Theory of Isomorphous Replacement in Aluminosilicates

R. M. Barrer and J. Klinowski

Phil. Trans. R. Soc. Lond. A 1977 **285**, 637-676
doi: 10.1098/rsta.1977.0107

THEORY OF ISOMORPHOUS REPLACEMENT IN ALUMINOSILICATES

By R. M. BARRER, F.R.S. and J. KLINOWSKI
Physical Chemistry Laboratories, Chemistry Department, Imperial College, London SW7 2AY

(*Received* 1 *March* 1976)

CONTENTS

In § 1 the statistical thermodynamic treatment of ion exchange has been developed for a system in which there is one kind of exchange site (for example, sodalite or felspar). In an earlier treatment (Barrer & Falconer 1956) it was assumed that when two entering ions occupied adjacent sites an extra energy could arise which was not present when these ions did not occupy nearest neighbour positions. It was also assumed that despite this pair-wise additive extra energy the distribution of ions on sites was random. This latter assumption has now been removed, the consequences of its removal examined, and the resultant treatment applied to calculation of characteristic isotherm contours, thermodynamic equilibrium, free energy function for the mixed crystals, miscibility gaps between end members of the exchange and the influence of temperature and other factors upon such gaps. The treatment can represent and explain many of the features established experimentally in exchanges involving zeolites, felspars, felspathoids and clay minerals, especially when it is extended, as has been done in § 2, to allow for situations in which there is more than one kind of exchange site, a situation which is common among zeolites. After considering the general case of *n* different site groups in the exchanger and deriving expressions for the chemical potentials and equilibrium constants in terms of contributions from component site groups, calculations have been made in § 2 of representative isotherm contours for the particular situations:

(i) Two site groups, each fully exchangeable by ion A and ion B.
(ii) Two site groups, one excluding ion A and the other excluding ion B.
(iii) Two site groups, one available for both A and B and the other only for B.

For the first situation the occurrence of miscibility gaps has also been investigated.

In § 3 the theory has been extended to isomorphous replacements of the types Na, Al $\rightleftarrows$ Si and Ca, Al $\rightleftarrows$ Na, Si in tectosilicate frameworks. Certain tectosilicates have nearly fixed Al/Si ratios while in others these ratios may vary within wide limits. In addition it is found experimentally that in tectosilicates Al/Si ratios do not exceed unity. The treatment developed can satisfy these three characteristics. The free energy function plotted against Al content exhibits a minimum the position, depth and sharpness of which depend upon the values of certain constants which have a clear physical meaning. The compositions of some zeolites and felspathic minerals have been interpreted in terms of the free energy function.

GENERAL INTRODUCTION

Isomorphous replacement is one of the most important chemical processes characterizing both natural and synthetic aluminosilicates. Such replacement can occur by cation exchanges of the kinds

$$\mathrm{Na} \rightleftarrows \mathrm{K}, \qquad 2\mathrm{Na} \rightleftarrows \mathrm{Ca}.$$

Although these reactions are very simple in terms of their stoichiometry investigations of ion exchange in zeolites, felspathoids, felspars and clay minerals have revealed a number of situations for which quantitative treatments are either inadequate or do not exist. These situations include the following:

case	example
1. There is one kind of cation site available for both cations	Sodalite hydrate and ions Li, Na, Ag (Barrer & Falconer 1956). Alkali metal felspar and Na and K (Orville 1963). Clay minerals and alkali and alkaline earth metal cations (Barrer & Jones 1971).
2. There is more than one kind of cation site available for both cations	Many zeolites and common cations (Smith 1971; Sherry 1971; Barrer, Davies & Rees 1969; Barrer & Munday 1971*a*, *b*, *c*; Barrer & Klinowski 1974*b*). Cancrinite hydrate and Li, Na and Ag (Barrer & Falconer 1956)

3. There is more than one kind of cation site, all types available for one cation but some not available for the other	Some zeolites and cations of disparate sizes (Barrer & Falconer 1956; Barrer, Papadopoulos & Rees 1967)
4. Cations of one kind occupy only certain types of site; cations of the other kind occupy only sites of another type	Faujasite with Na and tetramethylammonium (Barrer, Buser & Grütter 1956)

A statistical thermodynamic treatment of case 1 has been given (Barrer & Falconer 1956), as have formal treatments of case 2 (Barrer & Klinowski 1972) and of case 3 (Barrer, Klinowski & Sherry 1973). It will be a purpose of this work to improve the statistical thermodynamic formulation for case 1 and to extend this formulation to other cases (§§ 1 and 2).

However, the isomorphous replacements involved in cation interchange are not the only kinds or indeed even the most important. Other processes are exemplified by the following reactions

$$\mathrm{Na, Al} \rightleftarrows \mathrm{Si}, \qquad \mathrm{Ca, Al} \rightleftarrows \mathrm{Na, Si}.$$

The first of these is often found among both natural and synthetic zeolites (see, for example, Breck 1974); the second is exemplified among the felspars (Bragg & Claringbull 1965). No theoretical treatment of these reactions exists and accordingly a further objective will be the statistical thermodynamic treatment of these substitutions (§ 3).

1. CATION EXCHANGE ON A HOMOGENEOUS GROUP OF EXCHANGE SITES

(a) *Introduction*

Barrer & Falconer (1956) made a first approximation to the statistical thermodynamics of exchange by adapting the theory of localized adsorption with interaction (Lacher 1937; Fowler & Guggenheim 1939). Barrer & Falconer assumed a random distribution of cations among sites even when extra energy changes occurred whenever two entering ions occupied adjacent sites. Despite this the treatment successfully accounted for three major kinds of exchange isotherm: ideal (extra energy approximately zero); sigmoid (extra energy positive (endothermic)); or showing two-phase regions (extra energy sufficiently negative). For uni-univalent exchanges a physical interpretation was also obtained of the nearly linear plots of $\ln K_c$ against cation equivalent fractions which are sometimes observed experimentally (K_c is defined in equation (1.3)).

These successes suggest that an advance could result if the assumption of random distribution of ions on exchange sites was removed and the study extended to include exchanges involving multivalent cations. The consequences are examined in § 1 for a single homogeneous group of exchange sites as found in certain minerals (general introduction).

(b) *The ion-exchange reaction*

The general exchange reaction is

$$Z_{\mathrm{A}}\,\mathrm{B}_{\mathrm{c}}^{Z_{\mathrm{B}}^{+}} + Z_{\mathrm{B}}\,\mathrm{A}_{\mathrm{s}}^{Z_{\mathrm{A}}^{+}} \rightleftarrows Z_{\mathrm{A}}\,\mathrm{B}_{\mathrm{s}}^{Z_{\mathrm{B}}^{+}} + Z_{\mathrm{B}}\,\mathrm{A}_{\mathrm{c}}^{Z_{\mathrm{A}}^{+}}, \tag{1.1}$$

where ions of species A have a charge Z_{A}^{+} and ions of B have a charge Z_{B}^{+}. The subscripts c and s refer to the crystalline phase and solution, respectively. The rational thermodynamic equilibrium constant K_a is then

$$K_a = \frac{A_{\mathrm{c}}^{Z_{\mathrm{B}}}(m_{\mathrm{s}}^{\mathrm{B}})^{Z_{\mathrm{A}}} f_{\mathrm{A}}^{Z_{\mathrm{B}}} \gamma_{\mathrm{B}}^{Z_{\mathrm{A}}}}{B_{\mathrm{c}}^{Z_{\mathrm{A}}}(m_{\mathrm{s}}^{\mathrm{A}})^{Z_{\mathrm{B}}} f_{\mathrm{B}}^{Z_{\mathrm{A}}} \gamma_{\mathrm{A}}^{Z_{\mathrm{B}}}}, \tag{1.2}$$

where A_c and B_c are equivalent cation fractions of A and B in the aluminosilicate and m_s^A, m_s^B are molalities in the solution. f_A, f_B, γ_A and γ_B are the corresponding activity coefficients.

We now define a quotient K_c related to ion selectivity by

$$K_c = \frac{A_c^{Z_B}(m_s^B)^{Z_A}\,\gamma_B^{Z_A}}{B_c^{Z_A}(m_s^A)^{Z_B}\,\gamma_A^{Z_B}} = \frac{A_c^{Z_B}(a_s^B)^{Z_A}}{B_c^{Z_A}(a_s^A)^{Z_B}}, \tag{1.3}$$

where the a_s are activities in solution. If we replace molalities in solution by equivalent cation fractions A_s and B_s, then (Barrer & Klinowski 1972)

$$K_a' = K_a\,Q = \frac{A_c^{Z_B}\,B_s^{Z_A}f_A^{Z_B}\,\Gamma}{B_c^{Z_A}A_s^{Z_B}f_B^{Z_A}}, \tag{1.4}$$

where

$$Q = Z_B^{Z_A}/[Z_A^{Z_B}(Z_A\,m_s^A+Z_B\,m_s^B)^{(Z_A-Z_B)}] \tag{1.5}$$

$$\Gamma = \gamma_B^{Z_A}/\gamma_A^{Z_B}. \tag{1.6}$$

The activity coefficients γ_A and γ_B in the solution refer at all times to the molarity scale, even when (equation (1.4)) the actual concentrations have been, for convenience, expressed as equivalent fractions. When cation concentrations are so expressed $(Z_A\,m_s^A+Z_B\,m_s^B)$ must also be given to define the absolute concentration of each aqueous ion.

(c) *The model*

A crystal in which there is only one kind of exchange site will be considered. In tectosilicates one may have more crystallographic cationic *sites* than there are framework *charges*. It follows that some sites then remain unfilled. If we consider a system containing cations A and B and including unfilled sites, O, the following pairs are involved:

OO, AO, BO, AA, AB, BB.

We make the following assumptions:

(i) When two entering ions, A, occupy adjacent sites, an additional change in energy of the crystal takes place. This change in energy is set equal to $2w_{AA}/\nu$ where w_{AA} is an energy term and ν is the coordination number of a site with respect to other sites. Of the above list of possible cation pairs, AA is the only pair which produces this extra energy, over and above the binding energy of unpaired A cations.

(ii) The change in energy is additive with respect to N_{AA}, the number of AA pairs, independently of whether these pairs are in clusters or isolated.

In the crystal there are N_A cations of A and N_B cations of B, distributed among N identical sites. The number of distinguishable ways of distributing the ions among the sites is

$$\frac{N!}{N_A!\,N_B!\,(N-N_A-N_B)!}. \tag{1.7}$$

We are at present concerned only with the cation exchange in an already formed and permanent aluminosilicate framework the amount of which is constant. The partition function for that amount of the anionic framework carrying one negative charge will be denoted by P_L so that if N_0 is the total charge the framework partition function is $P_L^{N_0}$ where

$$N_0 = Z_A\,N_A+Z_B\,N_B. \tag{1.8}$$

The partition function for the mixed crystal is then written as

$$P = \frac{N!}{N_A!\,N_B!\,(N-N_A-N_B)!}\,J_A^{N_A}\,J_B^{N_B}\,J_G^{N_G}\,P_L^{N_0}\,P^{\text{int}}. \tag{1.9}$$

In equation (1.9) J_A and J_B are the partition functions of a cation of A and B, respectively, in the anionic framework. There is a configurational part, $C(N_G)$, in the partition function of the N_G guest molecules. If J'_G is the partition function of a single intracrystalline guest throughout §§ 1, 2 and 3, we will for simplicity write $J_G^{N_G}$ for $C(N_G)\,(J'_G)^{N_G}$ because $J_G^{N_G}$ will not here be evaluated. In zeolites the guest is usually water but in some felspathoids it may be NaCl, Na_2CO_3, Na_2SO_4 and other species. In felspars and certain felspathoids there are no guest molecules so that $J_G^{N_G}$ can be omitted. In the general case N_G, J_G and P_L may change with cationic composition. P^{int} allows for the contribution to P arising from the extra energy $2w_{AA}/\nu$ when a pair of A ions occupy adjacent sites (assumptions (i) and (ii)).

(*d*) *Complete and incomplete exchange*

All quantities under the factorial in the partition function given by equation (1.9) must be greater than or equal to, zero. Thus also

$$N - N_A - N_B \geqslant 0$$

which divided by N_0 gives

$$\eta - A_c/Z_A - B_c/Z_B \geqslant 0,$$

where $\eta = N/N_0$. It follows that the crystal can be obtained in pure B-form only if $\eta \geqslant 1/Z_B$; and in pure A-form only if $\eta \geqslant 1/Z_A$. When η is greater than both $1/Z_A$ and $1/Z_B$ exchange can always proceed to completion; if the value of η lies between $1/Z_A$ and $1/Z_B$ there is incomplete exchange. If A is the entering ion, exchange can only be incomplete when $Z_A < Z_B$ *and* $\eta < 1/Z_A$. It is obvious that for cations of equal valence the exchange can always proceed to completion. Multiplying the previous inequality by $Z_A Z_B$ we obtain

$$Z_A(Z_B\eta - 1) - A_c(Z_B - Z_A) \geqslant 0,$$

which leads to the maximum equivalent fraction of A in the crystal as the lower of the two values:

$$A_c^{\max} = \frac{Z_A(Z_B\eta - 1)}{Z_B - Z_A}; \quad A_c^{\max} = 1.$$

TABLE 1. $A_c^{\max}$ FOR DIFFERENT Z_A, Z_B AND η

$Z_A = 1;\ Z_B = 2$		$Z_A = 1;\ Z_B = 3$		$Z_A = 2;\ Z_B = 3$	
η	$A_c^{\max}$	η	$A_c^{\max}$	η	$A_c^{\max}$
0.5	0	$\frac{1}{3}$	0	$\frac{1}{3}$	0
0.6	0.2	0.4	0.1	0.4	0.4
0.7	0.4	0.5	0.25	0.45	0.7
0.8	0.6	0.6	0.4	0.5	1.0
0.9	0.8	0.7	0.55		
1.0	1.0	0.8	0.7		
		0.9	0.85		
		1.0	1.0		

Table 1 gives the values of $A_c^{\max}$ for several combinations of Z_A and Z_B and different values of η. The behaviour predicted in table 1 may be illustrated for the case $Z_A = 1$, $Z_B = 2$ with reference to anorthite, the unit cell content of which is $4(CaAl_2Si_2O_8)$. The four cation sites available per unit cell are already occupied by four Ca^{2+} ions. To replace one Ca^{2+} by $2Na^+$ would require an additional site – one more than is available. Accordingly no exchange of this kind is possible. Any reaction would have to be of the kind

$$\text{Ca, Al} \longrightarrow \text{Na, Si}$$

to be discussed later (§ 3).

(*e*) *The ion-exchange equilibria*

The relation between the partition function and the Helmholtz free energy, F, is

$$F = -kT \ln P. \tag{1.10}$$

To calculate the logarithm of the partition function given by equation (1.9) Stirling's approximation is applied to all factorial terms. In the algebra which follows we have assumed $\Delta N > 0$. For the case when $\Delta N = (N - N_\mathrm{A} - N_\mathrm{B}) = 0$ the terms in $\Delta N \ln \Delta N$ must be omitted in equation (1.11) onwards. From equations (1.9) and (1.10) we have

$$\begin{aligned} F = -kT[&N \ln N - N_\mathrm{A} \ln N_\mathrm{A} - N_\mathrm{B} \ln N_\mathrm{B} - \Delta N \ln \Delta N + N_\mathrm{A} \ln J_\mathrm{A} \\ &+ N_\mathrm{B} \ln J_\mathrm{B} + N_\mathrm{G} \ln J_\mathrm{G} + N_0 \ln P_\mathrm{L}] + F^{\mathrm{int}}, \end{aligned} \tag{1.11}$$

where F^{int} is $-kT \ln P^{\mathrm{int}}$. The crystal may be considered as a solid solution of two components, $\mathrm{AL_A}$ and $\mathrm{BL_B}$ where $\mathrm{L_A}$ is the amount of anionic framework associated with an A ion and carrying anionic charge $\mathrm{Z_A}$ and $\mathrm{L_B}$ is this amount of framework associated with B and carrying anionic charge $\mathrm{Z_B}$. If Si/Al $= \delta$ then

$$\mathrm{AL_A} = \mathrm{A}[(\mathrm{Si}_\delta\mathrm{Al})\,\mathrm{O}_{2(1+\delta)}]_{Z_\mathrm{A}}; \quad \mathrm{BL_B} = \mathrm{B}[(\mathrm{Si}_\delta\mathrm{Al})\,\mathrm{O}_{2(1+\delta)}]_{Z_\mathrm{B}}.$$

The numbers of lattice-forming units $\mathrm{AL_A}$ and $\mathrm{BL_B}$ are then respectively equal to the total numbers N_A and N_B of ions A and B in the exchanger. If for the exchanger capable of full exchange for either A or B ions the standard states for $\mathrm{AL_A}$ and $\mathrm{BL_B}$ are defined as pure A-crystal ($\mathrm{AL_A}$) and pure B-crystal ($\mathrm{BL_B}$) then the standard quantities can be calculated from the values of partition functions *per mol* of $\mathrm{AL_A}$ and $\mathrm{BL_B}$. If N_G changes with electrolyte dilution N_G^* is the value of N_G in pure $\mathrm{AL_A}$ in equilibrium with infinitely dilute solution containing ion A; $N_\mathrm{G}^\vartriangle$ is the value of N_G in pure $\mathrm{BL_B}$ in equilibrium with infinitely dilute solution. We put $n_\mathrm{G}^* = N_\mathrm{G}^*/N_0$ and $n_\mathrm{G}^\vartriangle = N_\mathrm{G}^\vartriangle/N_0$. Let J_A^*, J_G^* and P_L^* be the values of J_A, J_G and P_L at the standard state with respect to A; the corresponding quantities superscripted with a triangle refer to the standard state with respect to B. The required standard chemical potentials are

$$\left.\begin{aligned} F_{\mathrm{AL_A}}^{\ominus} = \mu_{\mathrm{AL_A}}^{\ominus} = -RT \ln P_{\mathrm{AL_A}}^{\ominus} = -RT[&\mathrm{Z_A}\eta \ln \mathrm{Z_A}\eta - (\mathrm{Z_A}\eta - 1) \ln (\mathrm{Z_A}\eta - 1) \\ &+ \ln J_\mathrm{A}^* + \mathrm{Z_A} n_\mathrm{G}^* \ln J_\mathrm{G}^* + \mathrm{Z_A} \ln P_\mathrm{L}^* - \mathit{\Delta}_\mathrm{A}^*], \\ F_{\mathrm{BL_B}}^{\ominus} = \mu_{\mathrm{BL_B}}^{\ominus} = -RT \ln P_{\mathrm{BL_B}}^{\ominus} = -RT[&\mathrm{Z_B}\eta \ln \mathrm{Z_B}\eta - (\mathrm{Z_B}\eta - 1) \ln (\mathrm{Z_B}\eta - 1) \\ &+ \ln J_\mathrm{B}^\vartriangle + \mathrm{Z_B} n_\mathrm{G}^\vartriangle \ln J_\mathrm{G}^\vartriangle + \mathrm{Z_B} \ln P_\mathrm{L}^\vartriangle], \end{aligned}\right\} \tag{1.12}$$

where $\mathit{\Delta}_\mathrm{A}^*$ is the value of F^{int}/kT in pure A-crystal calculated for N_A = Avogadro's number. Since in pure B-crystal $F^{\mathrm{int}} = 0$ there is no term corresponding with $\mathit{\Delta}_\mathrm{A}^*$ for B-crystal.

