K–Na exchange equilibria between muscovite–paragonite solid solution and hydrothermal chloride solutions

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ABSTRACT. Three ion exchange equilibrium isotherms between muscovite–paragonite solid solution and 2-molal KCl–NaCl aqueous solutions have been studied at (1) 420 °C, 1 kbar, (2) 420 °C, 2 kbar, and (3) 550 °C, 2 kbar. The $\Delta G°$ (Joules) $\pm 2\sigma$ of the ion exchange reaction are: $\Delta G°$ (1) $= -17\,259 \pm 686$, $\Delta G°$ (2) $= -18\,268 \pm 560$, $\Delta G°$ (3) $= -16\,018 \pm 336$. The excess mixing parameters ('subregular solution') of the solid solution (at 1 bar) have been calculated:

$$W_{\text{parag.}}(\text{J/mol}) = 5996 \pm 1816 \ (420\ °C)$$
$$6348 \pm 624 \ (550\ °C)$$
$$W_{\text{muscov.}}(\text{J/mol}) = 14\,781 \pm 1448 \ (420\ °C)$$
$$16\,785 \pm 554 \ (550\ °C)$$

The corresponding binodal compositions are (muscovite mol fraction): 12–56 % at 420 °C, 1 bar and 15–51 % at 550 °C, 1 bar. The compositions of micas in equilibrium with perthites (high structural state) at 400, 500, 600 °C, and 2 kbar are respectively: $X_{\text{mus}} = 91$, 86, and 82 %.

The mixing properties of the solution were estimated using the speciation of two molal chloride solutions calculated from the dissociation constants of NaCl and KCl in aqueous solution. Although NaCl appears to be substantially more dissociated than KCl, the resulting excess free energy of mixing of the hydrothermal (Na,K)Cl solution was found less than 500 J at temperatures above 400 °C and pressures up to 2 kbar.

The difference in Gibbs free energy of formation (from the elements at 25 °C, 1 bar) between NaCl and KCl in two molal aqueous solutions is proposed:

$$\Delta G°_{\text{KCl}} - \Delta G°_{\text{NaCl}} = -18\,152 - 19.41\ T \text{ Joules (at 2 kbar).}$$

KEYWORDS: muscovite, paragonite, ion exchange, chloride solutions.

IN a preceding work (Pascal and Roux, 1982) we reviewed the experimental data on equilibrium between hydrothermal (Na,K)Cl solutions and sodi-potassic silicates. This enabled us to propose an estimate of the difference in Gibbs free energy of formation (from the elements at 25 °C, 1 bar) between KCl and NaCl in aqueous solution of molality > 0.5, between 400 and 800 °C and 1 and 2 kbar. The set of experimental data studied was

found to be remarkably self-consistent. However, the need has emerged for more accurate data on the equilibrium between paragonite–muscovite solid solutions and hydrothermal (Na,K)Cl solutions.

In this paper we present three new isotherms at 420 °C, 1 and 2 kbar and 550 °C, 2 kbar. These new data, along with another isotherm obtained by Chatterjee and Flux (pers. comm.) at 7 kbar and 620 °C, cover large P, T ranges (limited by the stability of the mica solid solution) where the dissociation constant of NaCl and KCl are known. We have therefore attempted to improve the thermodynamic treatment of these ion-exchange equilibria taking into account the dissociation of the salt, and estimating the effect on the macroscopic properties of the hydrothermal solutions.

Experimental procedure

A gel on the join muscovite–paragonite and a (Na,K)Cl–H$_2$O solution were sealed in a gold capsule. The solids crystallized and equilibrated with the solutions during the run in a conventional cold-seal pressure vessel. After the run the solutions and solids were recovered quantitatively, by freezing the gold capsule in liquid nitrogen (to prevent loss of solution), cutting it open, and flushing its content into a plastic vial. The solution was then diluted and analysed by flame photometry for K and Na. For the 550 °C isotherm, the bulk composition of the mica was also determined by flame photometry, taking care of Al interferences. When the solid was not analysed, its composition was calculated from that of the solution after the experiment, assuming that the total number of alkali elements in the hydrothermal solution did not vary during the experiment (e.g. due to the solubility of the mica in the hydrothermal solution), from the relations:

$$N' \cdot n' + X' \cdot x' = N'' \cdot n'' + X'' \cdot x'' \tag{1}$$
$$n' = n'' \tag{2}$$
$$x' = x'' \tag{3}$$

where X, N, are the mole fractions of the K end-member in the solid and solution respectively, x and n the number of moles of alkali in the solid and solution respectively. (') stands for starting material, ('') for final products.

Table I summarizes the experimental data (composition, and weights of starting and run products) for each isotherm. Because special care was taken to ensure an accurate recovery of the solution, it was possible to make a direct check of the validity of relation (2) which was found to be satisfied within analytical uncertainty for most of the runs. For those runs where the solid was analysed there was a good agreement between the analysed and calculated compositions of the solid.

