

INDIRECT CALCULATION OF THE PARTIAL FREE ENERGY OF ALBITE AND ORTHOCLASE IN ALKALI FELDSPAR. [1]

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Orville in his thesis "Alkali ion exchange between vapor and feldspar phases" [2] suggests a method for calculating the partial molar free energy of the pure alkali phases in the mixed crystal region. Orville studied the equilibrium of solubility of K^+ and Na^+ in a vapor phase and in the alkali feldspar crystals; the vapor phase consisted of a 2-n solution of KCl and NaCl with different ratios of K and Na. The results for different temperatures at 2000 bars are given in Figure 3 of his paper in this volume (page FFF).

The concentration ratio $\frac{K}{K+Na}$ for feldspar and coexisting chloride solution is given in Table 1.

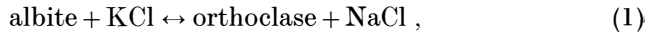
Table 1.

$\frac{K}{K+Na}$	-ratio in alkali feldspar and coexisting vapor phase (after Orville).									
$t = 700^\circ C$	feldspar	4	17	31	58	74	90	95	96	%
	vapor	16	23	25	28	34	51	71	75	%
$t = 600^\circ C$	feldspar	4	9	12	misc.gap	68	84	95	96	%
	vapor	18	21	23	23	32	50	75	%

[1] Manuscript submitted November 21st 1962.

[2] In press in the American Journal of Science. We thank Dr. Orville for kindly making the manuscript of his paper available to us.

From the equation of chemical equilibrium



follows the relation of the partial free energy:

$$F_{\text{NaCl}} - F_{\text{KCl}} = F_{\text{alb}} - F_{\text{or}} = \Delta F_{\text{feldspar}} \quad (2)$$

If one assumes an ideal mixture of the alkali chloride solution, one can calculate the partial free energy as a function of the mole fraction x by

$$F(x) = F(l) + RT \ln x \quad (3)$$

where $F(l)$ is the free energy of the pure end members.

From the assumptions mentioned above one can calculate the left side of equation (2) which is demonstrated in Figure 1 for 700° ; the left side of the figure shows the partial free energy for NaCl and KCl in the solution of the H_2O -phase, the right side $F_{\text{NaCl}} - F_{\text{KCl}} = \Delta F_{\text{chloride}}$. The values of Table 1 allow us to construct the $\Delta F_{\text{feldspar}}$ curve from the known $\Delta F_{\text{chloride}}$ values; for instance at 700° the

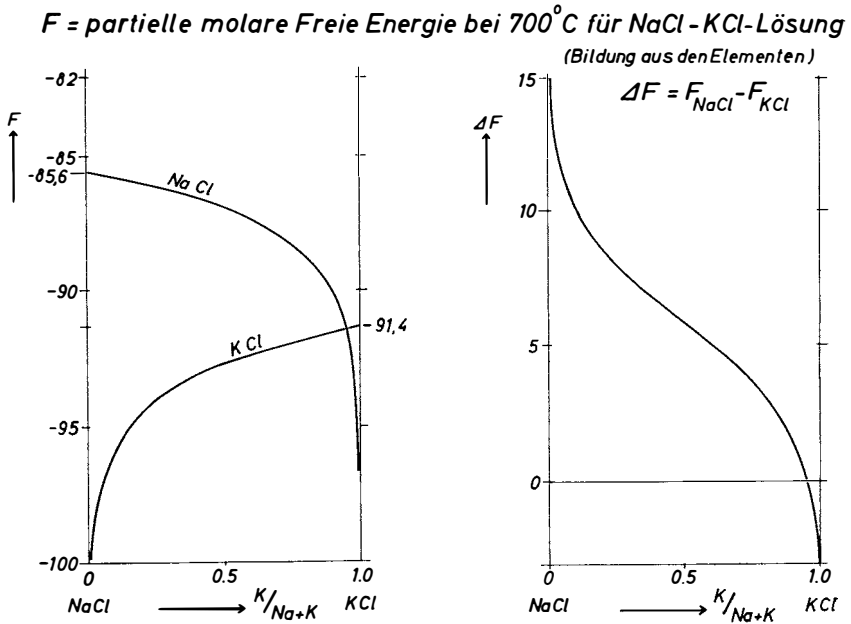


Fig. 1.

$F =$ partielle molare Freie Energie bei 700°C für Alkalifeldspäte

(aus $\text{Na(K)}\text{flüssig}, \frac{1}{4}\text{O}_2, \frac{1}{2}\text{Al}_2\text{O}_3, 3\text{SiO}_2$)

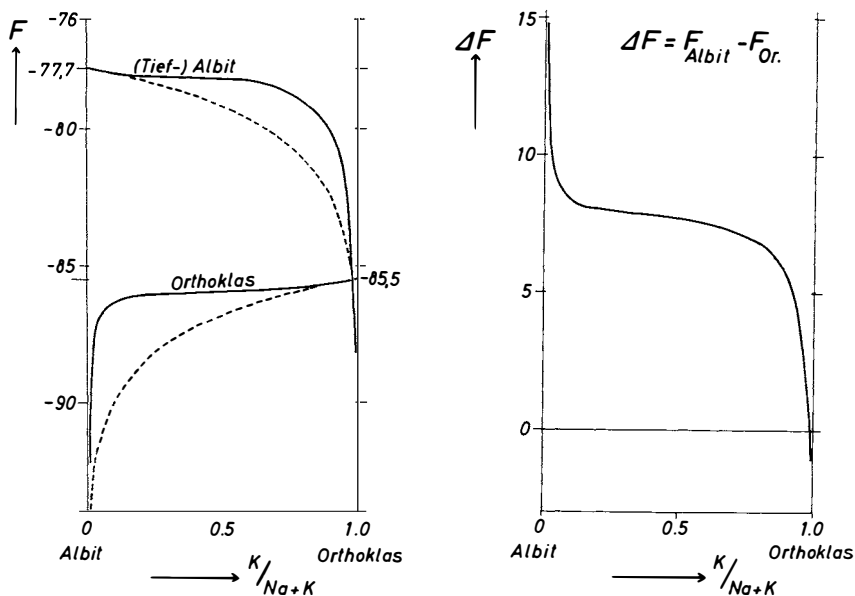


Fig. 2.