The thermodynamic equilibrium constant for the exchange reaction (1.1) is

$$\ln K_a = (\mathrm{Z_A}\mu_{\mathrm{BL_B}}^{\ominus} - \mathrm{Z_B}\mu_{\mathrm{AL_A}}^{\ominus} + \mathrm{Z_B}\mu_{\mathrm{A_s}}^{\ominus} - \mathrm{Z_A}\mu_{\mathrm{B_s}}^{\ominus})/RT. \tag{1.13}$$

Taking $\mu_{\mathrm{AL_A}}^{\ominus}$ and $\mu_{\mathrm{BL_B}}^{\ominus}$ from equation (1.12) we obtain for $\ln K_a$

$$\begin{aligned} \ln K_a = {} & \mathrm{Z_A}(\mathrm{Z_B}\eta - 1) \ln (\mathrm{Z_B}\eta - 1) - \mathrm{Z_B}(\mathrm{Z_A}\eta - 1) \ln (\mathrm{Z_A}\eta - 1) + \mathrm{Z_A Z_B}\eta \ln (\mathrm{Z_A}/\mathrm{Z_B}) \\ & + \ln (J_\mathrm{A}^*)^{\mathrm{Z_B}}/(J_\mathrm{B}^\vartriangle)^{\mathrm{Z_A}} - \mathrm{Z_B}\mathit{\Delta}_\mathrm{A}^* + \mathrm{Z_A Z_B} \ln (P_\mathrm{L}^*/P_\mathrm{L}^\vartriangle) \\ & + \mathrm{Z_A Z_B} n_\mathrm{G}^* \ln J_\mathrm{G}^* - \mathrm{Z_A Z_B} n_\mathrm{G}^\vartriangle \ln J_\mathrm{G}^\vartriangle + \chi, \end{aligned} \tag{1.14}$$

where

$$\chi = (\mathrm{Z_B}\mu_{\mathrm{A_s}}^{\ominus} - \mathrm{Z_A}\mu_{\mathrm{B_s}}^{\ominus})/RT. \tag{1.15}$$

For $\mathrm{Z_A} = \mathrm{Z_B} = \mathrm{Z}$, equation (1.14) greatly simplifies.

(*f*) *The evaluation of* F^{int}

If we consider a system containing cations A, B ... and including unfilled sites, O, the following pairs are involved:

$$\text{OO, AO, BO} \ldots \text{AA, AB} \ldots \text{BB}, \ldots$$

N_{AA} will influence the numbers of other pairs, but these numbers are not required for our calculation of F^{int} since all pairs except AA do not produce any extra energy term. It has been shown (Barrer & Klinowski, in preparation) that F^{int} is not affected by the numbers of other pairs and that the expression obtained for F^{int} in the case of adsorption of a single substance (Lacher 1937; Fowler & Guggenheim 1939) applies. This expression is

$$F^{\text{int}} = kT\nu\left\{N_{\text{A}}\ln\frac{2(1-\theta_{\text{A}})}{D_{\text{AA}}-2\theta_{\text{A}}}+\tfrac{1}{2}N\ln\frac{D_{\text{AA}}-2\theta_{\text{A}}}{D_{\text{AA}}(1-\theta_{\text{A}})}\right\}, \tag{1.16}$$

where

$$\left.\begin{aligned} D_{\text{AA}} &= [1-4\theta_{\text{A}}(1-\theta_{\text{A}})\,\alpha_{\text{AA}}]^{\frac{1}{2}}+1,\\ \alpha_{\text{AA}} &= 1-\exp\left(-2w_{\text{AA}}/\nu kT\right),\\ \theta_{\text{A}} &= N_{\text{A}}/N = A_{\text{c}}/Z_{\text{A}}\eta. \end{aligned}\right\} \tag{1.17}$$

Barrer & Falconer (1956) assumed that the siting of ions A was random and therefore used the simpler expression for F^{int}

$$F^{\text{int}} = (N_{\text{A}}^2/N)\,w_{\text{AA}}. \tag{1.18}$$

(*g*) *Calculation of chemical potentials*

The chemical potentials μ_{AL_A} and μ_{BL_B} are

$$\mu_{\text{AL}_\text{A}} = \boldsymbol{L}(\partial F/\partial N_{\text{A}})_{\text{BL}_\text{B}};\quad \mu_{\text{BL}_\text{B}} = \boldsymbol{L}(\partial F/\partial N_{\text{B}})_{\text{AL}_\text{A}}, \tag{1.19}$$

where $\boldsymbol{L}$ is the Avogadro number.

The conditions of equation (1.19) can be met by adding more BL_B to a mixture containing a fixed amount of AL_A and vice versa. This operation involves increasing the total amount of the crystalline phase, and therefore increases N, the total number of sites available for cations (which may exceed $Z_{\text{A}}N_{\text{A}}+Z_{\text{B}}N_{\text{B}}$). From consideration of electrical neutrality (equation (1.8)) we have

$$N = \eta(Z_{\text{A}}N_{\text{A}}+Z_{\text{B}}N_{\text{B}}), \tag{1.20}$$

where, for the exchanger to be fully convertible into a univalent cationic form, one must have $N/N_0 = \eta \geqslant 1$. It follows that

$$(\partial N/\partial N_{\text{A}})_{\text{BL}_\text{B}} = Z_{\text{A}}\eta;\quad (\partial N/\partial N_{\text{B}})_{\text{AL}_\text{A}} = Z_{\text{B}}\eta. \tag{1.21}$$

In order to obtain general expressions for the chemical potentials μ_{AL_A} and μ_{BL_B} one must know how $J_{\text{A}}, J_{\text{B}}, J_{\text{G}}$, N_{G} and P_{L} vary with the cationic composition of the crystal. We assume that these quantities are independent of N_{A} and N_{B}.

The numbers of cations may be replaced by equivalent fractions A_{c} and B_{c}, where

$$N_{\text{A}} = N_0A_{\text{c}}/Z_{\text{A}};\quad N_{\text{B}} = N_0B_{\text{c}}/Z_{\text{B}}. \tag{1.22}$$

One then obtains the following expressions for the chemical potentials in equation (1.19):

$$\left.\begin{aligned} \mu_{\text{AL}_\text{A}} = {} & -RT[Z_{\text{A}}\eta\ln\eta-(Z_{\text{A}}\eta-1)\ln\left(\eta-A_{\text{c}}/Z_{\text{A}}-B_{\text{c}}/Z_{\text{B}}\right)\\ & +\ln Z_{\text{A}}+Z_{\text{A}}n_{\text{G}}\ln J_{\text{G}}+\ln J_{\text{A}}+Z_{\text{A}}\ln P_{\text{L}}-\ln A_{\text{c}}-\Delta_{\text{A}}],\\ \mu_{\text{BL}_\text{B}} = {} & -RT[Z_{\text{B}}\eta\ln\eta-(Z_{\text{B}}\eta-1)\ln\left(\eta-A_{\text{c}}/Z_{\text{A}}-B_{\text{c}}/Z_{\text{B}}\right)\\ & +\ln Z_{\text{B}}+Z_{\text{B}}n_{\text{G}}\ln J_{\text{G}}+\ln J_{\text{B}}+Z_{\text{B}}\ln P_{\text{L}}-\ln B_{\text{c}}-\Delta_{\text{B}}], \end{aligned}\right\} \tag{1.23}$$

where

$$\left.\begin{aligned}\Delta_{\mathrm{A}} &= \frac{1}{kT}\left(\frac{\partial F^{\mathrm{int}}}{\partial N_{\mathrm{A}}}\right)_{\mathrm{BL_B}},\\ \Delta_{\mathrm{B}} &= \frac{1}{kT}\left(\frac{\partial F^{\mathrm{int}}}{\partial N_{\mathrm{B}}}\right)_{\mathrm{AL_A}}.\end{aligned}\right\} \tag{1.24}$$

To obtain the chemical potentials Barrer & Falconer (1956) carried out the differentiation in equation (1.19) with respect to A_{c} and B_{c} instead of N_{A} and N_{B}. This overlooks the fact that one may not vary the equivalent fraction of one cation while keeping the equivalent fraction of the other cation constant. Consequently, their equations (7) are incorrect; this however does not affect the expression for K_a given in that paper or indeed any of its conclusions. For identity with the definition of chemical potentials

$$\left.\begin{aligned}\mu_{\mathrm{AL_A}}/RT &= \mu^{\ominus}_{\mathrm{AL_A}}/RT+\ln A_{\mathrm{c}}f_{\mathrm{A}},\\ \mu_{\mathrm{BL_B}}/RT &= \mu^{\ominus}_{\mathrm{BL_B}}/RT+\ln B_{\mathrm{c}}f_{\mathrm{B}}.\end{aligned}\right\} \tag{1.25}$$

The activity coefficients of $\mathrm{AL_A}$ and $\mathrm{BL_B}$ are then

$$\left.\begin{aligned}\ln f_{\mathrm{A}} &= (Z_{\mathrm{A}}\eta-1)\ln\left(\frac{Z_{\mathrm{A}}Z_{\mathrm{B}}\eta-Z_{\mathrm{B}}A_{\mathrm{c}}-Z_{\mathrm{A}}B_{\mathrm{c}}}{Z_{\mathrm{A}}Z_{\mathrm{B}}\eta-Z_{\mathrm{B}}}\right)+\Delta_{\mathrm{A}}-\Delta^{*}_{\mathrm{A}},\\ \ln f_{\mathrm{B}} &= (Z_{\mathrm{B}}\eta-1)\ln\left(\frac{Z_{\mathrm{A}}Z_{\mathrm{B}}\eta-Z_{\mathrm{B}}A_{\mathrm{c}}-Z_{\mathrm{A}}B_{\mathrm{c}}}{Z_{\mathrm{A}}Z_{\mathrm{B}}\eta-Z_{\mathrm{A}}}\right)+\Delta_{\mathrm{B}}.\end{aligned}\right\} \tag{1.26}$$

For $Z_{\mathrm{A}} = Z_{\mathrm{B}}$ the first terms on the right in equations (1.26) is zero.

(*h*) *Evaluation of the quantities* Δ

The quantities Δ defined by equation (1.24) are evaluated by partial differentiation of F^{int} with respect to N_{A} or N_{B}. We shall obtain these for two different expressions for F^{int}: the first order approximation, used by Barrer & Falconer, which assumes random siting of cations (equation (1.18)); and the refined expression, similar to the Lacher–Fowler–Guggenheim treatment of adsorption with interaction and including the entropy effect (equation (1.16)). Using the Barrer–Falconer expression we obtain

$$\left.\begin{aligned}\Delta_{\mathrm{A}} &= \frac{w_{\mathrm{AA}}}{Z_{\mathrm{A}}\eta kT}(1-B^{2}_{\mathrm{c}}),\\ \Delta_{\mathrm{B}} &= -\frac{Z_{\mathrm{B}}w_{\mathrm{AA}}}{Z^{2}_{\mathrm{A}}\eta kT}A^{2}_{\mathrm{c}}\\ \Delta^{*}_{\mathrm{A}} &= \frac{w_{\mathrm{AA}}}{Z_{\mathrm{A}}\eta kT}.\end{aligned}\right\} \tag{1.27}$$

The refined treatment was found to give

$$\left.\begin{aligned}\Delta_{\mathrm{A}} &= \nu\left[\tfrac{1}{2}(Z_{\mathrm{A}}\eta)\ln\frac{D_{\mathrm{AA}}-2\theta_{\mathrm{A}}}{D_{\mathrm{AA}}(1-\theta_{\mathrm{A}})}+\ln\frac{2(1-\theta_{\mathrm{A}})}{D_{\mathrm{AA}}-2\theta_{\mathrm{A}}}\right]\\ \Delta_{\mathrm{B}} &= \tfrac{1}{2}(Z_{\mathrm{B}}\eta\nu)\ln\frac{D_{\mathrm{AA}}-2\theta_{\mathrm{A}}}{D_{\mathrm{AA}}(1-\theta_{\mathrm{A}})},\\ \Delta^{*}_{\mathrm{A}} &= \nu\left[\tfrac{1}{2}(Z_{\mathrm{A}}\eta)\ln\frac{D^{*}_{\mathrm{AA}}-2\theta^{*}_{\mathrm{A}}}{D^{*}_{\mathrm{AA}}(1-\theta^{*}_{\mathrm{A}})}+\ln\frac{2(1-\theta^{*}_{\mathrm{A}})}{D^{*}_{\mathrm{AA}}-2\theta^{*}_{\mathrm{A}}}\right],\end{aligned}\right\} \tag{1.28}$$

where θ^{*}_{A}, D^{*}_{AA} and Δ^{*}_{A} are the values of θ_{A}, D_{AA} and Δ_{A} at $A_{\mathrm{c}} = 1$. For $w_{\mathrm{AA}}/kT = 0$ (no interaction) all quantities in equations (1.27) and (1.28) are zero. Further, for $\nu \to \infty$ we have

$\alpha_{AA} \to 0$ and $D_{AA} \to 2$, and the quantities in equations (1.28) approach the corresponding quantities in equations (1.27), so that the difference between results obtained using the two approximations then tends to zero. It can also be demonstrated that for $Z_A = \eta = 1$ and thus $\theta_A^* = 1$ the value of Δ_A^* from both expressions for F^{int} is w_{AA}/kT.

A comment may be made concerning the empirical near-linear plots of $\ln K_c$ against A_c or B_c, first observed by Kielland (1935), which require that

$$\left.\begin{aligned} \ln f_A &= 2.303\, C B_c^2, \\ \ln f_B &= 2.303\, C A_c^2, \end{aligned}\right\} \tag{1.29}$$

where C is a constant. First, it can be seen from equations (1.26)–(1.28) that for $\eta > 1$ the expression for F^{int} given in equation (1.16) cannot lead to truly linear plots of $\ln K_c$ against A_c, even for a uni-univalent exchange. Secondly, for the Barrer–Falconer expression for F^{int} (equation (1.18)), and if $Z_A \neq Z_B$, linear plots cannot be obtained either, because of the first term on the right in equations (1.26). On the other hand, if $Z_A = Z_B$ this first term vanishes and equations (1.26) reduce to equations (1.29), where, as shown by Barrer & Falconer (1956)

$$C = -\frac{w_{AA}}{2.303 Z_A \eta k T}. \tag{1.30}$$

(i) *The free energy function*

By dividing equation (1.11) by N_0 and replacing numbers of cations and sites by equivalent cation fractions one obtains

$$\begin{aligned} \frac{F}{N_0 kT} + s_2 \equiv g(F) = -\eta \ln \eta + \frac{A_c}{Z_A} \ln \frac{A_c}{Z_A} + \frac{B_c}{Z_B} \ln \frac{B_c}{Z_B} \\ + \left(\eta - \frac{A_c}{Z_A} - \frac{B_c}{Z_B}\right) \ln \left(\eta - \frac{A_c}{Z_A} - \frac{B_c}{Z_B}\right) + s_1 A_c + \frac{F^{\text{int}}}{N_0 kT}, \end{aligned} \tag{1.31}$$

where

$$\left.\begin{aligned} s_1 &= \ln \left(J_B^{1/Z_B} / J_A^{1/Z_A}\right), \\ s_2 &= \frac{1}{Z_B} \ln J_B + n_G \ln J_G + \ln P_L. \end{aligned}\right\} \tag{1.32}$$

The J are assumed to be independent of A_c, and we have a given total charge, N_0, of the crystal and assumed constant N_G. The quantity $(F/N_0 kT + s_2) \equiv g(F)$ will therefore be plotted against the cation fraction, A_c, of the incoming cation. The properties of the function $g(F)$ will be discussed later.