The run durations were 3 weeks for the 550 °C isotherm and 3 to 5 months for the 420 °C isotherms. There was evidence that the equilibrium between the solid and the solution was achieved: (a) the runs using different starting materials (muscovite or paragonite gels) gave identical

TABLE I. Muscovite-Paragonite ion-exchange isotherms : experimental data

Composition of the starting products:

K_S: K mol/Kg of starting solution

Na_S: Na mol/Kg of starting solution

m_S: weight of starting solution (mg)

K_G: K mol/Kg of gel

Na_G: Na mol/Kg of gel

m_G: weight of gel(mg)

Analyses of the mica and the solution after run:

K-m: micro-mol K after run in the solution;

Na-m: ""   Na   ""

X_m: $\frac{K}{Na+K}$ of the mica: wet chemical analysis of the bulk solid phase after run, 0 if n.d.;

X_c: $\frac{K}{Na+K}$ of the mica: calculated from the composition of the starting products and the analysis of the solution;

N_m: $\frac{K}{Na+K}$ of the solution: flame-photometry;

Run	K_s	Na_s	m_s	K_g	Na_g	m_g	K-m	Na-m	%recov.	X_m	X_c	N_m	$\frac{K^+}{KCl}$	$\frac{Na^+}{NaCl}$	$\gamma_\pm$	γ_{H_2O}	dG_N^{ex}/dN
420°, 1 kb																	
1.23	0.1808	1.725	111.6	0.0	2.746	91.40	5.650	207.4	100.2	0.0	0.05792	0.02652	0.0250	0.253	0.316	1.004	-691.3
1.24	0.2851	1.627	118.6	0.0	2.746	94.00	7.780	216.0	98.68	0.0	0.1005	0.03477	0.0250	0.252	0.316	1.004	-684.9
1.25	0.3659	1.551	116.1	0.0	2.746	77.20	9.060	212.5	99.60	0.0	0.1575	0.04088	0.0250	0.252	0.316	1.004	-680.0
1.27	0.5664	1.362	121.8	0.0	2.746	76.10	10.12	220.8	98.32	0.0	0.2809	0.04382	- 2 micas coexisting -				
1.29	1.114	0.8468	121.7	0.0	2.746	90.50	9.830	226.5	99.03	0.0	0.5057	0.04159					
1.30	1.404	0.5738	120.7	0.0	2.746	74.50	14.32	221.8	98.89	0.0	0.7577	0.06065	0.0241	0.245	0.316	1.004	-650.6
1.31	1.632	0.3596	114.9	0.0	2.746	64.80	28.25	196.9	98.39	0.0	0.8925	0.1255	0.0245	0.248	0.319	1.004	-610.2
1.33	1.899	0.1087	123.3	0.0	2.746	76.70	39.95	200.2	97.02	0.0	0.9160	0.1664	0.0246	0.249	0.322	1.004	-581.7
1.34	2.014	0.0	112.5	0.0	2.746	78.80	33.69	193.4	100.2	0.0	0.8919	0.1484	0.0243	0.246	0.320	1.004	-590.5
1.35	0.0	1.895	116.4	2.629	0.0	59.60	19.70	197.2	98.36	0.0	0.8722	0.09081	0.0258	0.259	0.320	1.004	-658.6
1.36	0.0825	1.817	117.6	2.629	0.0	62.80	26.43	202.1	102.2	0.0	0.9022	0.1157	0.0260	0.261	0.321	1.003	-642.6
1.37	0.1808	1.725	117.2	2.629	0.0	62.70	33.70	187.3	98.96	0.0	0.9220	0.1525	0.0263	0.263	0.324	1.003	-618.7
1.38	0.3659	1.551	118.4	2.629	0.0	71.00	53.08	169.6	98.13	0.0	0.9423	0.2384	0.0271	0.269	0.329	1.003	-559.7
1.39	0.5664	1.362	123.3	2.629	0.0	77.20	77.50	157.3	98.74	0.0	0.9574	0.3301	0.0282	0.277	0.337	1.003	-489.9
420°, 2 kb																	
2.2	0.1808	1.725	130.6	0.0	2.746	113.8	5.630	242.2	99.59	0.0	0.05747	0.02272	0.0172	0.426	0.362	1.006	-1674
2.3	0.2851	1.627	113.1	0.0	2.746	94.30	5.950	211.2	100.4	0.0	0.10165	0.02740	0.0171	0.425	0.362	1.006	-1663
2.4	0.3659	1.551	162.4	0.0	2.746	135.0	9.430	298.7	99.01	0.0	0.1346	0.03060	0.0171	0.424	0.362	1.006	-1656
2.5	0.4673	1.455	168.8	0.0	2.746	115.4	11.74	313.7	100.3	0.0	0.2120	0.03607					
2.6	0.5664	1.362	144.5	0.0	2.746	92.80	10.28	263.7	98.33	0.0	0.2802	0.03752					
2.7	0.8381	1.106	124.8	0.0	2.746	91.40	9.930	131.7	58.38	0.0	0.3490	0.07009	- 2 micas coexisting -				
2.8	1.114	0.8468	153.7	0.0	2.746	121.2	14.93	279.0	97.52	0.0	0.4685	0.05080					
2.10	1.632	0.3596	81.20	0.0	2.746	62.30	10.68	152.0	100.6	0.0	0.7126	0.06566	0.0163	0.412	0.362	1.006	-1560
2.11	1.780	0.2202	122.0	0.0	2.746	58.20	28.11	210.9	97.93	0.0	0.8744	0.1176					
2.12	1.899	0.1087	99.20	0.0	2.746	73.20	19.31	179.5	99.80	0.0	0.8408	0.09715	0.0164	0.413	0.363	1.006	-1503
