ with increasing temperature. Our experimental and X-ray diffraction data indicate that the low-temperature, non-isostructural nepheline–kalsilite solvus is stable up to at least 1000°C at
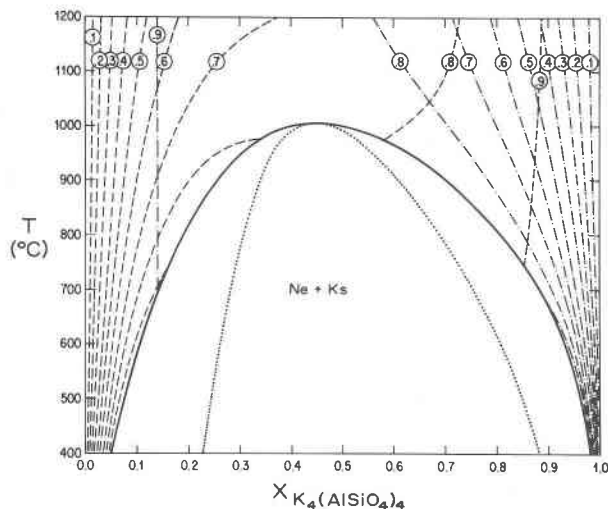
Fig. 6. Solvus, spinodal, and subsolidus isoactivity contours for the $Na_3K(AlSiO_4)_4$-$K_4(AlSiO_4)_4$ system at 2.0 kbar calculated from the polybaric Margules equations (23)–(24). ——— = solvus; ········ = spinodal; ·–·–·– = isoactivity contours for the $Na_3K(AlSiO_4)_4$ component; -------- = isoactivity contours for the $K_4(AlSiO_4)_4$ component.

0.5, 2.0, and 5.0 kbar, but we did not conduct experiments at temperatures above 1000°C at any of these pressures. Consequently, we are unable to provide evidence to either support or refute Tuttle and Smith's inferences regarding the nature of the high-temperature termination of the nepheline–kalsilite solvus.

Petrologic applications

Our $(Na,K)_3K(AlSiO_4)_4$ phase-equilibrium data have indirect but significant applications to natural nepheline-bearing rocks. Our nepheline–kalsilite solvus data give approximate T–X limits of stability for natural nepheline–kalsilite pairs, but this is of minor petrologic importance because: (1) rocks containing both nepheline and kalsilite are comparatively rare; and (2) rates of nepheline–kalsilite exsolution are very rapid, even at temperatures as low as 500°C (Yund *et al.,* 1972). Consequently, instances of direct application of $(Na,K)_3K(AlSiO_4)_4$ solvus data in geothermometry are infrequent, and final equilibration temperatures for natural nepheline–kalsilite pairs obtained from these data will generally be very low and of limited practical value in deciphering the crystallization history of the host rock (Tuttle and Smith, 1958). On the other hand, $(Na,K)_3K(AlSiO_4)_4$ solvus data are of significant practical value in deriving equations of state for $(Na,K)_3K(AlSiO_4)_4$ crystalline solutions. As discussed previously, such equations can be used to calculate nepheline–kalsilite solvi

and activities of the $Na_3K(AlSiO_4)_4$ and $K_4(AlSiO_4)_4$ components in $(Na,K)_3K(AlSiO_4)_4$ crystalline solutions. However, application of these calculated solvi and activities is not restricted to the $Na_3K(AlSiO_4)_4$–$K_4(AlSiO_4)_4$ system; with certain assumptions and approximations, and equations of state for alkali feldspars, they also can be used to derive subsolidus alkali feldspar–$(Na,K)_3K(AlSiO_4)_4$ nepheline phase relations in the $NaAlSiO_4$–$KAlSiO_4$–SiO_2 ($\pm H_2O$) system. Moreover, equations of state for alkali feldspar and nepheline–kalsilite crystalline solutions can be employed to calculate final equilibration temperatures of alkali feldspar–nepheline pairs in natural rocks (Perchuk and Ryabchikov, 1968; Powell and Powell, 1977; Blencoe and Ferry, 1977). The reliability of these calculated temperatures depends in part upon the extent to which the equations of state accurately represent the activity–composition relations of the crystalline solutions, and uncertainties regarding the accuracies of calculated activities are a major problem in such geothermometric calculations. Consequently, it is instructive to compare activity–composition relations for $(Na,K)_3K(AlSiO_4)_4$ crystalline solutions calculated from our solvus data and the Margules, van Laar, and quasichemical solution models.