(j) *The ion-exchange isotherms*

The following comments can be made on equation (1.14)

(i) s_1, η and Δ_A^* (which is a function of w_{AA}/kT, ν, η, Z_A, Z_B) are *primary* quantities, dependent only on the properties of the crystal, and determining the affinity of exchange. The calculated K_a is the *secondary* quantity dependent on the above primary quantities and the quantity χ given by equation (1.15). K_a will therefore have different values depending on which approximation for F^{int} we choose, and cannot be assigned *a priori*. It is evident from the captions to figures 1–6 how the different values of intrinsic physical properties of the crystal can result in very different values for K_a.

(ii) If we are considering specific ion pairs, χ can be evaluated from standard electrode potentials, $E^\ominus$. That is, $\mu^\ominus = -|Z|\, F E^\ominus$ for an ion of charge Z and where F is the Faraday constant. Thus χ is a known constant for any specific cation pair.

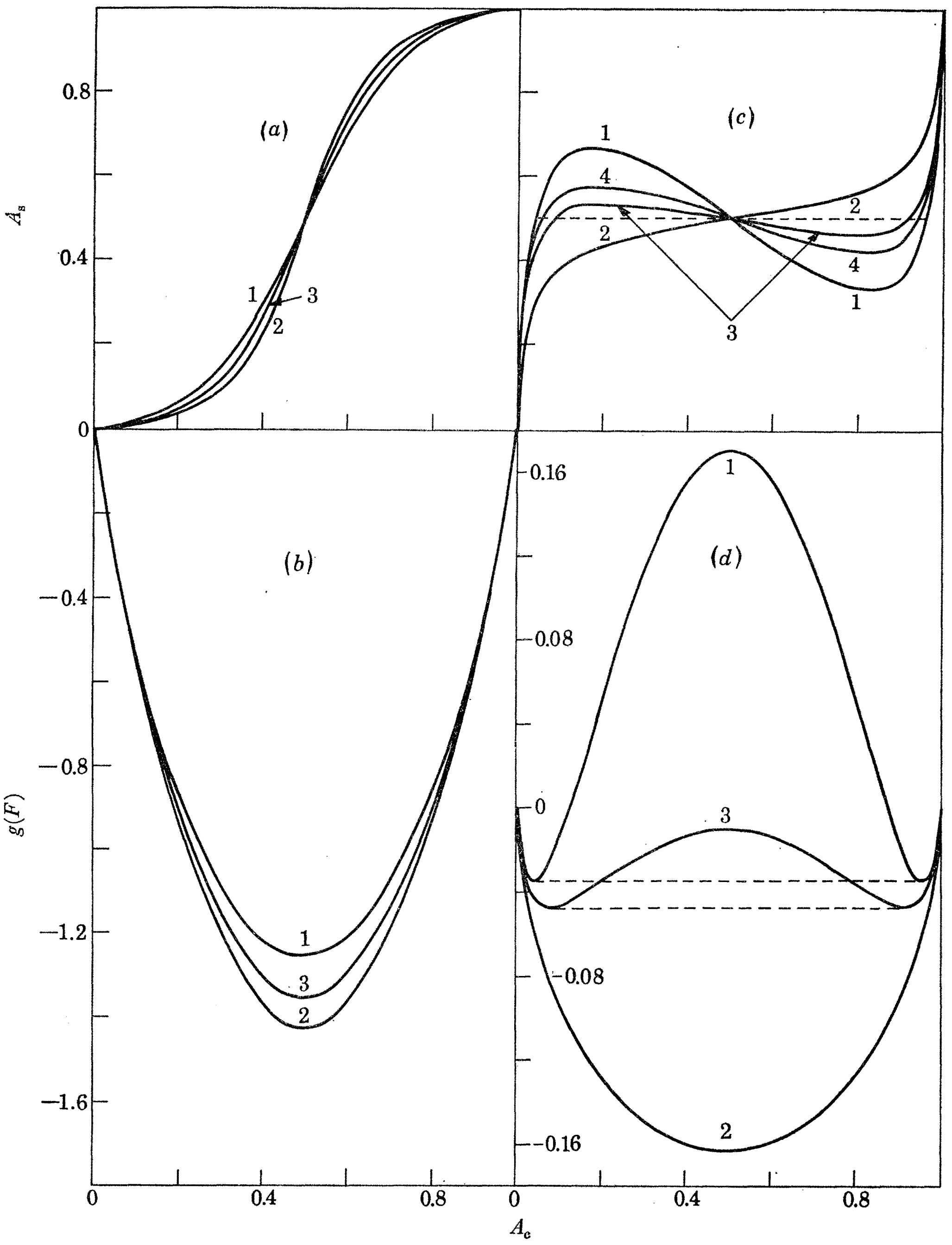

FIGURE 1. The curves of $g(F)$ against A_c (lower graphs) and the ion-exchange isotherms (upper graphs) for $Z_A = Z_B = 1$ and $\eta = 1$. Curves 1 were obtained from the Barrer–Falconer expression for F^{int}; curves 2–4 were obtained from a refined expression with $\nu = 2$ (curves 2); $\nu = 4$ (curves 3) and $\nu = 6$ (curves 4). For (a) and (b), $w_{AA}/kT = 2.303$; $s_1 = -2.303$; for (c) and (d), $w_{AA}/kT = -3.454$, $s_1 = 3.454$. $K_a^{(1)} = K_a^{(2)} = K_a^{(3)} = K_a^{(4)} = 1.0$ for all values of w_{AA}/kT. All isotherms were calculated assuming $\chi = 0$. Miscibility gaps are indicated by dashed lines. Curves 4 are omitted in (a), (b) and (d) for clarity.

(iii) For $Z_A = Z_B$ the sum of the first three terms in equation (1.14) is zero. This is not the case however, when $Z_A \neq Z_B$. Consequently, even for no pair-wise interaction ($w_{AA}/kT = 0$) each assigned value of η will lead to a different isotherm. This can be seen by comparing figure 5*b* and figure 6*b*.

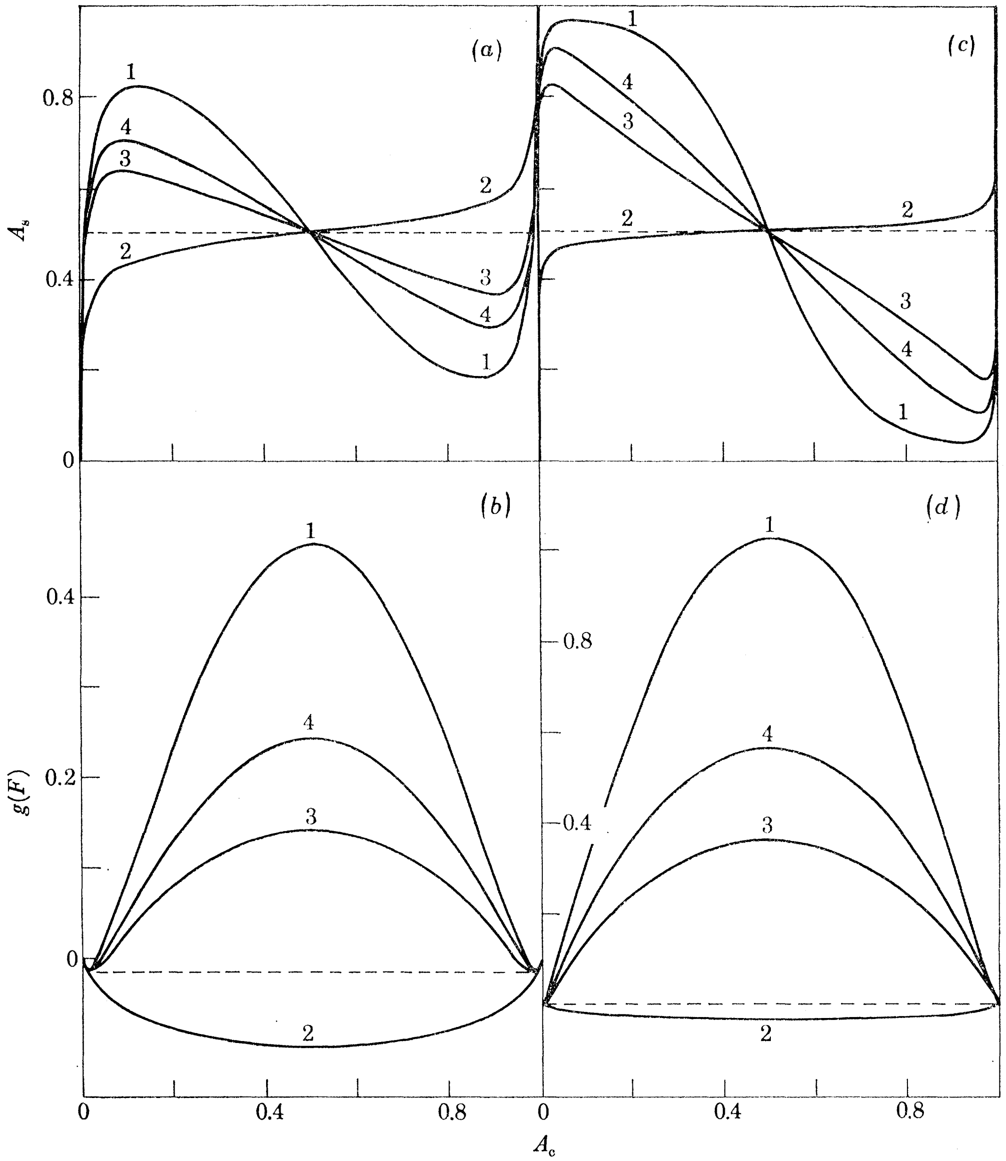

Figure 2. The curves of $g(F)$ against A_c (lower graphs) and the ion-exchange isotherms (upper graphs) for $Z_A = Z_B = 1$ and $\eta = 1$. Curves are numbered as in figure 1. For (*a*) and (*b*), $w_{AA}/kT = -4.605$, $s_1 = 4.605$; for (*c*)–(*d*), $w_{AA}/kT = -6.908$, $s_1 = 6.908$. $K_a^{(1)} = K_a^{(2)} = K_a^{(3)} = K_a^{(4)} = 1.0$ for all values of w_{AA}/kT.

Characteristic ion-exchange isotherms (figures 1–6) were calculated as follows. The parameters Z_A, Z_B, ν, w_{AA}/kT, η, s_1 and $(Z_A m_s^A + Z_B m_s^B)$ were specified. w_{AA}/kT was given such values as to lead, in the Barrer–Falconer approximation for F^{int}, to $C = -1$, $+1.5$, $+2$ and $+3$ respectively (equation (1.30)). For easiest presentation of the results, s_1 was given such a value as to lead, in conjunction with other variables, to $QK_a = 1$ (equation (1.4)) when the Barrer–Falconer expression was used. This was done to obtain isotherms not too close to the axis on the diagrams, and thus easily comparable. $(Z_A m_s^A + Z_B m_s^B)$ was taken to be 0.01 M; at low ionic strengths the ratio of the activity coefficients in the solution is very close to, and was taken as, unity. The calculations were performed for values of η of 1 and 2. Next, K_a was calculated from equation (1.14), using both the crude and the refined expressions for F^{int}. For generality, no particular pair of cations was chosen and it was assumed that $\chi = 0$. The value of χ, being only an additive term, does not affect the conclusions. In any case, instances of two cations producing $\chi \approx 0$ can be found in practice (the pair K⁺/Rb⁺). Next, the ratio of activity coefficients in the crystal was calculated from equations (1.26) for each value of A_c using a computer program.

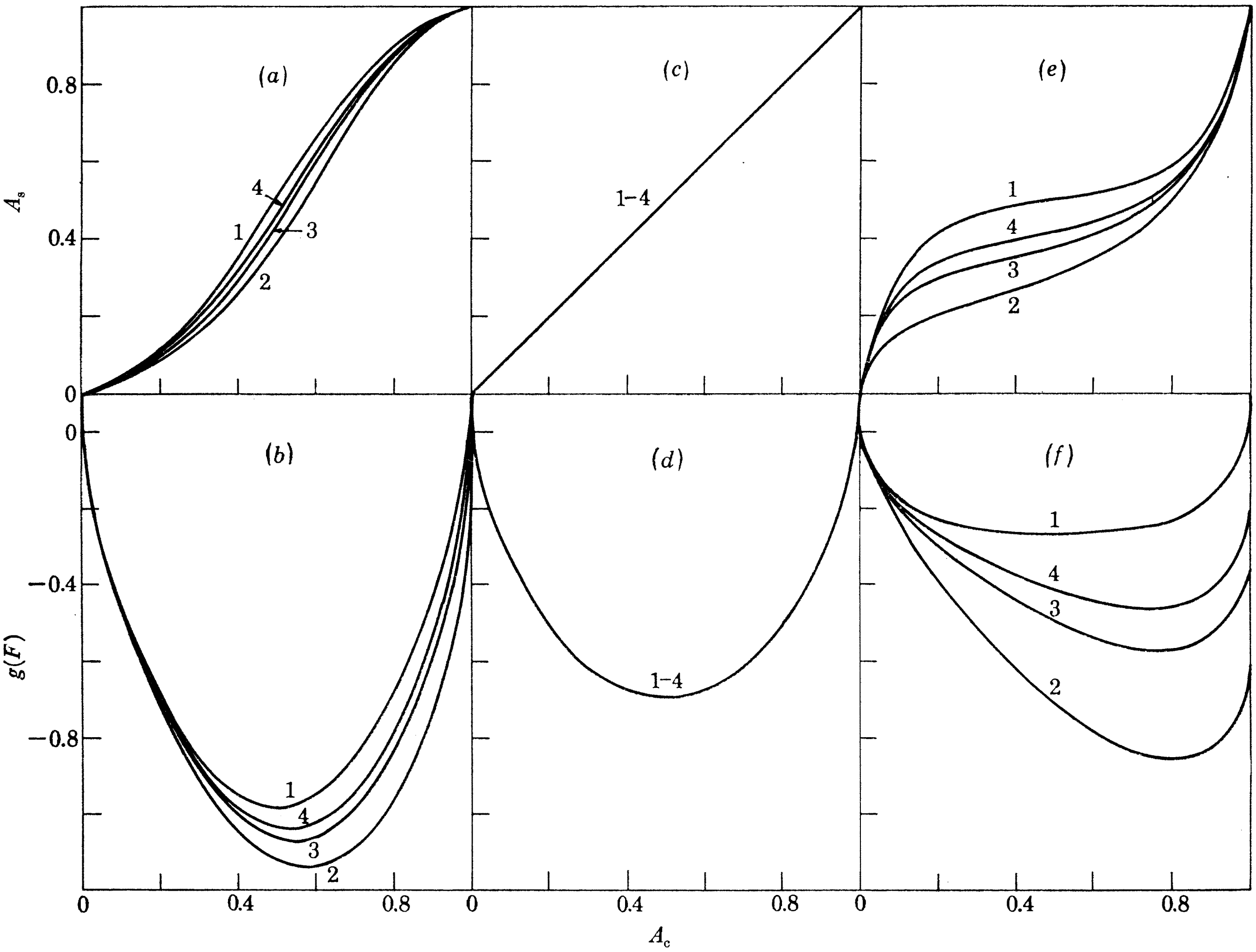

FIGURE 3. The curves of $g(F)$ against A_c and the ion-exchange isotherms for $Z_A = Z_B = 1$ and $\eta = 2$. Curves are numbered as in figure 1. For (a) and (b), $w_{AA}/kT = 2.303$, $s_1 = -1.151$, $K_a^{(1)} = 1.0$, $K_a^{(2)} = 1.370$, $K_a^{(3)} = 1.178$, $K_a^{(4)} = 1.116$; for (c) and (d), $w_{AA}/kT = 0$, $s_1 = 0$, $K_a^{(1)} = K_a^{(2)} = K_a^{(3)} = K_a^{(4)} = 1.0$; for (e) and (f), $w_{AA}/kT = -3.454$, $s_1 = 1.727$, $K_a^{(1)} = 1.0$, $K_a^{(2)} = 1.950$, $K_a^{(3)} = 1.436$, $K_a^{(4)} = 1.278$.

A_s was then calculated for each A_c from the implicit equation (1.2). The results were drawn in figures 1–6 as plots of A_s against A_c. The properties of the ion-exchange isotherms are discussed later.

(k) *Calculation of the function g(F)*

As in the expression for K_a (equation (1.14)), the expression for $g(F)$ (equation (1.31)) contains A_c as the independent variable and the constant parameters Z_A, Z_B, ν, w_{AA}/kT, η and s_1. As $g(F)$

describes only the properties of the crystal, it is not necessary to specify $(Z_A m_s^A + Z_B m_s^B)$ or to make any assumptions regarding χ. $g(F)$ has then been calculated from equation (1.31), as a function of A_c using a computer program, for each of the two expressions for F^{int}. The influence of each parameter has been explored and, to facilitate discussion, $g(F)$ has been plotted alongside the isotherms for the same values of the parameters (figures 1–6). The conclusions are as follows.