2.13	2.014	0.0	167.9	0.0	2.746	102.0	80.26	252.6	98.42	0.0	0.9163	0.2411	0.0181	0.437	0.372	1.005	-1248
2.14	0.0	1.895	105.0	2.629	0.0	56.80	18.43	173.8	96.64	0.0	0.8723	0.09586	0.0181	0.440	0.366	1.005	-1563
2.15	0.0825	1.817	114.0	2.629	0.0	98.70	30.97	186.1	100.3	0.0	0.9172	0.1427	0.0187	0.447	0.369	1.005	-1481
2.16	0.1808	1.725	110.1	2.629	0.0	104.9	39.03	170.8	100.0	0.0	0.9307	0.1860	0.0191	0.453	0.371	1.005	-1400
2.17	0.3659	1.551	117.1	2.629	0.0	67.30	53.62	170.3	99.77	0.0	0.9384	0.2395	0.0197	0.461	0.375	1.005	-1292
2.18	0.5664	1.362	96.70	2.629	0.0	57.20	62.35	125.0	100.5	0.0	0.9516	0.3328	0.0210	0.477	0.281	1.004	-1088
2.19	0.8381	1.106	120.7	2.629	0.0	65.10	102.1	126.5	97.43	0.0	0.9784	0.4467	0.0229	0.500	0.391	1.004	-797
2.20	1.114	0.8468	124.2	2.629	0.0	61.70	139.4	101.0	98.88	0.0	0.9826	0.5798	0.0260	0.533	0.407	1.003	-374.6
2.21	1.404	0.5738	119.8	2.629	0.0	88.70	169.4	65.43	99.12	0.0	0.9883	0.7214	0.0311	0.579	0.430	1.003	+238.4
550°, 2 kb																	
3.1	0.06433	2.770	100.0	0.0	2.746	66.90	3.796	267.9	95.86	0.01575	0.01346	0.01397	0.0164	0.1118	0.321	1.003	-308.7
3.2	0.1284	2.440	166.2	0.0	2.746	161.0	9.177	366.3	87.96	0.02420	0.02467	0.02444	0.0183	0.1245	0.323	1.003	-337.3
3.3	0.2535	1.854	162.6	0.0	2.746	124.4	15.24	319.5	97.68	0.07588	0.07500	0.04553	0.0222	0.1494	0.329	1.002	-389.3
3.4	0.5138	1.571	153.5	0.0	2.746	181.3	17.28	294.7	97.49	0.1184	0.1228	0.05539	0.0224	0.1506	0.330	1.002	-388.4
3.5	1.006	1.013	162.9	0.0	2.746	110.9	25.36	304.2	100.2	0.0	0.4550	0.07695	- 2 micas coexisting -				
3.6	0.5138	1.571	85.80	1.617	1.057	67.50	18.63	148.6	93.49	0.7447	0.7385	0.1114	0.0228	0.1531	0.334	1.002	-371.2
3.7	1.498	0.530	164.6	0.0	2.746	111.6	30.89	300.1	99.15	0.6787	0.7030	0.09333	0.0229	0.1536	0.333	1.002	-380.4
3.8	1.006	1.013	107.3	1.617	1.057	73.30	48.80	166.8	99.53	0.8969	0.9052	0.2263	0.0241	0.1614	0.343	1.002	-340.5
3.9	0.0	2.344	110.4	2.629	0.0	62.70	33.73	214.1	95.77	0.8062	0.7864	0.1361	0.0208	0.1405	0.332	1.002	-335.4
3.10	2.009	0.0	170.0	0.0	2.746	132.1	47.10	305.7	103.3	0.8341	0.8159	0.1335	0.0232	0.1555	0.336	1.002	-368.3
3.11	0.06433	2.770	168.0	2.629	0.0	124.7	65.01	399.7	97.59	0.8315	0.8298	0.1399	0.0171	0.1162	0.329	1.003	-280.2
3.12	0.1284	2.440	163.5	2.629	0.0	117.5	64.01	324.0	92.40	0.8577	0.8437	0.1650	0.0192	0.1298	0.332	1.002	-301.4
3.13	0.2535	1.854	156.7	2.629	0.0	112.9	70.07	267.9	102.3	0.8927	0.9032	0.2073	0.0234	0.1566	0.341	1.002	-339.6
3.14	1.498	0.530	111.1	1.617	1.057	76.40	94.94	130.6	100.1	0.9560	0.9551	0.4209	0.0259	0.1711	0.360	1.002	-259.0
3.15	0.5138	1.571	163.5	2.629	0.0	174.3	108.2	225.9	98.02	0.9401	0.9424	0.3239	0.0246	0.1637	0.351	1.002	-298.5
3.16	1.006	1.013	156.5	2.629	0.0	98.80	163.7	149.6	99.16	0.9703	0.9705	0.5225	0.0275	0.1802	0.372	1.002	-209.4
3.17	1.498	0.530	167.5	2.629	0.0	143.0	252.9	83.27	98.96	0.9891	0.9877	0.7523	0.0314	0.2015	0.406	1.001	-41.6
3.19	1.884	0.1280	164.1	2.629	0.0	115.6	306.4	20.29	98.97	0.9980	0.9983	0.9379	0.0379	0.2350	0.452	1.0007	+203.4
3.21	1.282	0.8478	109.4	0.0	2.746	130.4	17.15	223.1	103.1	0.0	0.3454	0.07138					
3.22	1.003	1.174	108.7	0.0	2.746	68.00	21.00	222.6	102.9	0.5010	0.4745	0.08621					
3.23	0.8021	1.408	113.4	0.0	2.746	165.1	17.74	232.1	99.68	0.0	0.1614	0.07101	- 2 micas coexisting -				
3.24	0.5770	1.671	102.4	0.0	2.746	72.00	16.02	224.5	104.5	0.0	0.2213	0.06661					
3.25	0.3772	1.904	141.1	0.0	2.746	75.30	20.09	307.9	101.9	0.1697	0.1620	0.06125					
3.26	0.2027	2.108	112.8	0.0	2.746	67.70	11.55	256.2	102.7	0.06241	0.06253	0.04314	0.0204	0.1382	0.326	1.003	-364.0