$\Delta F_{\text{chloride}}$ for $x=0.28$ is equal to the $\Delta F_{\text{feldspar}}$ of the coexisting feldspar with $x=0.58$ (see Figure 2). From this $\Delta F_{\text{feldspar}}$ curve it is possible to construct the F_{albite} and $F_{\text{orthoclase}}$ curves from the free energy of the end members, remembering that the curve has to show a continuous slope, because no miscibility gap exists at 700° . (The stippled lines give the curves for an ideal mixed crystal). The actual curves indicate by their nearly horizontal slopes in the range $x=0.20-0.70$ the proximity of a miscibility gap at lower temperatures. In the same manner the calculations were done for 600°C (Figure 3). In the unstable region of the miscibility gap the curves are dotted, because these values cannot be realized in nature.

The method of Orville seems well suited for calculating partial free energies for other mixed crystal minerals.

The F -values for the feldspars were calculated from the heat of formation of the oxides, except for Na_2O and K_2O ; the free energy of the chlorides was calculated from the elements; an extrapolation

was made for the hydration energy of the chlorides, because these values are not known from the literature.

The following data were used for calculating the free energy values (Tables 2 and 3).

Table 2. Thermodynamic constants (after Handbook of Physics and Chemistry, 43th Ed. 1961-62).

$$C_p = a + b \cdot T + c \cdot T^2 + d \cdot T^{-2} \text{ cal/grad mole}$$

	<i>a</i>	<i>b</i> ·10 ³	<i>c</i> ·10 ⁶	<i>d</i> ·10 ⁻⁵	S298°·K
Na ₂ O	15.70	5.40	—	—	17.4 cal/grad mole
K ₂ O	15.9	6.4	—	—	23.4
Al ₂ O ₃	26.12	4.39	—	-7.27	12.19
SiO ₂ (β)	11.22	8.20	—	-2.70	10.00
NaAlSi ₃ O ₈	63.78	11.71	—	-16.78	49.20
KAlSi ₃ O ₈	63.83	12.90	—	-17.05	52.50
Na liquid	8.95	-4.58	2.54	—	14.0
K liquid	8.88	-4.56	2.94	—	16.9
Cl ₂	8.76	0.27	—	-0.65	53.29
NaCl	10.76	4.20	—	—	17.30
KCl	10.93	3.76	—	—	19.76
O ₂	8.27	0.258	—	-1.877	49.00

Table 3(a). Formation from oxydes.

	Δ <i>H</i> 25 °C	Δ <i>F</i> 700 °C	Δ <i>F</i> 600 °C
low albite	-41.2	-44.5	-44.0 Kcal/mole
high albite	-39.0	-42.3	-41.8
orthoclase	-56.3	-60.0	-59.3

Table 3(b). Formation from elements (liquid metals).

	Δ <i>H</i> 25 °C	Δ <i>F</i> 700 °C	Δ <i>F</i> 600 °C
$\frac{1}{2}$ Na ₂ O		-33.2	-35.0 Kcal/mole
$\frac{1}{2}$ K ₂ O		-25.5	-27.4
NaCl	-98.86	-76.66	-78.94
KCl	-100.74	-78.08	-80.41

Table 3(c). Hydration energy.

Δ <i>F</i>	25 °C	700 °C	600 °C
NaCl	-2.15	-9.07	-8.07 Kcal/mole
KCl	-1.23	-13.35	-11.57

The used Δ*F* values of Figure 1 are the sums of Table 3(b) and 3(c); the values of Figure 2 and 3 are the sums of the Δ*F* values in Tables 3(a) and 3(b).

F = partielle molare Freie Energie bei 600° C für Alkalifeldspäte

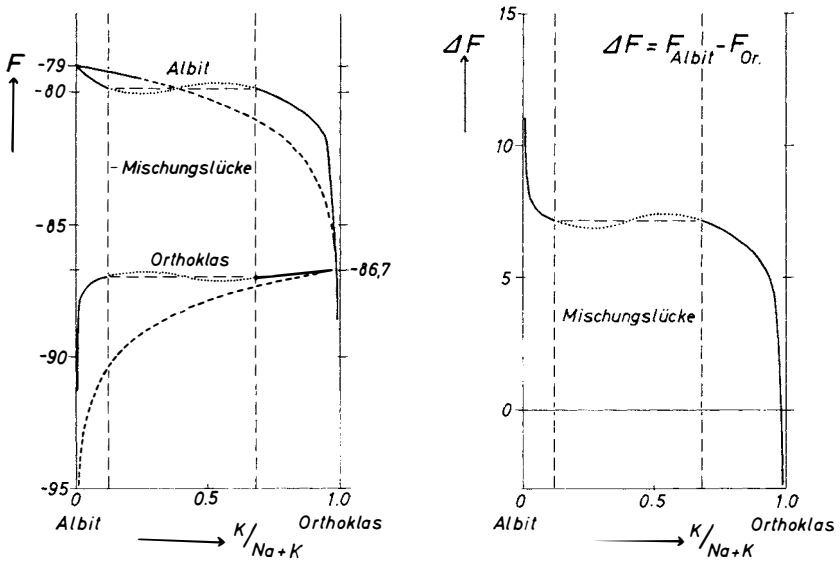


Fig. 3.