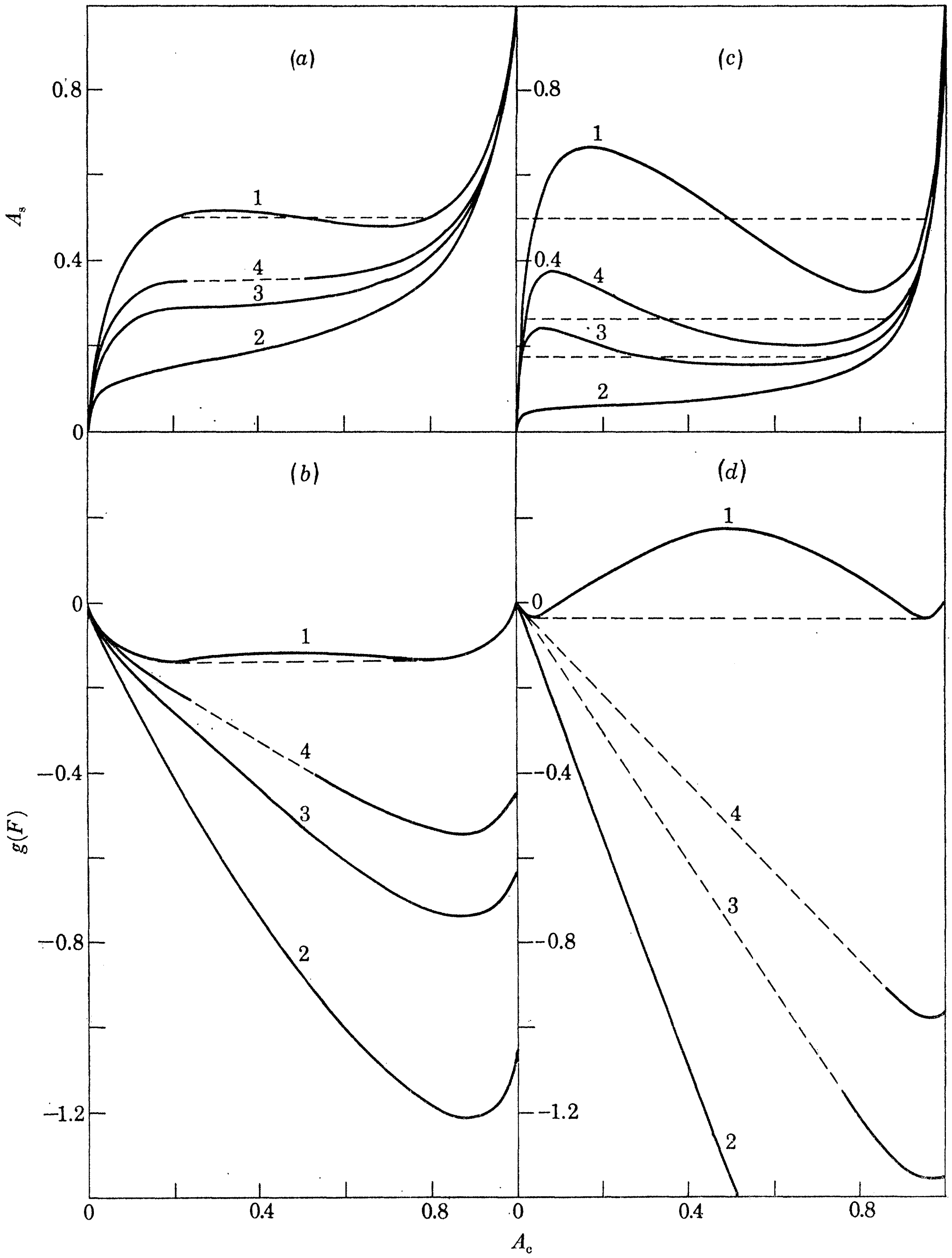

FIGURE 4. The curves of $g(F)$ against A_c and the ion-exchange isotherms for $Z_A = Z_B = 1$ and $\eta = 2$. Curves are numbered as in figure 1. For (*a*) and (*b*), $w_{AA}/kT = -4.605$, $s_1 = 2.303$, $K_a^{(1)} = 1.0$, $K_a^{(2)} = 3.025$, $K_a^{(3)} = 1.876$, $K_a^{(4)} = 1.539$; for (*c*) and (*d*), $w_{AA}/kT = -6.908$, $s_1 = 3.454$, $K_a^{(1)} = 1.0$, $K_a^{(2)} = 8.414$, $K_a^{(3)} = 3.804$, $K_a^{(4)} = 2.569$.

Firstly, the free energy curve always begins to decrease as A_c increases from zero or decreases from unity. This is on account of the logarithmic function in the entropy of mixing. Secondly, the course of $g(F)$ against A_c for intermediate compositions depends principally on the value and sign of w_{AA}/kT. Three cases can be distinguished.

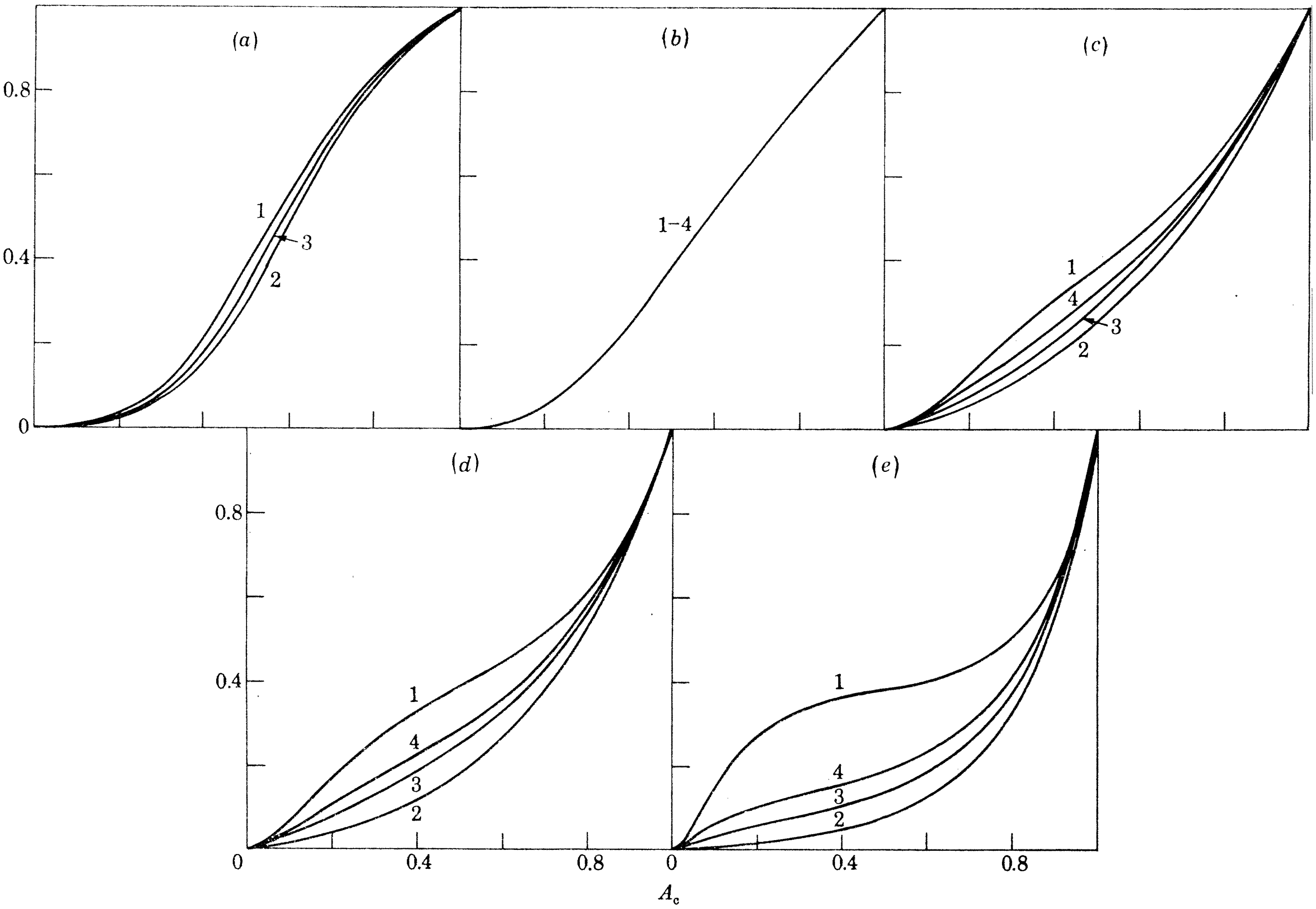

FIGURE 5. The ion-exchange isotherms for $Z_A = 2$, $Z_B = 1$ and $\eta = 1$. Curves are numbered as in figure 1. For (a), $w_{AA}/kT = 2.303$, $s_1 = 2.074$ $K_a^{(1)} = 0.02$, $K_a^{(2)} = 0.02739$, $K_a^{(3)} = 0.02355$, $K_a^{(4)} = 0.02232$; for (b), $w_{AA}/kT = 0$, $s_1 = 2.649$, $K_a^{(1)} = K_a^{(2)} = K_a^{(3)} = K_a^{(4)} = 0.02$; for (c), $w_{AA}/kT = -3.454$, $s_1 = 3.513$, $K_a^{(1)} = 0.02$, $K_a^{(2)} = 0.03901$, $K_a^{(3)} = 0.02872$, $K_a^{(4)} = 0.02556$; for (d), $w_{AA}/kT = -4.605$, $s_1 = 3.800$, $K_a^{(1)} = 0.02$, $K_a^{(2)} = 0.06050$, $K_a^{(3)} = 0.03752$, $K_a^{(4)} = 0.03079$; for (e), $w_{AA}/kT = -6.908$, $s_1 = 4.376$, $K_a^{(1)} = 0.02$, $K_a^{(2)} = 0.1683$, $K_a^{(3)} = 0.07607$, $K_a^{(4)} = 0.05139$.

Case 1

When w_{AA}/kT is sufficiently negative (i.e. when the cations tend to segregate rather than form a homogeneous phase) the curve of $g(F)$ either contains a double minimum and a maximum (curve 1 in figure 1*d*) or is so shaped that a tangent line can be drawn below the curve and touching it at just two points (curve 4 in figure 4*d*). Whether the tangent line is horizontal or sloping depends entirely on the value of s_1 through the term $s_1 A_c$. s_1 can always be chosen so as to produce two minima of equal depth. Case 1 corresponds with two-phase regions (miscibility gaps).

Case 2

When $w_{AA}/kT = 0$ (the cations A are indifferent to their neighbours) $g(F)$ has a single minimum well away from either $A_c = 0$ or $A_c = 1$ (figure 3*d*). The precise position of this minimum is modified by s_1.

Case 3

When $w_{AA}/kT > 0$ (the cations A avoid each other) $g(F)$ has also a single minimum, but deeper than in case 2.

(*l*) *Comparison of isotherms and of free energy curves*

The application of the two different expressions for F^{int} leads to conclusions which can be summarized as follows:

(i) Equations (1.27) show that for a random distribution of cations in the crystal isotherms and the curves of $g(F)$ against A_c are independent of ν. This is not so in the more refined expression

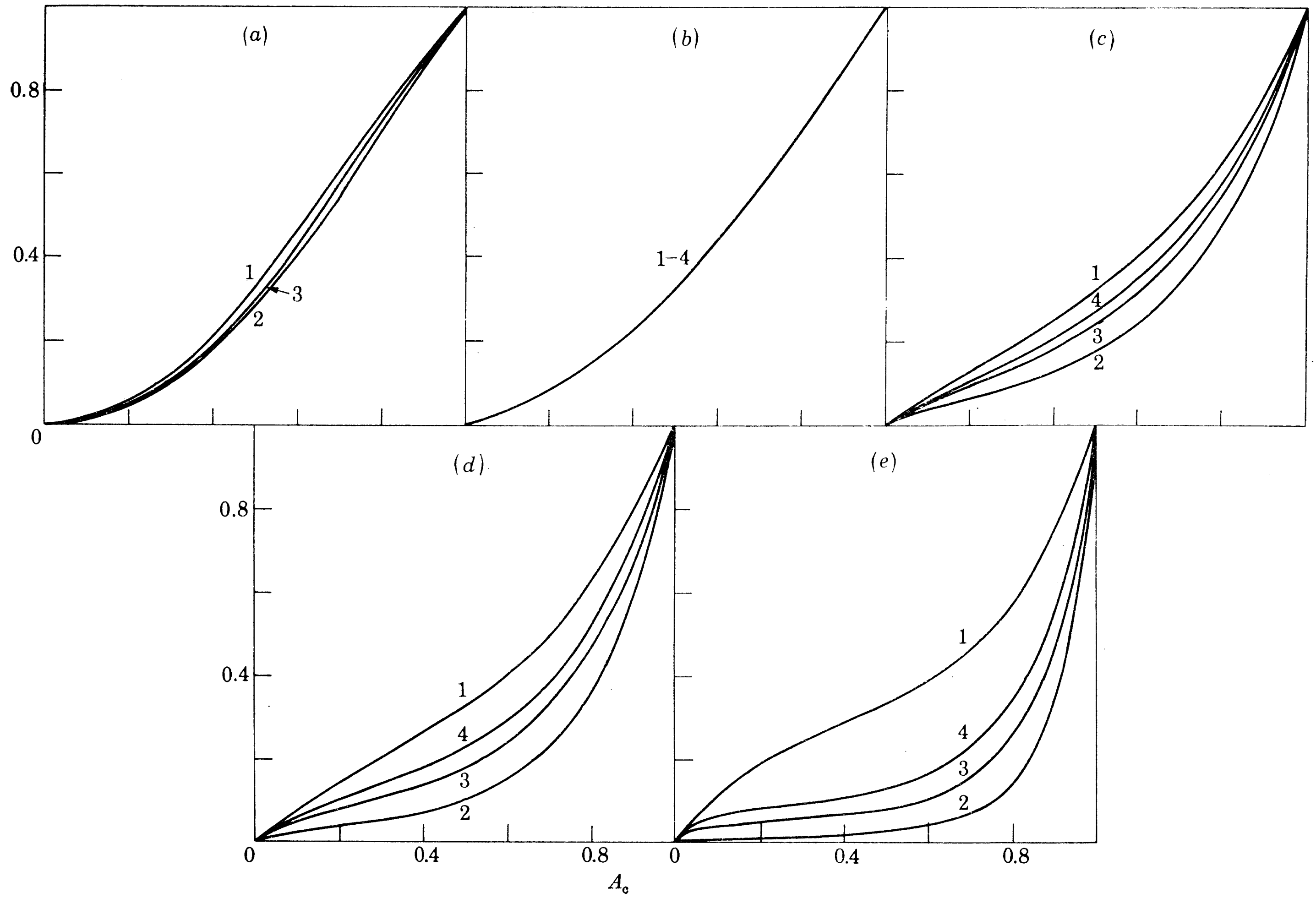

FIGURE 6. The ion-exchange isotherms for $Z_A = 2$, $Z_B = 1$ and $\eta = 2$. Curves are numbered as in figure 1. For (*a*), $w_{AA}/kT = 2.303$, $s_1 = 1.407$, $K_a^{(1)} = 0.02$, $K_a^{(2)} = 0.02654$, $K_a^{(3)} = 0.02359$, $K_a^{(4)} = 0.02244$; for (*b*), $w_{AA}/kT = 0$, $s_1 = 1.694$, $K_a^{(1)} = K_a^{(2)} = K_a^{(3)} = K_a^{(4)} = 0.02$; for (*c*), $w_{AA}/kT = -3.454$, $s_1 = 2.126$, $K_a^{(1)} = 0.02$ $K_a^{(2)} = 0.04922$, $K_a^{(3)} = 0.03157$, $K_a^{(4)} = 0.02699$; for (*d*), $w_{AA}/kT = -4.605$, $s_1 = 2.270$; $K_a^{(1)} = 0.02$, $K_a^{(2)} = 0.09257$, $K_a^{(3)} = 0.04520$, $K_a^{(4)} = 0.03429$; for (*e*), $w_{AA}/kT = -6.908$, $s_1 = 2.558$, $K_a^{(1)} = 0.02$, $K_a^{(2)} = 0.4177$, $K_a^{(3)} = 0.1211$, $K_a^{(4)} = 0.06794$.

(equations (1.28)). In accordance with the comments following equations (1.28) the difference between the plots obtained with these two expressions decreases as ν increases.

(ii) In uni-univalent exchanges with $\eta = 1$ the plots are symmetrical with respect to $A_c = 0.5$. Both approximations for F^{int} then lead to the same value of K_a. In view of equations (1.28) and (1.14) we have in this case

$$\ln K_a = -s_1 + \chi - w_{\text{AA}}/kT.$$

For $\eta > 1$ the plots can no longer be symmetrical, and each approximation leads to a different value of K_a. In uni-divalent exchanges the difference between the K_a obtained for different ν is considerable, and increases also with increased η. As a result the isotherms and the plots of $g(F)$ become very different in these cases (see, for instance, figures 2*c* and *d* and figures 4*c* and *d*). This shows that where $w_{\text{AA}}/kT < 0$ the assumption of random siting of ions A becomes very inadequate, particularly when $Z_{\text{A}} \neq Z_{\text{B}}$.

(iii) For random siting of cations the shape of all curves depends on the ratio $w_{\text{AA}}/\eta kT$ (related to Kielland's 'C'). In the more refined treatment the influence of w_{AA}/kT, η and additionally ν must be considered separately. For $w_{\text{AA}}/kT > 0$ the difference between curves calculated using the two approximations for F^{int} is small (figures 1*a*, 3*a*, 5*a*, 6*a*). Of course, when $w_{\text{AA}}/kT = 0$ both approximations produce the same isotherm and free energy curve. The difference referred to above becomes greater when $w_{\text{AA}}/kT < 0$ and thus the ions of A tend to cluster. Even so, the difference between various such curves is in fact less than it would at first appear from the theoretical plots, because of the miscibility gaps (figure 2*a*). The equilibrium course of exchange is then marked by the dashed lines.

(iv) In practice K_a can be determined from experimental ion-exchange isotherms, while ν and η can be found from crystallographic data. Z_{A} and Z_{B} are of course known. However, s_1 and w_{AA}/kT, although both clearly defined physical quantities, cannot be directly measured. In order to simulate an experimental isotherm, one has to find w_{AA}/kT and s_1 by trial and error, bearing in mind that they must be compatible with the experimentally measured value of K_a (equation (1.14)).