results, and (b) the scatter of the experimental points around the isotherm was very small and within analytical uncertainties (fig. 1).

Interpretation

These data, along with one isotherm at 7 kbar and 620 °C obtained by Chatterjee and Flux (pers. comm.), were used to calculate the mixing parameters of the mica solid solution and the ΔG_r° of the ion exchange reaction. At given P, T, and bulk chloride concentration in the fluid, the equilibrium condition can be written:

$$-RT \ln\left(\frac{X}{1-X}\frac{1-N}{N}\right) = \Delta G_r^\circ + dG_x^{ex}/dX - dG_n^{ex}/dN \quad (4)$$

$\Delta G_r^\circ = \Delta G_{muscovite}^f - \Delta G_{paragonite}^f - (\Delta G_{KCl}^f - \Delta G_{NaCl}^f)$.

G_x^{ex} = molar excess free energy of mixing of the solid solution.

G_n^{ex} = excess free energy of mixing of the fluid solution, related to 1 mole of chloride.

ΔG_{KCl}^f = free energy of formation of KCl solution related to one mole of chloride.

All presently determined isotherms involving chloride solutions [alkali-feldspar–fluid, plagioclase–fluid (Orville, 1972), Fe-Mg-biotite–fluid (Schulien, 1979), olivine–fluid (Schulien et al., 1970), etc.], have been interpreted assuming that the hydrothermal solution mixes ideally, i.e. $dG_n^{ex}/dN = 0$.

One may question the validity of this approximation. In none of the isotherms are the aqueous chlorides fully associated. According to Barnes and Ernst (1963), the mixing of associated salts in aqueous solution may be considered as ideal, and their activity coefficients close to 1. On the contrary, ionized salts activity coefficients are much smaller than 1: for example, Helgeson (1981) predicted that the dissociated fraction of NaCl in a 1-molal aqueous solution is about 80% at 400 °C and 1 kbar, and the resulting stoichiometric activity coefficient is about 0.3. In mixed NaCl–KCl fluids, the common ion effect results in KCl remaining widely associated while NaCl is partly ionic (cf. speciation calculations in appendix). Consequently, the stoichiometric activity coefficients of KCl and NaCl can be expected to be different, and the mixing of KCl and NaCl solutions may be nonideal.

Since K^+/KCl° and $Na^+/NaCl^\circ$ ratios are strongly dependent on bulk chloride molality, $\Delta G_{KCl}^f - \Delta G_{NaCl}^f$ is expected to change with concentration, and thus ΔG_r°. Such an effect has been investigated by Lagache and Weisbrod (1977), who measured the composition of a KCl–NaCl fluid in
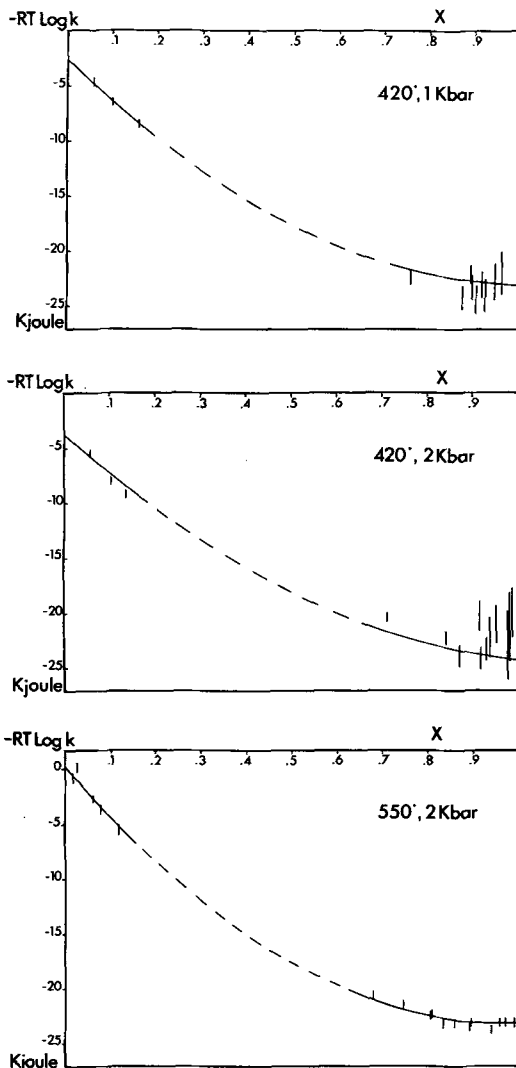

FIG. 1. Experimental data points and fitted curves of the function $Z = -RT \ln \{X/(1-X)\cdot(1-N)/N\}$ where X, N are K-end-member mole fractions in the solid and fluid phases respectively.