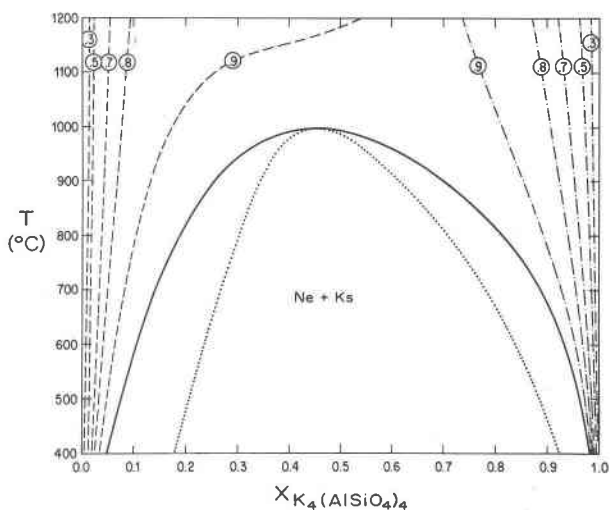Figures 6 and 7 are calculated T–X phase diagrams for the $Na_3K(AlSiO_4)_4$–$K_4(AlSiO_4)_4$ system at 2.0 kbar. Subsolidus phase relations and activities in

Fig. 7. Solvus, spinodal, and subsolidus isoactivity contours for the $Na_3K(AlSiO_4)_4$-$K_4(AlSiO_4)_4$ system at 2.0 kbar calculated from the polybaric quasichemical equations (27)–(28). Labelling of curves (solid, dotted, dash-dot, and dashed) is the same as listed in the legend for Fig. 6. Note that the solvus and spinodal in this figure are essentially the same as in Fig. 6, but calculated activity-composition relations in the two figures are significantly different.

these figures were calculated from the polybaric Margules equations (23)–(24) (Fig. 6) and the polybaric quasichemical equations (27)–(28) (Fig. 7). The solvus, spinodal, and activity–composition relations at 2.0 kbar calculated from the polybaric van Laar equations (25)–(26) (not illustrated) are essentially identical to those given by the polybaric Margules equations. [Calculated T–X phase diagrams for the $Na_3K(AlSiO_4)_4$–$K_4(AlSiO_4)_4$ system at other pressures in the range one atm to 5.0 kbar show corresponding similarities and differences between the phase relations and activities calculated from the three models.] Each of the three models gives similar calculated solvi at 0.5, 2.0, and 5.0 kbar, but Figures 6 and 7 illustrate that the Margules and quasichemical models give significantly different calculated activity–composition relations for $(Na,K)_3K(AlSiO_4)_4$ crystalline solutions at 2.0 kbar. These figures show that the quasichemical model predicts greater nonideality for $(Na,K)_3K(AlSiO_4)_4$ crystalline solutions; that is, the Margules and quasichemical models both give calculated $Na_3K(AlSiO_4)_4$ and $K_4(AlSiO_4)_4$ activity coefficients that are generally $\gg 1.0$ at temperatures below 1200°C, but the quasichemical activity coefficients are systematically larger than those calculated from the Margules model. [This is evident from Figs. 6 and 7, because isoactivity curves calculated from the quasichemical model are more tightly clustered near the $Na_3K(AlSiO_4)_4$ and $K_4(AlSiO_4)_4$ sidelines.] Consequently, except for calculations of nepheline–kalsilite solvi, it is to be expected that activities calculated using equations (23)–(24) and (27)–(28) will yield significantly different results in $(Na,K)_3K(AlSiO_4)_4$ phase-equilibrium calculations; for example, in calculations of $(Na,K)_3K(AlSiO_4)_4$ phase relations in multicomponent systems such as $NaAlSiO_4$–$KAlSiO_4$–SiO_2 ($\pm H_2O$). We have performed various phase-equilibrium and geothermometric calculations involving nepheline–kalsilite crystalline solutions using activities obtained from two-parameter solution models and other methods, and we will report the results of these calculations in a subsequent paper.

Acknowledgments

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