(v) In uni-univalent exchanges the existence of miscibility gaps requires larger and larger values of w_{AA}/kT as η increases. This is evident from the comparison of figures 2 and 4. The existence of miscibility gaps is also very strongly dependent on the valency of the cations involved (compare figures 2 and 5). Miscibility gaps in uni-divalent exchanges are less likely than in uni-univalent exchanges. One such case of immiscibility in the Na $\rightleftarrows$ Sr exchange in a synthetic faujasite was reported (Olson & Sherry 1968). It is however not easy to analyse the isotherm in view of the high concentration of the external solutions used ($Z_{\text{A}} m_{\text{s}}^{\text{A}} + Z_{\text{B}} m_{\text{s}}^{\text{B}} = 0.1\,\text{M}$). For $Z_{\text{A}} \neq Z_{\text{B}}$ the position of the isotherm depends strongly on aqueous concentration (Barrer & Klinowski 1974*a*); also the ratio of aqueous activity coefficients is no longer nearly unity.

(*m*) *Limited mutual miscibility of the end members of exchange*

A line connecting the points $A_c = 0$ and $A_c = 1$ on the diagram of $g(F)$ against A_c represents the values of $g(F)$ for the *physical mixture* of separate A- and B-crystals, while the $g(F)$ for their *solution*, i.e. the (A, B) mixed crystal, is of course given by the function itself. Similarly, a line connecting any two points on the curve of $g(F)$ corresponding to compositions A_c' and A_c'' represents the values of $g(F)$ for the *physical mixture* of crystals of compositions A_c' and A_c''. For cases 2 and 3 such a line always corresponds to a higher free energy than the curve itself. However, for case 1 of § 1 (*k*) it is always possible to draw a straight line touching the plot of $g(F)$ against A_c at

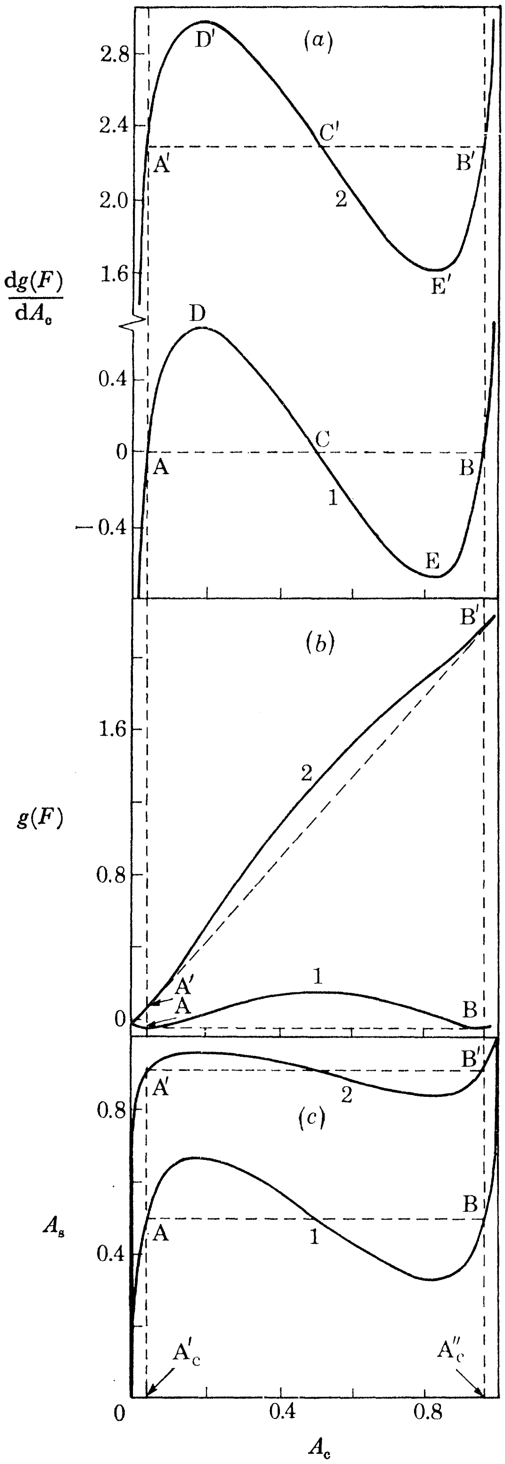

FIGURE 7. (*a*) Plots of $dg(F)/dA_c$ against A_c; (*b*) plots of $g(F)$ against A_c; (*c*) plots of A_s against A_c (ion-exchange isotherms) calculated for $Z_A = Z_B = 1$; $\eta = 1$ and $w_{AA}/kT = -3.454$. For curves 1 $s_1 = 3.454$; for curves 2 $s_1 = 5.756$. This choice of s_1 gives $K_a^{(1)} = 1.0$; $K_a^{(2)} = 0.1$ for curves 1 and 2 in (*c*), respectively. Pairs of points A, B and A′, B′ indicate the miscibility gaps.

just two points and lying entirely below. This is shown by the dashed lines connecting A, B and A′, B′ in figure 7 *b*. This means that there is a region within which a physical mixture of crystals of compositions A'_c and A''_c has a lower free energy than the homogeneous phase. The resulting mixture of crystals can have the overall composition anywhere between A'_c and A''_c; its $g(F)$ is simply a proportional intermediate value between the $g(F)$ of the two phases. In this region the calculated exchange isotherms develop a loop.

It is seen from figures 1–6 that the presence and the size of the two-phase region for a given pair of cations depends in the case of the Barrer–Falconer expression for F^{int} on the parameters w_{AA}/kT and η; and in the case of the refined expression for F^{int} additionally on ν. Conditions which must be fulfilled if a miscibility gap is to exist will be considered further.

By differentiating equation (1.31) with respect to A_c one obtains

$$\frac{\mathrm{d}g(F)}{\mathrm{d}A_c} = \frac{1}{Z_A}\ln\frac{A_c}{Z_A} - \frac{1}{Z_B}\ln\frac{B_c}{Z_B} + \left(\frac{1}{Z_B} - \frac{1}{Z_A}\right)\ln\left(\eta - \frac{A_c}{Z_A} - \frac{B_c}{Z_B}\right) + s_1 + \frac{\Delta_A}{Z_A} - \frac{\Delta_B}{Z_B}. \tag{1.33}$$

It follows that s_1 does not change the shape of $\mathrm{d}g(F)/\mathrm{d}A_c$ but only its position (compare curves 1 and 2 in figure 7 *a*). For the two phases to be at equilibrium, the work on going from A to B by path AB must be equal to the work for the path ADCEB, so that the integral

$$\int_{A'_c}^{A''_c} \frac{\mathrm{d}g(F)}{\mathrm{d}A_c}\,\mathrm{d}A_c$$

is equal to the area of the rectangle determined by the line A′B′ and its crossing points with the curve of $\mathrm{d}g(F)/\mathrm{d}A_c$ against A_c. A particular case of such a situation arises when both these areas are zero (curve 1 in figure 7 *a*). In the plot of $g(F)$ against A_c there are then two minima of equal depth (curve 1 in figure 7 *b*). The following conditions must be fulfilled for two phases in equilibrium:

(i) Pairs of points A, B and A′, B′ in figure 7 *b* must lie on *the same* tangential line to the plot of $g(F)$ against A_c. If the common tangent has intercept b, the equation of this tangent is

$$g(F) = \frac{\mathrm{d}g(F)}{\mathrm{d}A_c}A_c + b$$

and the slope is the same at A'_c and A''_c. Therefore, at these points

$$\left.\begin{aligned} b = [g(F)]' - \left[\frac{\mathrm{d}g(F)}{\mathrm{d}A_c}\right]' A'_c = [g(F)]'' - \left[\frac{\mathrm{d}g(F)}{\mathrm{d}A_c}\right]'' A''_c,\\ \left[\frac{\mathrm{d}g(F)}{\mathrm{d}A_c}\right]' = \left[\frac{\mathrm{d}g(F)}{\mathrm{d}A_c}\right]'', \end{aligned}\right\} \tag{1.34}$$

where $[g(F)]'$, $[g(F)]''$, $[\mathrm{d}g(F)/\mathrm{d}A_c]'$ and $[\mathrm{d}g(F)/\mathrm{d}A_c]''$ are the values of $g(F)$ and $\mathrm{d}g(F)/\mathrm{d}A_c$ at compositions A'_c and A''_c respectively. Inspection of equations (1.34) in conjunction with equations (1.31) and (1.33) shows that both equations (1.34) are independent of s_1.

(ii) A tangent touching $g(F)$ at two points implies two points of inflexion between A'_c and A''_c (Rushbrooke 1949 *b*); that is two points at which $\mathrm{d}^2g(F)/\mathrm{d}A_c^2 = 0$. The reason for this is obvious from figure 7 *a*. To find the points A'_c and A''_c, i.e. the limits of the miscibility gap, the implicit equations (1.34) were solved using a computer program. Calculations were made for different values of the coordination number ν and the results represented as plots of $-kT/w_{\text{AA}}$ against A_c, that is in a similar fashion to phase diagrams. The results are summarized below for uni-univalent exchanges. The Barrer–Falconer approximation leads to a universal 'phase diagram', independent of ν, provided one plots $-kT\eta/w_{AA}$ against A_c. This shows a miscibility gap which narrows as $-kT\eta/w_{AA}$ increases (figure 8*a*). Thus for a given material the miscibility gap narrows with increased temperature to vanish at $-kT\eta/w_{AA} = 0.5$ (in terms of equation (1.30) corresponding to $C = 0.87$). This is in agreement with the experiments of Orville (1963) in which the miscibility gap in Na $\rightleftarrows$ K exchange in felspars narrows and finally vanishes with increased temperature. For $\eta = 1$ and the refined expression for F^{int} the phase diagram is similar to that for the Barrer–Falconer approximation, but the two-phase region disappears at lower values of $-kT/w_{AA}$, depending on ν. For $Z_A = Z_B = 1$ and $\eta = 1$, equation (1.33) is symmetrical with respect to the point $A_c = 0.5$. Consequently the phase diagrams in figures 8*a* and *b* are symmetrical. The symmetry of the miscibility gap is sensitive to η. Figure 8*c* shows this gap for $\eta = 2$. When the temperature is high enough all the phase diagrams show only a single phase.

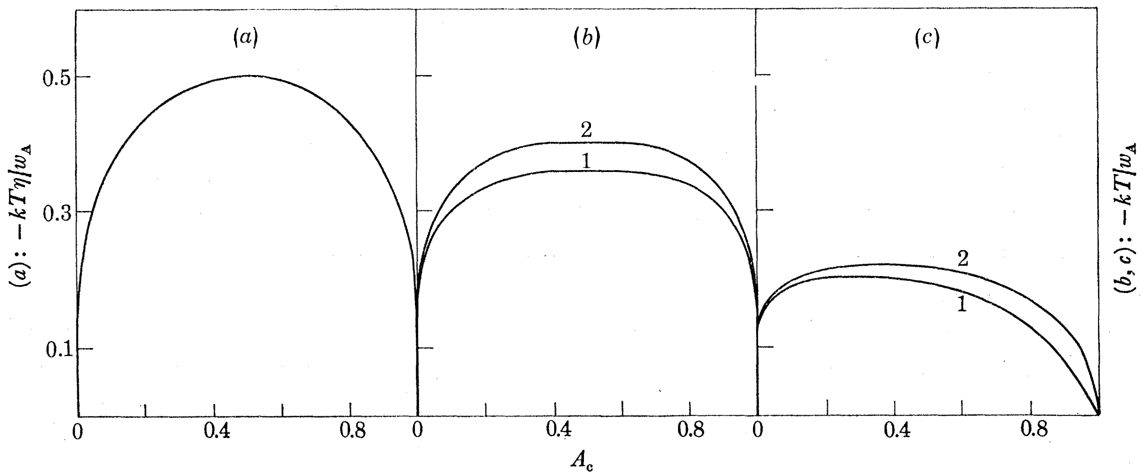

FIGURE 8. Plots of $-kT\eta/w_{AA}$ against A_c (figure 8*a*) and $-kT/w_{AA}$ against A_c (figures 8 *b*, *c*) for $Z_A = Z_B = 1$. (*a*) Barrer–Falconer approximation for F^{int}. (*b*) $\eta = 1$. For curve 1 $\nu = 4$; for curve 2 $\nu = 6$. (*c*) $\eta = 2$. Curves are numbered as in figure 8*b*.

It was next demonstrated numerically that the dashed line connecting the points on ion-exchange isotherms corresponding to A'_c and A''_c (e.g. figure 7*c*) always bisects the isotherm into parts of equal area. This was shown for all exchanges in which $Z_A = Z_B$, and also for $Z_A = 2$ and $Z_B = 1$. This property of ion-exchange isotherms is independent of η, w_{AA}/kT or K_a.

(*n*) *Discussion*

It is seen from many of the ion-exchange isotherms (e.g. figures 2*a* and *c*) and from the phase diagrams (figure 8) that the lower temperature boundaries of the two-phase regions often correspond with an extremely low content of the incoming cation in the crystal. Iiyama (1974) considered such low concentrations for a number of alkali and alkaline earth metal ion exchanges in aluminosilicates. He suggested a model involving 'forbidden' zones around each incoming ion which no other incoming ion, A, could occupy, but which were accessible to the ions B. Apart from the difficulty of explaining the required large forbidden zones this approach seems unsatisfactory in its quantitative aspect. The expression given for the maximum number of cations does not allow for the possibility that additional sites are excluded for A by *several* nearby ions of A, because, although the sites in question are outside the forbidden zones, these zones are too close together to permit another entering ion of A plus its exclusion zone to be inserted among them. On the other hand limited solid solubility as formulated in the present §1 is adequate to explain very low solubilities of the entering ion A in the B-rich medium (figure 8). There is no need to postulate, as did Iiyama, that low solubility means that replacement of B by A must be extremely endothermal. It is the extra negative energy $2w_{AA}/\nu$ which is involved when two ions A occupy adjacent sites which determines the boundaries of the phase diagram and hence the low solubility of A in the B-rich crystal and of B in the A-rich form. This energy need not be very great to produce the observed behaviour, as our analysis shows. It is not necessary that both A- and B-rich forms be realizable; the form with a little B in the A-rich matrix could be replaced by a third more stable structure with a quite different framework topology. For example, Rb-analcime is more stable that Rb-felspar and would tend to replace this in a K $\rightleftarrows$ Rb exchange in felspar (Barrer & McCallum 1953).

When there is limited mutual solid solubility of the end members of the exchange reactions the phase separation can be manifested in several ways. Firstly there would be physical separation of A-rich crystals from the parent B-rich ones, the amount of B-rich material decreasing as the amount of A-rich crystals increases. This is the equilibrium situation considered here. However, it is also possible for nuclei of A-rich phase to grow on or in a matrix of the parent phase, either as three dimensional domains, or, as in some (Na, K)-felspars, as perthitic structures in which layers of crystal rich in A alternate with layers rich in B (Bragg & Claringbull 1965). In layer silicates also there may be interlamellar cation layers rich in one ion interstratified with layers rich in the other (Sawhney 1967; Barrer & Brummer 1963).

In all cases where domain, perthitic or interstratified structures occur as a result of the tendency to phase separation, two extra, positive free energy terms are involved. These are due to strain arising from misfit between the chemically different parts, and to interfacial free energy. Because both are positive they tend to delay the appearance of the new phase beyond the true equilibrium points both for forward and reverse reactions. The result is hysteresis in the isotherms which may be extreme (Barrer & Falconer 1956) or small (Barrer & Munday 1971*c*) and which may result in some interesting history-dependent effects (Barrer & Hinds 1953). These considerations fall outside the scope of an equilibrium treatment but are of importance both in nature and in the laboratory.

2. Cation exchange when more than one kind of exchange site is present

(*a*) *Introduction*

In zeolites it is more usual than not to find the exchangeable cations in several crystallographically distinct kinds of position, so that a number of site groups need to be considered. Sites belonging to different groups are intimately mixed together throughout the crystals. For example figure 9 (Schoonheydt 1975) shows some of the positions which cations occupy in the faujasite structure. It is also known that in homoionic forms the cation populations in the different site groups may differ for different cations (cf. Smith 1971). This happens in part because the number of possible sites exceeds the number of cations needed to neutralize the negative charge of the framework. It also arises in part because the smallest scale local electrical neutrality is not fully achieved within the crystals, as shown by the strong affinity between zeolite sorbents and dipolar molecules (NH_3, H_2O, SO_2), indicating the presence of big local electrostatic fields, and between zeolite and quadrupolar molecules (N_2, CO_2) indicating large local field gradients. This evidence is supported by calculations of fields and field gradients within zeolites (Barrer & Gibbons 1963; Dempsey 1968; and Bonnin & Legrand 1975). Thus virtually equivalent, if incomplete, approaches to local electrical neutrality may be equally well satisfied by several distributions of the cationic charge between site groups. In this Part the general problem of exchange equilibrium on an exchanger providing more than one kind of site, and some limiting cases, will be considered.