equilibrium with a perthite at 600 °C and 2 kbar, and chloride molalities from 0.5 to 20 m. The KCl/NaCl ratio was found to be constant: because the feldspar solid solution properties are independent of chloride concentration, the thermochemical properties of the fluid appeared to be independent of chloride dissociation in the conditions investigated by these authors (the chlorides are weakly ionized at low fluid densities). At higher densities ($T < 450$ °C, $P > 2$ kbar), ionization is greater, especially for NaCl, and the validity of the
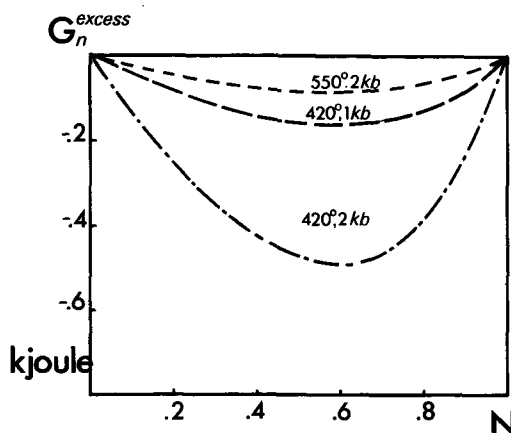
FIG. 2. Evaluation of the excess free energy of mixing of 2.2 molal $KCl-H_2O$ and $NaCl-H_2O$ solutions as a function of $N = KCl/(KCl + NaCl)$.

ideal mixing assumption must be checked. The excess free energy of mixing of KCl and NaCl solutions, G_n^{ex}, and dG_n^{ex}/dN have been derived from available data on the dissociation constants (Quist and Marshall, 1968a, b; Ritzert and Franck, 1968). The calculation is detailed in the appendix. The values of G_n^{ex} for 2.2 m solutions are plotted in fig. 2. The values of dG_n^{ex}/dN related to each experimental run (Table I) were used to calculate the mixing properties of the mica solid solution and ΔG_r° from relation (4).

Assuming that the mica solid solution follows the

so-called 'regular asymmetric' solution model then (4) can be rewritten as:

$$Z = \Delta G_r^\circ - dG_n^{ex}/dN + W_{G1}X(2-3X) + W_{G2}(1-X)(1-3X) \quad (5)$$

where $\quad Z = -RT\ln\left(\dfrac{X}{1-X}\dfrac{1-N}{N}\right).$

Z is an experimentally measured quantity, and the right hand side a linear function of the unknown ΔG_r°, W_{G1}, W_{G2}. We calculated simultaneously, by a least square fit, the values of ΔG_r° and W_G (1 bar), using the relation: $W_G = W_E - T \cdot W_S + P \cdot W_V$, with W_V from Eugster et al. (1972): $W_{V1} = 0.6646$ J/mol·bar, $W_{V2} = -0.4556$ J/mol·bar. Each measurement was weighed by the square reciprocal of the uncertainty on Z.

The results of the fits are given in fig. 1 and Table II. A similar calculation, assuming ideal mixing for the fluid ($dG_n^{ex}/dN = 0$), is given for comparison (Table III).

Discussion

Free energy of mixing of the fluid. The quality of the adjustments is good in all the concentration range investigated, for both non-ideal fluid mixing and ideal fluid mixing interpretations: no systematic differences between calculated and measured values of Z appear (fig. 1). The two series of fits lead to values of W_G which are close to one another (Tables II and III). As pointed out by Delbove and Sabatier (1974), it is difficult to draw

TABLE II. Numerical values of mica solid solution excess mixing parameters and ΔG_r° fitted on experimental data with calculated values of dG_n^{ex}/dN. Inferred values of the binodal compositions x_1^{ms}, x_2^{ms}, and of $\Delta G_{KCl}^\circ - \Delta G_{NaCl}^\circ$.

t (°C)	420	420	550
P (bars)	1000	2000	2000
ΔG_r°(J)	-17259	-18268	-16018
σ	343	280	168
W_{G1}(1 bar)	5996	4004	6348
σ	908	791	312
W_{G2}(1 bar)	14781	13687	16785
σ	724	586	277
$\rho(W_{G1},W_{G2})$ corr. coeff.	-0.78	-0.76	-0.60
Minim. funct. Deg. of freedom	4.4 / 9	22.3 / 11	18.2 / 15
Solvus 1 bar	0.12 , 0.56 (0.03) (0.03) -0.89	0.16 , 0.46 (0.05) (0.05) -0.98	0.15 , 0.51 (0.01) (0.01) -0.94
x_1^{ms}, x_2^{ms} 1 kbar	0.15 , 0.55 (0.04) (0.04) -0.90	0.21 , 0.40 (0.09) (0.09) -0.99	0.18 , 0.49 (0.02) (0.02) -0.96
(σ_1) (σ_2) 2 kbar $\rho(X_1,X_2)$	0.18 , 0.53 (0.06) (0.05) -0.92		0.22 , 0.45 (0.03) (0.03) -0.98
$\Delta G^\circ_{musc-para}$	-47396	-46559	-48701
$\Delta G^\circ_{KCl-NaCl}$	-30137	-28291	-32683

TABLE III. Numerical values of mica solid solution excess mixing parameters and ΔG_r° fitted on experimental data assuming $dG_n^{ex}/dN = 0$. Inferred values of the binodal compositions x_1^{ms}, x_2^{ms}, and of $\Delta G_{KCl}^\circ - \Delta G_{NaCl}^\circ$.