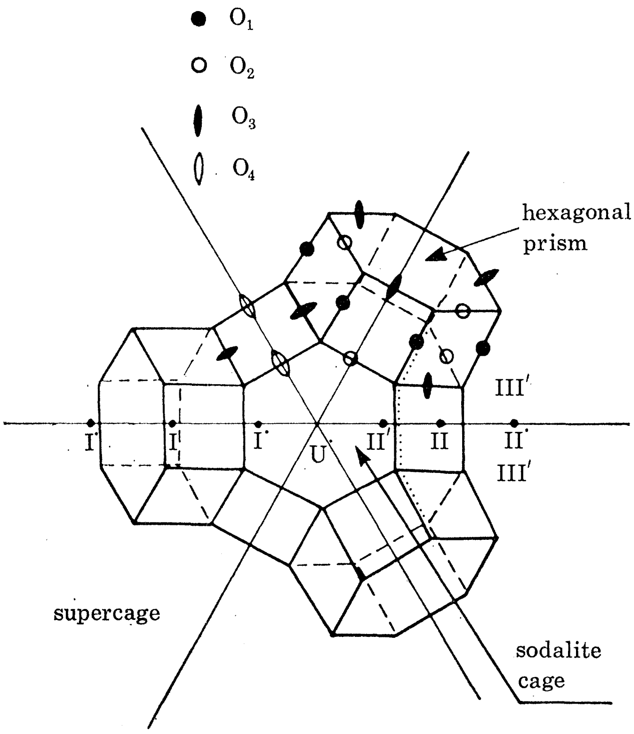

FIGURE 9. Cation positions in faujasite. Positions are numbered I, I$^{\cdot}$, U$^{\cdot}$, II′, II, II$^{\cdot}$ and III′. The diagram also indicates the four kinds of oxygen site.

(*b*) *The model*

There are assumed to be *n* kinds of site in the crystalline exchanger. The number of sites in the *i*th site group is N_i and the amount of cationic charge located on this site group is $N_{0,i}$ where

$$N_{0,i} = Z_A N_{A,i} + Z_B N_{B,i}. \tag{2.1}$$

$N_{A,i}$ and $N_{B,i}$ are the numbers of ions of A and B of charges Z_A and Z_B in the *i*th site group. The total cationic charge, N_0, is equal to the total anionic charge and is

$$N_0 = Z_A N_A + Z_B N_B = \sum_{i=1}^{n} N_{0,i} = \sum_{i=1}^{n} (Z_A N_{A,i} + Z_B N_{B,i}), \tag{2.2}$$

where N_A and N_B are the total numbers of ions A and B in the crystal. The $N_{0,i}$ could be functions of $N_{A,i}/N_{B,i}$ (§ 2 (*a*)). Also, if *N* is the total number of crystallographic sites available for cations

$$N = \sum_{i=1}^{n} N_i. \tag{2.3}$$

As before, the crystal may be considered as a solid solution of two components, AL_A and BL_B where L_A is the amount of anionic framework associated with an A ion and carrying anionic charge Z_A and L_B is this amount of framework associated with B and carrying anionic charge Z_B.

As noted in § 2 (*a*) total cation populations in a given site group may vary according to the nature of the cation so that various distributions of cations among site groups, different for different cations, may reasonably satisfy local electrical neutrality conditions. Accordingly the overall partition function P_t for the mixed crystal is written as

$$P_t = \sum_{N_{\mathrm{A},i},\,N_{\mathrm{B},i}} P, \tag{2.4}$$

where

$$P = \prod_{i=1}^{n} P_i = \prod_{i=1}^{n} \frac{N_i!}{N_{\mathrm{A},i}!\,N_{\mathrm{B},i}!\,(N_i-N_{\mathrm{A},i}-N_{\mathrm{B},i})!}\,J_{\mathrm{A},i}^{N_{\mathrm{A},i}}J_{\mathrm{B},i}^{N_{\mathrm{B},i}}J_{\mathrm{G},i}^{N_{\mathrm{G},i}}P_{\mathrm{L},i}^{N_{0,i}} \tag{2.5}$$

$J_{\mathrm{A},i}$ and $J_{\mathrm{B},i}$ are respectively the partition function of a cation A, and a cation B in the *i*th site group. $J_{\mathrm{G},i}^{N_{\mathrm{G},i}}$, the partition function for the $N_{\mathrm{G},i}$ guest molecules, includes the configurational term $C(N_{\mathrm{G},i})$ as in § 1. $P_{\mathrm{L},i}$ is the partition function for that amount, $[(\mathrm{Si}_\delta\mathrm{Al})\mathrm{O}_{2(1+\delta)}]^-$, of framework carrying one negative charge and associated with the *i*th group. The $N_{0,i}$, $N_{\mathrm{G},i}$, J_i and $P_{\mathrm{L},i}$ may firstly be functions of the overall composition of the mixed crystal of $\mathrm{AL_A}$ and $\mathrm{BL_B}$. In addition the $N_{0,i}$ and J_i would not for a fixed composition depend on the assigned values of the $N_{\mathrm{A},i}$ and $N_{\mathrm{B},i}$ in equation (2.4). The J_i contain terms $\exp(-\epsilon_i/kT)$ where ϵ_i is the energy of binding in the *i*th site group. If the choices of $N_{\mathrm{A},i}$ and $N_{\mathrm{B},i}$ in the summation in equation (2.4) result in serious local disbalances of positive and negative charge then, through the terms $\exp(-\epsilon_i/kT)$, the $J_{\mathrm{A},i}$ and $J_{\mathrm{B},i}$ will be very small for such distributions so that the corresponding terms of the summation will also become very small. For pure A-crystal and pure B-crystal the corresponding partition functions follow from equation (2.4) by omitting terms $N_{\mathrm{B},i}$, $J_{\mathrm{B},i}$ or $N_{\mathrm{A},i}$, $J_{\mathrm{A},i}$ respectively from the factorials and summation in the expression for P_t.

For the exchange reaction

$$Z_{\mathrm{B}}A_{\mathrm{s}} + Z_{\mathrm{A}}(\mathrm{BL_B}) \rightarrow Z_{\mathrm{A}}B_{\mathrm{s}} + Z_{\mathrm{B}}(\mathrm{AL_A}) \tag{2.6}$$

the thermodynamic equilibrium constant is given by equation (1.14). For the exchanger capable of full exchange for either A or B ions the standard states of $\mathrm{AL_A}$ and $\mathrm{BL_B}$, defined as in § 1 as pure A-crystal ($\mathrm{AL_A}$) and pure B-crystal ($\mathrm{BL_B}$), then the standard chemical potentials derived from equation (2.4) are

$$F^{\ominus}_{\mathrm{AL_A}} = \mu^{\ominus}_{\mathrm{AL_A}} = -RT\ln P^{\ominus}_{\mathrm{AL}} = -RT\sum_{N_{\mathrm{A},i}} P, \tag{2.7}$$

$$F^{\ominus}_{\mathrm{BL_B}} = \mu^{\ominus}_{\mathrm{BL_B}} = -RT\ln P^{\ominus}_{\mathrm{BL_B}} = -RT\sum_{N_{\mathrm{B},i}} P. \tag{2.8}$$

The term $(Z_{\mathrm{B}}\mu^{\ominus}_{\mathrm{A_s}} - Z_{\mathrm{A}}\mu^{\ominus}_{\mathrm{B_s}})$ in equation (1.14) is readily obtained from the standard electrode potentials of the ions A and B in solution and K_a can be obtained from experimental data by the method of Gaines & Thomas (1953). Thus $(Z_{\mathrm{A}}\mu^{\ominus}_{\mathrm{BL_B}} - Z_{\mathrm{B}}\mu^{\ominus}_{\mathrm{AL_A}})$ can be found. Alternatively, in principle K_a may be calculated from $(Z_{\mathrm{B}}\mu^{\ominus}_{\mathrm{A_s}} - Z_{\mathrm{A}}\mu^{\ominus}_{\mathrm{B_s}})$ and the standard state partition functions $P^{\ominus}$. In practice, however, the $P^{\ominus}$ cannot be evaluated for this most general case, but the summation in equation (2.4) is replaced by its largest term, P, with no sensible error.

If one now considers P'_i for one equivalent of cationic charge on the *i*th site group one may readily show that $\ln P_i = X_i \ln P'_i$ where $X_i = N_{0,i}/N_0$ is the fraction of one equivalent represented in equation (2.5) by $N_{0,i}$. Accordingly one may rewrite equation (2.5) as

$$P = \prod_{i=1}^{n} P_i'^{X_i} \tag{2.9}$$

Using equation (2.5) and the standard relation between the partition function and the Helmholtz free energy F of the crystal one obtains for each site group

$$F_i = -kT[N_i \ln N_i - N_{A,i} \ln N_{A,i} - N_{B,i} \ln N_{B,i} - \Delta N_i \ln \Delta N_i + N_{A,i} \ln J_{A,i} + N_{B,i} \ln J_{B,i} + N_{G,i} \ln J_{G,i} + N_{0,i} \ln P_{L,i}], \tag{2.10}$$

and for the entire crystal
$$F = -\sum_{i=1}^{n} F_i = -\sum_{i=1}^{n} X_i F'_i, \tag{2.11}$$
where $F'_i = -kT \ln P'_i$ and $\Delta N_i = N_i - N_{A,i} - N_{B,i}$.

(*c*) *All site groups fully exchangeable with respect to both* A *and* B

Pure B-crystal is the starting material. Assume that the electrical charge on each site group must be neutralized by cations on this site group only (i.e. the $N_{0,i}$ are now independent of the composition of the crystal). As before, the standard states are pure A- and B-crystals. $(\mu^{\ominus}_{AL_A})_i$ and $(\mu^{\ominus}_{BL_B})_i$ are chemical potentials when $N_{B,i} = 0$ and $N_{A,i} = 0$ respectively. $J_{A,i} = J^{*}_{A,i}$ when $N_{B,i} = 0$, and $J_{B,i} = J^{\vartriangle}_{B,i}$ when $N_{A,i} = 0$. From equation (2.10) one has when $N_{A,i}$ = Avogadro's number of lattice-forming units AL_A, so that $N_{A,i}kT = RT$,

$$(\mu^{\ominus}_{AL_A})_i = -RT[Z_A \eta_i \ln Z_A \eta_i - (Z_A \eta_i - 1) \ln (Z_A \eta_i - 1) + \ln J^{*}_{Ai} + Z_A n^{*}_{Gi} \ln J^{*}_{Gi} + Z_A \ln P^{*}_{Li}], \tag{2.12}$$

where $J^{*}_{G,i}$ and $P^{*}_{L,i}$ are the values of $J_{G,i}$ and $P_{L,i}$ for $N_{B,i} = 0$. η_i is defined as the ratio $N_i/N_{0,i}$ and $n_{G,i} = N_{G,i}/N_{0,i}$. Also, for $(BL_B)_i$

$$(\mu^{\ominus}_{BL_B})_i = -RT[Z_B \eta_i \ln Z_B \eta_i - (Z_B \eta_i - 1) \ln (Z_B \eta_i - 1) + \ln J^{\vartriangle}_{B,i} + Z_B n^{\vartriangle}_{G,i} \ln J^{\vartriangle}_{G,i} + Z_B \ln P^{\vartriangle}_{L,i}], \tag{2.13}$$

where $J^{\vartriangle}_{B,i}$, $n^{\vartriangle}_{G\ i}$ and $P^{\vartriangle}_{L,i}$ are the values of $J_{B,i}$, $n_{G,i}$ and $P_{L,i}$ for $N_{A,i} = 0$. We then have for the thermodynamic equilibrium constant on the *i*th site group

$$\ln K_i = (Z_A (\mu^{\ominus}_{BL_B})_i - Z_B (\mu^{\ominus}_{AL_A})_i + Z_B \mu^{\ominus}_{A_s} - Z_A \mu^{\ominus}_{B_s})/RT \tag{2.14}$$

while $\ln K_a$ is given as before by equation (1.13). From equations (2.12)–(2.14) one obtains

$$\ln K_i = Z_A (Z_B \eta_i - 1) \ln (Z_B \eta_i - 1) - Z_B (Z_A \eta_i - 1) \ln (Z_A \eta_i - 1) + Z_A Z_B \eta_i \ln (Z_A/Z_B) + \ln (J^{*Z_B}_{A,i}/J^{\vartriangle Z_A}_{B,i}) + Z_A Z_B \ln (P^{*}_{L,i}/P^{\vartriangle}_{L,i}) + Z_A Z_B n^{*}_{G,i} \ln J^{*}_{G,i} - Z_A Z_B n^{\vartriangle}_{G,i} \ln J^{\vartriangle}_{G,i} + \chi, \tag{2.15}$$

where $\chi = (Z_B \mu^{\ominus}_{A_s} - Z_A \mu^{\ominus}_{B_s})/RT$ (equation (1.15)). Also, as expected from equation (2.9),

$$\ln K_a = \sum_{i=1}^{n} X_i \ln K_i. \tag{2.16}$$

In this way, the individual and the overall equilibrium constants are expressed in terms of defined physical quantities. For $Z_A = Z_B = Z$ equation (2.15) simplifies and becomes independent of η_i. If the J_i are constant and independent of the degree of exchange, each site group is ideal, i.e. $(K_c)_i = K_i$. Barrer & Klinowski (1972) derived the following expression for the overall Kielland quotient, K_c, in terms of these quotients, $(K_c)_i$, for the individual site groups:

$$K_c = \left(\sum_{i=1}^{n} X_i A_i\right)^{Z_B} \Bigg/ \left(\sum_{i=1}^{n} X_i A_i^{Z_B/Z_A} (K_c)_i^{-1/Z_A}\right)^{Z_A}. \tag{2.17}$$

When there is more than one site group, the result of this division is a polynomial with an infinite number of terms in A_i. K_c cannot therefore be constant, which would be necessary for the overall exchange to be ideal. Consider a crystal containing several groups of sites, the behaviour of each site group being that described in § 1. This involves specifying Z_A, Z_B, η_i, ν_i, $w_{AA,i}/kT$ and K_i for each site group. The ratio of activity coefficients, $E_i = f_{A,i}^{Z_B}/f_{B,i}^{Z_A}$ is then calculated for any given A_i using equations (1.26). It is assumed that the extra energy arises only when a pair AA belongs to the same group of sites. The overall ion-exchange isotherms are calculated as follows. Since each site group is in equilibrium with the same aqueous solution, A_s for any given A_i is calculated from the equation:

$$K_i Q(1-A_i)^{Z_A}(A_s)^{Z_B} - (A_i)^{Z_B}(1-A_s)^{Z_A}\,\Gamma E_i = 0, \tag{2.18}$$

where Q and Γ have been defined by equations (1.5) and (1.6) respectively. Further, the composition of any other site group, j, can be calculated from the relation

$$\frac{K_i(1-A_i)^{Z_A}}{E_i A_i^{Z_B}} = \frac{K_j(1-A_j)^{Z_A}}{E_j A_j^{Z_B}}. \tag{2.19}$$

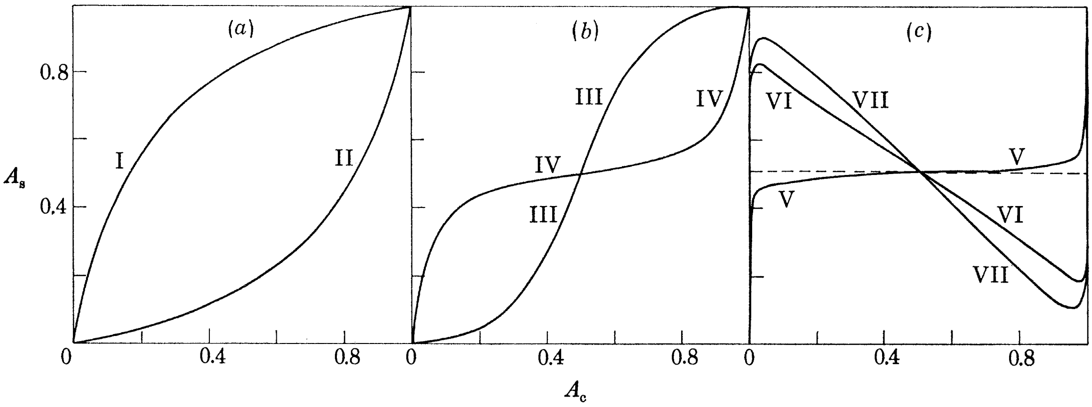

FIGURE 10. Ion-exchange isotherms for different values of w_{AA}/kT in uni-univalent exchanger composed of a single group of sites described by the model considered in § 1. $\eta = 1$. (*a*) For curve I, $w_{AA}/kT = 0$ and $K_a = 0.2$; for curve II, $w_{AA}/kT = 0$ and $K_a = 5$. The shape of curves does not depend on η and ν (ideal isotherms). (*b*) For curve III, $w_{AA}/kT = 2.303$, $\nu = 4$ and $K_a = 1$; for curve IV, $w_{AA}/kT = -2.303$, $\nu = 4$ and $K_a = 1$. (*c*) $w_{AA}/kT = -6.908$ and $K_a = 1$. For curve V, $\nu = 2$, for curve VI, $\nu = 4$; for curve VII, $\nu = 6$. Miscibility gaps are marked with the dashed line for VI and VII.

Equation (2.18) has been solved for A_s and equation (2.19) for A_j using a computer program. The overall equivalent cation fraction of A in the crystal is then

$$A_c = \sum_{i=1}^{n} X_i A_i, \tag{2.20}$$

where the individual X_i are known. The ion-exchange isotherms are plotted as A_s against A_c. Calculations were performed for a crystal containing two groups of sites with different kinds of non-ideality. Results are given in figures 10–12 and can be summarized as follows:

(i) As predicted from equation (2.17), figure 11*a* shows that even two ideal isotherms, I and II in figure 10*a*, do not produce an overall ideal isotherm. For example, curve 2 in figure 11*a* corresponds with $K_a = \sqrt{(5 \times 0.2)} = 1$, and yet the isotherm is not a straight line.