t (°C)	420	420	550	620	620
P (bars)	1000	2000	2000	7000	2000
ΔG_r°(J)	-16598	-16552	-15592	-13409	
σ	343	280	168		
W_{G1}(1 bar)	6075	4443	6689		
σ	908	791	312		
W_{G2}(1 bar)	14803	13652	16649		
σ	724	586	277		
$\rho(W_{G1},W_{G2})$ corr. coeff.	-0.78	-0.76	-0.60		
Minim. funct. Deg. of freedom	4.1 / 9	19.5 / 11	18.0 / 15		
Solvus 1 bar	0.12 , 0.56 (0.03) (0.03) -0.88	0.17 , 0.46 (0.05) (0.05) -0.98	0.16 , 0.50 (0.02) (0.02) -0.95		
x_1^{ms}, x_2^{ms} 1 kbar	0.15 , 0.55 (0.04) (0.04) -0.90	0.23 , 0.46 (0.10) (0.10) -0.99	0.19 , 0.48 (0.02) (0.02) -0.96		
(σ_1) (σ_2) 2 kbar $\rho(X_1,X_2)$	0.18 , 0.53 (0.06) (0.06) -0.91		0.24 , 0.44 (0.04) (0.04) -0.98		
$\Delta G^\circ_{musc-para}$	-47396	-46559	-48701	-45658	
$\Delta G^\circ_{KCl-NaCl}$	-30798	-29907	-33109	-32249	-37065

conclusions from one exchange isotherm on the mixing properties of both solid and hydrothermal solutions. However, it seems that the hydrothermal solution mixture is close to ideal, at any K/Na ratio, even at those conditions where NaCl is appreciably ionic. This conclusion is supported by the very small order of magnitude of G_n^{ex} calculated from conductivity data (fig. 2). Further, for (Na,K)Cl solutions, the independence of fluid composition equilibrated with a perthite, both on pressure (Iiyama, 1970) and on concentration (Orville, 1972; Lagache and Weisbrod, 1977) indicates that the excess free energy of mixing for (Na,K)Cl solutions is not much changed even by large changes in ionization.

Mixing properties of the solids. The good quality of Z adjustments has been pointed out above; no systematic deviation can be observed even close to the end members of the solutions as is the case with alkali feldspar. The four isotherms give consistent values of the W_G of the mica with a small dependence on temperature which is considered a good test of the adequacy of the mixing model chosen for the mica.

The values of W_{G1} and W_{G2} at 420 and 550 °C were used to calculate the miscibility gap: the binodal values X_1, X_2 of $X_{muscovite}$ at 1 bar, 1 kbar, and 2 kbar are given in Tables II and III. The uncertainties in X_1 and X_2 were calculated from the uncertainties on the fitted values of W_{G1} and W_{G2}. However, the binodal compositions at pressures different from the experimental pressure cannot be relied upon, because the accuracy of W_V values was not considered, especially concerning polytypism problems. A more detailed discussion of the mixing properties of the mica solid solution will be published by Chatterjee and Flux.
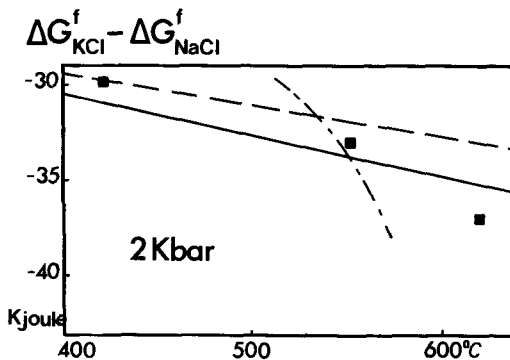

FIG. 3. Values of $\Delta G_{KCl-NaCl}^{\circ}$: solid squares (this study); solid line, determination from feldspar-fluid equilibria; dashed line, determination from nepheline-fluid equilibria; dashed curve, determination from mica-fluid equilibria (the three latter lines from Pascal and Roux, 1982).

Values of $\Delta G_{KCl-NaCl}^{\circ}$. The values of $\Delta G_n^{\circ} = \Delta G_{KCl}^{\circ} - \Delta G_{NaCl}^{\circ} = \Delta G_r^{\circ} - (\Delta G_{muscovite}^{\circ} - \Delta G_{paragonite}^{\circ})$ derived of the adjustments of Z function (thermochemical data for the micas from Helgeson et al., 1978) have been recast on the same plot used by Pascal and Roux, 1982 (fig. 3).

The value of $\Delta G_n^{\circ}(620°, 2\,kbar)$ was obtained from the experimental data of Chatterjee and Flux at 7 kbar (pers. comm.). The pressure correction down to 2 kbar was estimated using the experimental determination of the $KCl/(KCl + NaCl)$ ratio in aqueous solution equilibrated with a perthite at 600 °C and pressures from 1 to 7 kbar (Iiyama, 1970). For each equilibrium, $\Delta G_r^{ofeldspar}(600\ °C, P)$ was calculated (P from 1 to 7 kbar), assuming an ideal state for the fluid and using for the feldspars the mixing parameters derived from the two-phase data of Lagache and Weisbrod (1977) and Luth (1972):

$$W_{Ab}\ (J) = 9180 - 1.322\ T(K) + 0.3991\ P(bar);$$
$$W_{Or}\ (J) = 25\,598 - 9.518\ T(K) + 0.4686\ P(bar).$$

$\Delta G_n^{\circ}(600°, P)$ was calculated from $\Delta G_r^{\circ}(600°, P)$ (Iiyama ion exchange data up to 7 kbar), and free energies of formation from Helgeson et al. (1980):

$$\Delta G_n^{\circ}(600°, 2\ kbar) = -33\,756\ J,$$
$$\Delta G_n^{\circ}(600°, 7\ kbar) = -28\,941\ J.$$

The pressure effect on ΔG_n° between 2 and 7 kbar at 620° is believed to be satisfactorily approximated by that at 600°.

The results obtained are in very good agreement in both absolute magnitude and temperature dependence with our previously proposed values. The values of ΔG_n° at 2 kbar (Table III) are represented by:

$$\Delta G_{KCl}^{\circ} - \Delta G_{NaCl}^{\circ} = -18\,152 - 19.41\ T_{(K)}\ \text{Joules}.$$

Conclusions

Although Na salts are much more dissociated than K salts in mixed aqueous solutions, no significant deviation from ideal mixing of these solutions can be detected from the ion-exchange data. This is consistent with the evaluation of the free energy of mixing based upon the speciation determination.

The mica s.s. W_G and ΔG_n° adjusted from our isotherms, together with their counterpart for alkali feldspars, have been used to determine the muscovite mole fraction in the mica coexisting with two alkali feldspars (disordered): 0.91 at 400 °C, 0.86 at 500 °C, 0.82 at 600 °C. These results resolve the problem noticed by Gunter and Eugster (1980) who, in a similar calculation, found that the mica was a nearly pure paragonite at 500 and 600 °C

TABLE IV. Conventional dissociation constants of aqueous KCl and NaCl and Debye-Huckel activity coefficient parameters A and B (molal units). In these units, A and B depend on the molality and the density of the solution: the values have been estimated for 2.2 m solutions; for mixed KCl-NaCl solutions, A and B have been approximated by:

$A = N\ A_{KCl} + (1-N)A_{NaCl}$ and $B = N\ B_{KCl} + (1-N)B_{NaCl}$.

$(\mathring{a} \approx 3.72\ 10^{-8}cm\ )$.

T ($^\circ$C)	P (bar)	$\log \dfrac{a_K{}^+ a_{Cl}{}^-}{a_{KCl}{}^\circ}$	$\log \dfrac{a_{Na}{}^+ a_{Cl}{}^-}{a_{NaCl}{}^\circ}$	A_{KCl}	A_{NaCl}	$B_{KCl} 10^{-8}$	$B_{NaCl} 10^{-8}$
420	1000	-2.57	-1.43	1.40	1.45	0.394	0.406
420	2000	-2.31	-0.65	1.08	1.11	0.379	0.389
550	2000	-2.78	-1.87	1.51	1.56	0.397	0.409

[using the composition of the fluid in equilibrium with a perthite (Lagache and Weisbrod, 1977), various data on the compositions of fluids at equilibrium with micas, and the mica s.s. Margules parameters deduced from the solvus determination by Chatterjee and Froese, 1975].

The miscibility gap calculated from the W_G parameters is smaller than that directly determined by Chatterjee and Froese (1975). This result is consistent with the composition of natural coexisting muscovite (62% muscovite) and paragonite (12% muscovite) observed in sillimanitic rocks from New Mexico, where the metamorphic conditions have been estimated to 4.5-5 kbar and 550 °C (Grambling, 1984).

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Appendix

(a) <u>Speciation determination</u>. The reaction of dissociation of KCl is: (1) $KCl^\circ + k\ H_2O = K(H_2O)_i^+ + Cl(H_2O)_j^-$ According to Quist and Marshall (1968a and b), the hydration number of the KCl° (and $NaCl^\circ$) molecules is 2; this hydration number is increased of k (k' for NaCl) by the ionisation of 1 mole of KCl (NaCl). Quist and Marshall(op. cit.) proposed <u>k</u> = 9 and k'= 10 for our experimental conditions. Recently, Wood et al. (1984) checked that these values allow a good representation of the salt solutions properties.

$K(H_2O)_i^+$ and $Cl(H_2O)_j^-$ will be designated by K^+ and Cl^- The equilibrium between ions and neutral molecules is expressed by :(2) $k\ \mu_{H_2O} + \mu_{KCl^\circ} - \mu_{K^+} - \mu_{Cl^-} = 0$ The chemical potentials, ν_i, are of the form:

$$\mu_{H_2O} = \mu_{H_2O}^\circ - RT\ \frac{\Sigma n_{(solutes)}}{n_{H2O}} + RT\ \ln \gamma_{H_2O}$$

$$(3)\quad \mu_{KCl^\circ} = \mu_{KCl^\circ}^\circ + RT\ \ln(\frac{n_{KCl^\circ}\ \gamma_{KCl^\circ}}{n_{H_2O}}\ 55.51)$$

$$\mu_{K^+Cl^-} = \mu_{K^+} + \mu_{Cl^-} = \mu_{K^+Cl^-}^\circ + 2\ RT\ \ln \frac{\gamma_\pm\ n_{K^+Cl^-}}{n_{H_2O}}\ 55.51$$