(ii) By combining an isotherm with a miscibility gap with any continuous isotherm (figures 11*c* and *d*) one obtains a resultant isotherm with a miscibility gap. For instance, as pointed out in § 1 (l), a sufficiently high and negative w_{AA}/kT results in a miscibility gap. These features are preserved in the composite isotherms. The size and position of the resultant miscibility gap depends on the relative population of each site group participating in the composite isotherm. It is seen that diverse isotherm contours can be obtained. Some metastable contours are unusual in the immiscibility range. However, the real course of equilibrium exchange in the miscibility gap is that given by the dashed lines, as explained in § 1. In practice isotherms showing immiscibility are also subject to hysteresis (Barrer & Munday 1971; Barrer & Falconer 1956) arising from the difficulty of nucleating the new phase on or in a matrix of the parent phase.

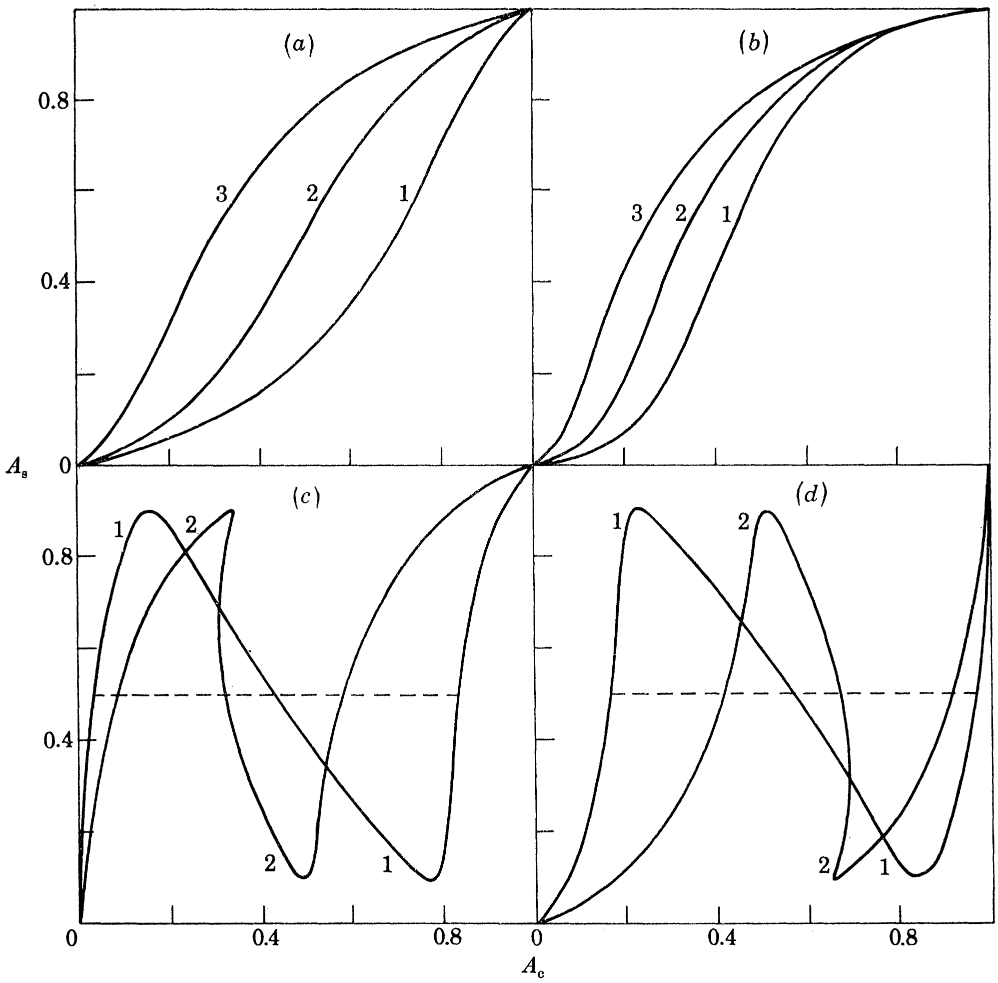

FIGURE 11. Overall ion-exchange isotherms for a crystal with two groups of sites. For curves 1 the relative population of the first site group, $X_1 = 0.2$; for curves 2 $X_1 = 0.5$; for curves 3 $X_1 = 0.8$. For clarity only curves 1 and 2 are shown in (c) and (d). Miscibility gaps, whose horizontal position is common for both curves, are marked with dashed lines. (a) First site group has properties described by curve I; second site group by curve II in figure 10a. (b), (c) and (d) give combination isotherms for (b) I+III; (c) I+VII; and (d) II+VII.

(d) *Two site groups: one excluding* A *and the other excluding* B

In aluminosilicates not all kinds of site need be available to both exchange cations. For instance, as noted in the General Introduction, in faujasite all of several types of site are available to the sodium cation (Smith 1971), while tetramethylammonium cations must, for reasons of size, occupy exclusively sites nearer the middle of the large faujasite cages. As a first approximation, we consider all the sites available only to sodium as group 1, and the sites nearer the middle of large cavities as group 2. Sodium cations are not expected appreciably to occupy group 2 sites. The model reduces in its simplest form to considering two site groups, one accessible only to ions A, the other available only to ions B.

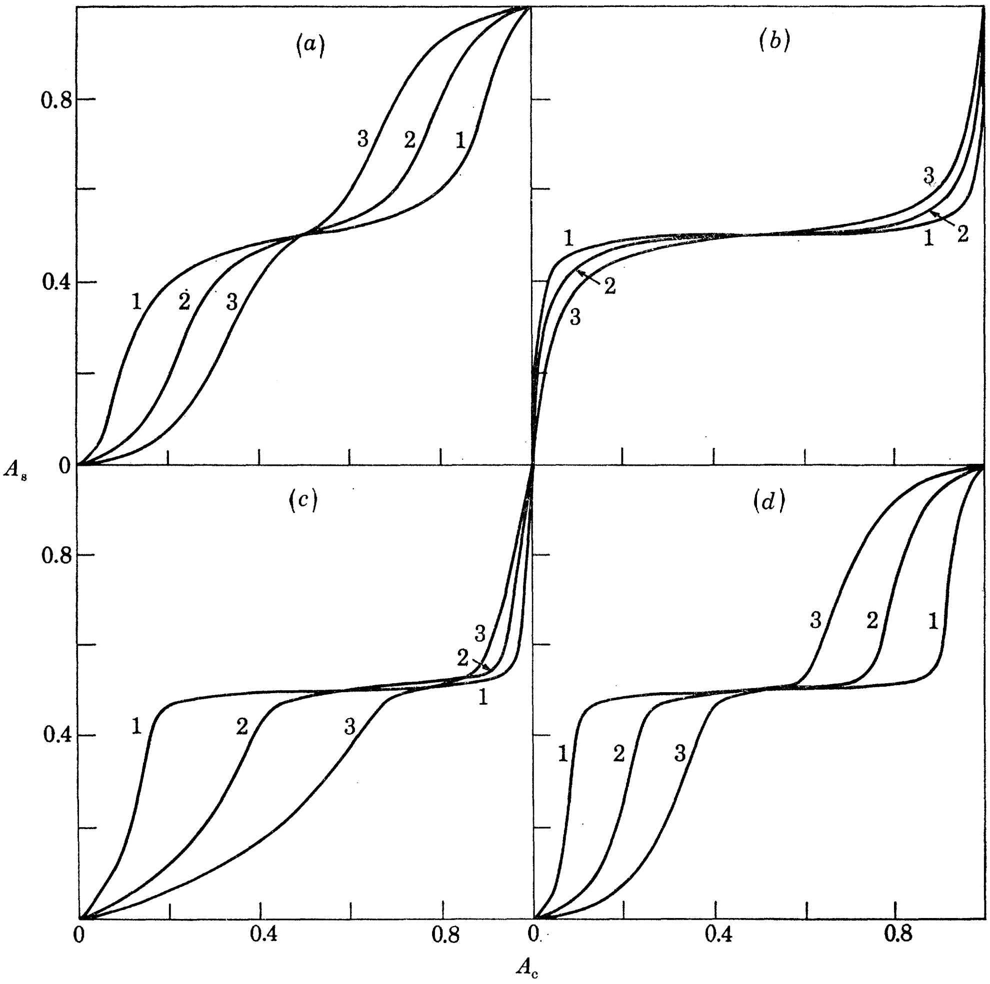

FIGURE 12. Overall ion-exchange isotherms for a crystal with two groups of sites. For curves 1 $X_1 = 0.2$; for curves 2 $X_1 = 0.5$; for curves 3 $X_1 = 0.8$. (*a*), (*b*), (*c*) and (*d*) give combination isotherms for (*a*) III+IV; (*b*) IV+V; (*c*) II+V; (*d*) III+V.

Equation (2.5) does not require that all site groups be accessible to both A and B. When some types of site admit only one kind of ion, the appropriate $N_{A,i}$ or $N_{B,i}$ in equation (2.5) are zero. When there are just two site groups one accessible only to A and the other only to B, ion exchange cannot be reconciled with the requirement in § 2 (*c*) that the negative framework charge on each site group be neutralized by cations on this site group only. Cations on both types of intermixed site must neutralize a *common* electrical charge. It does not follow, however, that the crystal is completely exchangeable with respect to both cations. The theoretical limit of exchange with respect to the incoming ion, A, is determined by the number of A ions required to neutralize the framework charge. On the other hand, this absolute limit may not be reached for other reasons.

One may be that the size of A cations restricts their number in a cavity for lack of space; another, the limited polarizability of the anionic framework and resultant local charge disbalance as ions B on one site group are replaced by ions A on the other. Consider site groups 1 and 2 having a total charge N_0. While this charge can be neutralized by cations A on sites 1 and cations B on sites 2, the framework charge appropriate to either group of sites must remain constant throughout the exchange. P_{L1} and P_{L2} are the partition functions for the amount of framework carrying one negative charge and associated with the site groups 1 and 2 respectively. Let there be N_1 sites of type 1 available for cation A and N_2 sites of type 2 available only for B. If N_A ions of A and N_B ions of B are present one has

$$N_0 = N_{0,1} + N_{0,2} = Z_A N_A + Z_B N_B. \tag{2.21}$$

The partition function for this amount of mixed crystal is

$$P = \frac{N_1!}{N_A!(N_1-N_A)!} \frac{N_2!}{N_B!(N_2-N_B)!} J_A^{N_A} J_B^{N_B} J_G^{N_G} P_{L1}^{Z_A N_A} P_{L2}^{Z_B N_B}, \tag{2.22}$$

where the J and the P_L may be functions of the cationic composition. All quantities under the factorial in equation (2.22) must be greater than or equal to zero. One must therefore have

$$\left.\begin{aligned} N_1 - N_A &\geqslant 0, \\ N_2 - N_B &\geqslant 0. \end{aligned}\right\} \tag{2.23}$$

Dividing the above by N_0, and setting $N_1/N_0 = \eta_1$ and $N_2/N_0 = \eta_2$ one has

$$\left.\begin{aligned} \eta_1 - A_c/Z_A &\geqslant 0, \\ \eta_2 - B_c/Z_B &\geqslant 0. \end{aligned}\right\} \tag{2.24}$$

For pure B-form to exist, one must have $\eta_2 \geqslant 1/Z_B$. The absolute limit to exchange with respect to the incoming ion A is the smaller of the two quantities

$$\left.\begin{aligned} A_c^{\max} &= Z_A \eta_1, \\ A_c^{\max} &= 1. \end{aligned}\right\} \tag{2.25}$$

As already noted, however, $A_c^{\max}$ can be lower than the above theoretical value.

When ion exchange cannot proceed to completion the exchange reaction can be represented as

$$\underset{\text{(component 1)}}{[B_{1/Z_B} L]_c} + \alpha_{\max}[A_{1/Z_A}^{Z_A+}]_s \rightleftarrows \underset{\text{(component 2)}}{[A_{\alpha\max/Z_A} B_{(1-\alpha_{\max})/Z_B} L]_c} + \alpha_{\max}[B_{1/Z_B}^{Z_B+}]_s, \tag{2.26}$$

where $\alpha_{\max}$ is the number of equivalents of $[A^{Z_A+}]_s$ which reacts with one equivalent of B-crystal to produce maximally exchanged material. It follows that $0 < \alpha_{\max} < 1$. Also, $\alpha_{\max}$ is determined by whichever of the three causes (number of sites available for A; charge disbalance; large size of A ions) imposes the lowest limit to exchange.

All realizable solid compositions can be considered as solid solutions of component 1 with component 2. By mixing q_1 moles of component 1 and q_2 moles of component 2 we arrive at a composition for which the numbers N_A and N_B are as follows:

$$\left.\begin{aligned} N_A &= \frac{q_2 Z_B \alpha_{\max}}{Z_B \alpha_{\max} + Z_A(1-\alpha_{\max})}, \\ N_B &= q_1 + \frac{q_2 Z_A(1-\alpha_{\max})}{Z_B \alpha_{\max} + Z_A(1-\alpha_{\max})}, \end{aligned}\right\} \tag{2.27}$$

In addition

$$\left.\begin{aligned} N_1 &= \eta_1 N_0 = Z_A \eta_1 N_A + Z_B \eta_1 N_B, \\ N_2 &= \eta_2 N_0 = Z_A \eta_2 N_A + Z_B \eta_2 N_B. \end{aligned}\right\} \tag{2.28}$$

From equation (2.22), using Stirling's approximation, one has

$$\begin{aligned} F = -kT[&N_1 \ln N_1 + N_2 \ln N_2 - N_A \ln N_A - N_B \ln N_B - (N_1 - N_A) \ln (N_1 - N_A) \\ &- (N_2 - N_B) \ln (N_2 - N_B) + N_A \ln J_A + N_B \ln J_B + N_G \ln J_G \\ &+ Z_A N_A \ln P_{L1} + Z_B N_B \ln P_{L2}]. \end{aligned} \tag{2.29}$$

For the incomplete exchange the standard states are the pure B-crystal (component 1) in which $N_A = A_c = 0$; and the pure component 2, i.e. the crystal maximally exchanged with respect to A ($A_c = \alpha_{\max}$; $B_c = 1 - \alpha_{\max}$). Standard chemical potentials $\mu_1^\ominus$ and $\mu_2^\ominus$ of components 1 and 2 then follow.

On multiplying the equation of the exchange reaction (equation (2.26) by $Z_A Z_B$ one obtains for K_a

$$\begin{aligned} \ln K_a &= \frac{Z_A \mu_1^\ominus - (Z_B A_c^{\max} + Z_A B_c^{\min}) \mu_2^\ominus + Z_B A_c^{\max} \mu_{A_s}^\ominus - Z_A A_c^{\max} \mu_{B_s}^\ominus}{RT} \\ &= \ln \frac{(a_S^B)^{Z_A A_c^{\max}} (y_2)^{(Z_B A_c^{\max} + Z_A B_c^{\min})}}{(a_S^A)^{Z_B A_c^{\max}} (y_1)^{Z_A}} = \ln K_c + \ln \frac{f_1^{Z_A}}{f_2^{(Z_B A_c^{\max} + Z_A B_C^{\min})}}, \end{aligned} \tag{2.30}$$

where y_1 and y_2 are equivalent fractions of components 1 and 2, respectively, and f_1 and f_2 are the appropriate activity coefficients. One has the following relation for the composite material:

$$\left.\begin{aligned} A_c &= y_2 A_c^{\max}, \\ B_c &= 1 - y_2 A_c^{\max}. \end{aligned}\right\} \tag{2.31}$$

In order to obtain general expressions for the activity coefficients f_1 and f_2 one must know how the individual partition functions J_A, J_B, J_G, P_{L1} and P_{L2} and the number of guest molecules, N_G, vary with the cationic composition of the crystal. For the calculations all these quantities are assumed independent of N_A and N_B. Differentiating equation (2.29) partially with respect to the numbers of moles of q_1 and q_2 and bearing in mind equations (2.27) and (2.28) one obtains for the chemical potentials of components 1 and 2

$$\left.\begin{aligned} \mu_1 = -RT[&Z_B \eta_1 \ln Z_A \eta_1 + Z_B \eta_2 \ln Z_B \eta_2 - \ln B_c - Z_B \eta_1 \ln (Z_A \eta_1 - A_c) \\ &- (Z_B \eta_2 - 1) \ln (Z_B \eta_2 - B_c) + \ln J_B + Z_B n_G \ln J_G + Z_B \ln P_{L2}], \\ \mu_2 = -\frac{RT}{Z_B A_c^{\max} + Z_A B_c^{\min}}[&Z_A Z_B \eta_1 \ln Z_A \eta_1 + Z_A Z_B \eta_2 \ln Z_B \eta_2 - Z_B A_c^{\max} \ln A_c \\ &- Z_A B_c^{\min} \ln B_c - Z_B (Z_A \eta_1 - A_c^{\max}) \ln (Z_A \eta_1 - A_c) \\ &- Z_A (Z_B \eta_2 - B_c^{\min}) \ln (Z_B \eta_2 - B_c) + Z_B A_c^{\max} \ln J_A + Z_A B_c^{\min} \ln J_B \\ &+ Z_A Z_B n_G \ln J_G + Z_A Z_B A_c^{\max} \ln P_{L1} + Z_A Z_B B_c^{\min} \ln P_{L2}], \end{aligned}\right\} \tag{2.32}$$

where $n_G = N_G / N_0$ independently of the cationic composition.