(Prigogine and Defay, 1954), using the conventional standard states for the solvent and solutes. Relation (2) becomes:

$$(4)\ -\frac{\Delta G^\circ}{RT} = \ln\ (\frac{\gamma_\pm^2 n_{K^+}\ n_{Cl^-}}{\gamma_{KCl^\circ} n_{KCl^\circ}}\ \frac{55.51}{n_{H_2O}}) + k\ RT(\frac{n_{K^+} + n_{Cl^-} + n_{KCl^\circ}}{n_{H_2O}} - \ln \gamma_{H_2O})$$

$$= \ln C_{KCl}$$

At infinite dilution, C_{KCl} and C_{NaCl} are identical to the conventional dissociation constants expressed in molal units. (table IV). In a m-molal chloride solution, for the amount of fluid containing one mole of Cl :

$n_{K^+} = Nb$ (b = dissociated fraction of KCl)

$n_{Na^+} = (1-N)b'$ (b'= dissociated fraction of NaCl)

$n_{Cl^-} = Nb + (1-N)b'$

n_{H_2O}, number of moles of 'free' water (not including hydration water), is a function of N: $n_{H_2O}(N) = \frac{55.51}{m} - 2 - (Nkb + (1-N)k'b')$ In the mixed KCl-NaCl fluid, the distribution of species satisfies to the following relations (5):

$$\ln(\frac{\gamma_\pm^2 b(Nb + (1-N)b')}{\gamma_{KCl^\circ}(1-b)}\frac{55.51}{n_{H_2O}}) + kRT(\frac{N(1+b) + (1-N)(1+b')}{n_{H_2O}} - \ln \gamma_{H_2O}) = \ln C_{KCl}$$

and the equivalent for NaCl. The speciation is calculated with the activity coefficients :

- for molecular species, $\gamma = 1$

- for ions, the Debye-Hückel activity coefficient is:

$$\log \gamma_\pm = -\frac{A\ \sqrt{I}}{1 + B\mathring{a}\sqrt{I}}\qquad \begin{array}{l} I = \text{ionic strength in mol/kg } H_2O\quad (6) \\ (A, B, \mathring{a}\ \text{in table IV}) \end{array}$$

-for the solvent, the activity coefficient γ_{H_2O} is derived from $\gamma_\pm$ by the Gibbs-Duhem relation : $\frac{d(\ln \gamma_{H2O})}{dI} = \frac{A}{mn_{H2O}}\frac{\sqrt{I}}{(1 + B\mathring{a}\sqrt{I})^2}$

The dissociated fractions of KCl and NaCl and the activity coefficients for each run are indicated in table I. Using these rigorous equilibrium expressions, the concentrations may be expressed in molalities instead of molarities, without any significant difference in the results. On the contrary, a conventional calculation assuming $a(H_2O)=1$ would lead to much larger ionization degrees – and much larger excess free energies of mixing, inconsistent with the experimental data.

(b) Determination of $G_n^{ex}(N)$. $G_n^{ex}(N) = G_n^{mix}(N) - G_n^{ideal}(N)$ (7)

$G_{\underline{n}}^{mix}$ is expressed as $\Sigma n_i \nu_i$:

$n_{H_2O}\mu_{H_2O} + n_{KCl^\circ}\mu_{KCl^\circ} + n_{K^+Cl^-}\mu_{K^+Cl^-} + n_{NaCl^\circ}\mu_{NaCl^\circ} + n_{Na^+Cl^-}\mu_{Na^+Cl^-}$

Taking account of (2), $G_n^{mix}(N)$ becomes:

$$(8)\ G^{mix}(N) = (\frac{55.51}{m} - 2)\mu_{H_2O} + N(1-b)\mu_{KCl^\circ} + (1-N)(1-b')\mu_{NaCl^\circ}$$

$$(9)\ G_n^{ideal}(N) = NG_{KCl} + (1-N)G_{NaCl} + NRT\ \ln N + (1-N)RT\ \ln(1-N)$$

with: $G_{KCl} = G_n^{mix}(1)$ and $G_{NaCl} = G_n^{mix}(0)$.

(7) can be developped using the expressions of the chemical potentials (3):

$$G_n^{ex}(N) = NRT\ \ln(\frac{(1-b)}{(1-a)}\frac{n_{H_2O}(1)}{n_{H_2O}(N)}) + (1-N)RT\ \ln(\frac{(1-b')}{(1-a')}\frac{n_{H_2O}(0)}{n_{H_2O}(N)})$$

$$+ (\frac{55.51}{m} - 2)RT(\frac{N(1+a)}{n_{H_2O}(1)} + \frac{(1-N)(1+a')}{n_{H_2O}(0)} - \frac{N(1+b) + (1-N)(1+b')}{n_{H_2O}(N)})$$

$$+ (\frac{55.51}{m} - 2)RT(\ln \gamma_{H_2O}(N) - N\ln \gamma_{H_2O}(1) - (1-N)\ln \gamma_{H_2O}(0))$$

$$\frac{dG_n^{ex}}{dN} = RT\ \ln\frac{(1-b)(1-a')n_{H_2O}(1)}{(1-b')(1-a)n_{H_2O}(0)} + (\frac{55.51}{m} - 2)RT\ (\frac{1+a}{n_{H_2O}(1)} - \frac{1+a'}{n_{H_2O}(0)} - \ln\frac{\gamma_{H_2O}(1)}{\gamma_{H_2O}(0)})$$

Numerical values are given in table I.