It is seen from equations (2.32) that for the exchange on two site groups of which one excludes A and the other excludes B the ratio of activity coefficients in the crystal phase is a function of composition, even if the partition functions J_A, J_B, J_G, P_{L1} and P_{L2} are taken as constant. The exchange is thus always non-ideal, even when $A_c^{\max} = 1$ and even if $Z_A = Z_B = 1$. However, these simplifying assumptions allow one to express $\ln (f_2/f_1)$ in terms of the physical parameters

Z_A, Z_B, η_1, η_2 and $A_c^{\max}$. K_a depends upon Z_A, Z_B, η_1, η_2, J_A, J_B, J_G, P_{L1}, P_{L2}, $\mu^{\ominus}_{A_s}$ and $\mu^{\ominus}_{B_s}$ (equation (2.30)). Ion-exchange isotherms were then calculated as follows. For a given Z_A, Z_B, η_1 and η_2 it is assumed that the maximum extent of exchange, $A_c^{\max}$, is that given by equations (2.25). It is thus assumed that the extent of exchange is not limited by an unfavourable electrical charge distribution or by the size of the A cations, but merely by the number of sites available for A. The remaining variables were assumed to be such as to give $QK_a = 1$, where Q has been defined in equation (1.5). Thus in effect the equilibrium constant was assigned *a priori*. $(Z_A m_s^A + Z_B m_s^B)$ for the aqueous solution, was taken to be 0.01 M, at which the ratio, Γ of the aqueous activity coefficients is close to unity. Finally, the implicit equation (2.30) was solved for A_c for each value of A_s using a computer program. The results (figure 13) are very similar to the experimental results of Barrer, Papadopoulos & Rees (1967) for the exchange of sodium by organic cations in clinoptilolite.

(*e*) *Two site groups*: *one available for* A *and* B *and the other only for* B

There are N_1 sites of type 1 available for A and B and N_2 sites of type 2 available only for B. As before, pure B-crystal is the starting material. If the electrical charge associated with each site group had to be neutralized by cations on this site group only, the sites available exclusively for B would have to remain filled with a constant number of B cations at all times. This is the case of two groups of sites, one exchangeable and the other completely unexchangeable and has been adequately considered by Barrer, Klinowski & Sherry (1973). We therefore consider a more general situation of two types of site intimately mixed with one another, on which the cations neutralize a *common* anionic framework charge N_0. Let P_{L1} and P_{L2} be the partition functions for the amount of framework carrying one negative charge and associated with site groups 1 and 2 respectively. J_A, J_{B1} and J_{B2} are the appropriate partition functions for the cations. By reference to equation (2.26), all realizable solid compositions can again be considered as solid solutions of component 1 with component 2. If N_A ions of A are present and the numbers of B ions on each type of site are respectively N_{B1} and N_{B2} one has

$$\left.\begin{aligned} N_{01} &= Z_A N_A + Z_B N_{B1}, \\ N_{02} &= Z_B N_{B2}, \\ N_0 &= N_{01} + N_{02}. \end{aligned}\right\} \tag{2.33}$$

The partition function for this amount of mixed crystal is

$$P = \frac{N_1!}{N_A!\,N_{B1}!\,(N_1 - N_A - N_{B1})!}\,\frac{N_2!}{N_{B2}!\,(N_2 - N_{B2})!}\,J_A^{N_A} J_{B1}^{N_{B1}} J_{B2}^{N_{B2}} J_G^{N_G} P_{L1}^{N_{01}} P_{L2}^{N_{02}}, \tag{2.34}$$

where, as before, the J and the P_L may be functions of composition. All quantities under the factorial in equation (2.34) must be greater than or equal to zero. One must have therefore

$$\left.\begin{aligned} N_1 - N_A - N_{B1} &\geqslant 0 \\ N_2 - N_{B2} &\geqslant 0 \end{aligned}\right\} \tag{2.35}$$

Taking $N_1/N_0 = \eta_1$; $N_2/N_0 = \eta_2$ one obtains as a condition for the existence of pure B-crystal: $\eta_1 \geqslant 1/Z_B$ and $\eta_2 \geqslant 1/Z_B$. The absolute limit to exchange with respect to the incoming ion A is given by equations (2.25). It follows that for $Z_A \geqslant Z_B$ complete exchange should always be possible. The availability of sites for A is however not the only limitation. As before, there may be steric reasons (if cations A are very large) and electrical reasons for $A_c^{\max}$ to be lower than the theoretical value.

From equation (2.34) the free energy is given by

$$\begin{aligned} F = -kT[&N_1 \ln N_1 + N_2 \ln N_2 - N_A \ln N_A - N_{B1} \ln N_{B1} \\ &- (N_1 - N_A - N_{B1}) \ln (N_1 - N_A - N_{B1}) - N_{B2} \ln N_{B2} \\ &- (N_2 - N_{B2}) \ln (N_2 - N_{B2}) + N_A \ln J_A + N_{B1} \ln J_{B1} + N_{B2} \ln J_{B2} \\ &+ N_G \ln J_G + N_{01} \ln P_{L1} + N_{02} \ln P_{L2}]. \end{aligned} \tag{2.36}$$

The standard states are the pure B-crystal (component 1) in which $N_A = 0$; and the pure component 2, i.e. the crystal maximally exchanged with respect to A. The appropriate expressions for the standard chemical potentials $\mu_1^{\ominus}$ and $\mu_2^{\ominus}$ follow.

Let $p_2 = N_{02}/N_0 = Z_B N_{B2}/N_0$ and $p_1 = 1 - p_2$ be the fractions of the negative framework charge, N_0, which are neutralized by cations on site groups 1 and 2, respectively. $p_1^*, p_2^*, p_1^{\vartriangle}$ and $p_2^{\vartriangle}$ are the values of p_1 and p_2 at the standard states. The equilibrium constant for the exchange is given by equation (2.30). However, this equation is insufficient for obtaining ion-exchange isotherms. To calculate these one must know J_A, J_{B1}, J_{B2}, J_G, P_{L1}, P_{L2}, N_G and p_1 as functions of the cationic composition of the crystal. As a first approximation one may assume that all these except p_1 are independent of N_A and N_B, and that p_1 is a linear function of composition: $p_1 = [(p_1^* - p_1^{\vartriangle}) A_c/A_c^{\max}] + p_1^{\vartriangle}$. Differentiating equation (2.36) partially with respect to the number of moles of q_1 and q_2, and bearing in mind equations (2.27) and (2.28) one obtains for the chemical potentials of components 1 and 2:

$$\left.\begin{aligned} \mu_1 = -RT[&Z_B \eta_1 \ln \eta_1 + Z_B \eta_2 \ln Z_B \eta_2 + p_1^{\vartriangle} \ln Z_B - p_1^{\vartriangle} \ln (p_1 - A_c) \\ &- (Z_B \eta_1 - p_1^{\vartriangle}) \ln \left(\eta_1 - \frac{A_c}{Z_A} - \frac{p_1 - A_c}{Z_B}\right) - p_2^{\vartriangle} \ln p_2 - (Z_B \eta_2 - p_2^{\vartriangle}) \ln (Z_B \eta_2 - p_2) \\ &+ p_1^{\vartriangle} \ln J_{B1} + p_2^{\vartriangle} \ln J_{B2} + Z_B n_G \ln J_G + Z_B p_1^{\vartriangle} \ln P_{L1} + Z_B p_2^{\vartriangle} \ln P_{L2}], \\ \mu_2 = -\frac{RT}{(Z_B A_c^{\max} + Z_A B_c^{\min})} [&Z_A Z_B \eta_1 \ln Z_A Z_B \eta_1 + Z_A Z_B \eta_2 \ln Z_B \eta_2 \\ &- Z_B A_c^{\max} \ln Z_B A_c - Z_A (B_c^{\min} - p_2^*) \ln Z_A (B_c - p_2) - (Z_A Z_B \eta_1 - Z_B A_c^{\max} \\ &- Z_A B_c^{\min} + Z_A p_2^*) \ln (Z_A Z_B \eta_1 - Z_B A_c - Z_A B_c + Z_A p_2) - Z_A p_2^* \ln p_2 \\ &- Z_A (Z_B \eta_2 - p_2^*) \ln (Z_B \eta_2 - p_2) + Z_B A_c^{\max} \ln J_A + Z_A (B_c^{\min} - p_2^*) \ln J_{B1} \\ &+ Z_A p_2^* \ln J_{B2} + Z_A Z_B n_G \ln J_G + Z_A Z_B p_1^* \ln P_{L1} + Z_A Z_B p_2^* \ln P_{L2}. \end{aligned}\right\} \tag{2.37}$$

If site group 1 is completely exchangeable for cation A we have $p_1^* = A_c^{\max}$ and $p_2^* = B_c^{\min}$ and the second of equations (2.37) simplifies. Ion-exchange isotherms were calculated using the procedure outlined in § 2 (*d*). Equations (2.30) and (2.31) apply to the present model. Some isotherms are shown in figure 14. They are in general similar in shape to the isotherms considered in § 2 (*d*) (figure 13), but the curves with $K_a = 1$ are closer to straight lines than the corresponding isotherms in § 2 (*d*). This seems to result from the assumption that the p vary linearly with the cationic content of the crystal. The isotherms 1′, 2′ in figure 14 for $K_a = 10$ have contours similar to those observed when transition metal ammine ions exchange with NH_4^+ in mordenite (Barrer & Townsend 1976). Exchange at room temperature progressed only to about 50 %, and it was considered that NH_4^+ sited in the wide channels was exchangeable by metal-ammine ions, but NH_4^+ in the side pockets was not. This interpretation corresponds with the model considered here, of two kinds of site, one kind accessible to both ions and the other accessible only to one of the ions.

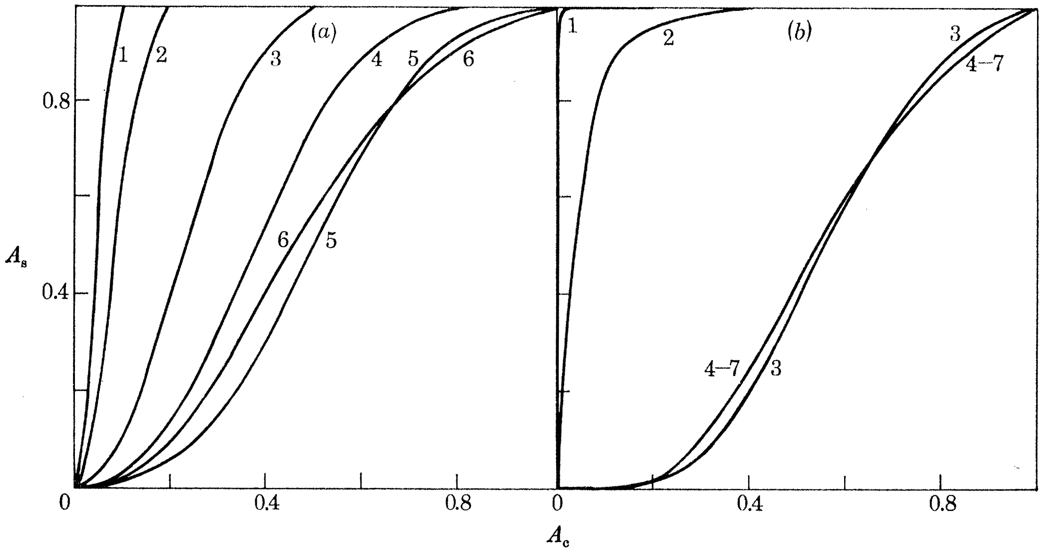

FIGURE 13. Ion-exchange isotherms for a crystal with two site groups. Sites of group 1 are available only for cation A, and sites of group 2 are available only for cation B. $K_a Q = 1$ and $(Z_A m_s^A + Z_B m_s^B) = 0.01$ M for all isotherms. $\eta_2 = 1$. For curves 1 $\eta_1 = 0.1$; for curves 2 $\eta_1 = 0.2$; for curves 3 $\eta_1 = 0.5$; for curves 4 $\eta_1 = 0.8$; for curves 5 $\eta_1 = 1$; for curves 6 $\eta_1 = 2$; for curves 7 $\eta_1 = 5$. (*a*) $Z_A = Z_B = 1$; (*b*) $Z_A = 2$; $Z_B = 1$. A_c^{max} was assumed to be that given by equations (2.28).

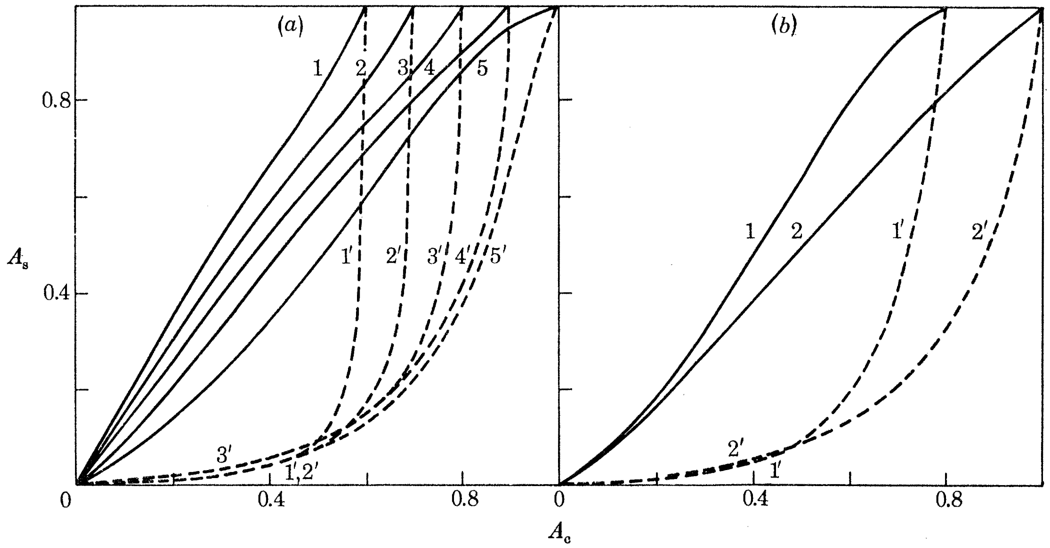

FIGURE 14. Ion-exchange isotherms for a crystal with two site groups. Sites of group 1 are available for cations A and B, and sites of group 2 are available only for cations B. The exchange is uni-univalent. Isotherms with $K_a = 1$ are drawn with solid lines, and isotherms with $K_a = 10$ are drawn with dashed lines. $p_1^A = 0.5$. (*a*) $\eta_1 = \eta_2 = 1$. For curves 1 and 1′ $p_1^* = A_c^{max} = 0.6$; for curves 2 and 2′ $p_1^* = A_c^{max} = 0.7$; for curves 3 and 3′ $p_1^* = A_c^{max} = 0.8$; for curves 4 and 4′ $p_1^* = A_c^{max} = 0.9$; for curves 5 and 5′ $p_1^* = A_c^{max} = 1.0$. (*b*) For curves 1 and 1′ $\eta_1 = \eta_2 = 1$, $p_1^* = 1.0$ and $A_c^{max} = 0.8$; for curves 2 and 2′ $\eta_1 = 2$, $\eta_2 = 1$, $p_1^* = A_c^{max} = 1.0$. $(m_s^A + m_s^B)$ is 0.01 M.

(*f*) *Concluding remarks*

The situations described in this section illustrate the effects of distinguishable configurations of cations upon the exchange isotherms. The calculations give isotherm contours which simulate well those of isotherms found in real situations considered to correspond with the cation sitings and restrictions assumed for the calculations. Because of the distributions of the cations between site groups, and because often, to neutralize the negative framework charge, only some of the sites in each site group need be occupied, there are many opportunities for cationic disorder in zeolites, even in the homoionic forms. One may consider further the positions in a given site group, for example those associated with the 6-ring windows between sodalite cages and 26-hedra in faujasite (position II in figure 9). Here small cations such as Na^+ may be located in the 6-ring whereas larger ions like Cs^+ must for steric reasons be centred outside the plane of the 6-ring (position $II^\cdot$ in figure 9). In the mixed crystals this introduces an additional element of cationic disorder, which however does not affect the counting of distinguishable configurations unless the positioning is so different as to constitute a new kind of site. The criterion for a new kind of site would be that when in the above illustration position $II^\cdot$ is occupied, position II adjacent to it can also be occupied. The counting of distinguishable configurations in the partition function must then take this into consideration. If on the other hand occupation of position $II^\cdot$ automatically requires that the position II be empty, then for the purpose of counting configurations positions II and $II^\cdot$ can be regarded as a single site group.

3. Replacement of silicon by aluminium

(a) *Introduction*

A very important aspect of the chemistry of tectosilicates referred to in the general introduction is the replacement of Si by Al in the anionic framework, accompanied by insertion of an electrochemical equivalent of cations, e.g.

$$Si^{4+} \rightleftarrows Al^{3+}, Na^+.$$

These replacements cannot be effected directly, but occur as a result of formation under different conditions. Some aluminosilicates tend to have fixed compositions (e.g. nepheline, $NaAlSiO_4$; kalsilite, $KAlSiO_4$; kaliophilite, $KAlSiO_4$; albite, $NaAlSi_3O_8$; potash felspar, $KAlSi_3O_8$; and anorthite, $CaAl_2Si_2O_6$). Others have variable Si/Al ratios according to the conditions of synthesis (e.g. chabazites with $1.08 < Si/Al < 3.9$ (Barrer & Baynham 1956; Gude & Sheppard 1966); faujasites with $1.0 < Si/Al < 3.0$ (Breck 1974*a*); zeolite L with $1.04 < Si/Al < 3.5$ (Barrer & Mainwaring 1972; Breck & Flanigen 1968)). Both situations must be explained by an adequate theoretical treatment of isomorphous replacement.

In the zeolites and in felspathoids of sodalite, cancrinite or scapolite families, water molecules or salts act as framework fillers and stabilisers (Barrer 1960; Barrer & Cole 1970). In view of the importance of tectosilicates such as those referred to above it is of much interest to consider various situations which can arise in isomorphous replacement in statistical thermodynamic terms. Such an attempt is presented in this section.

(b) *The framework*

Tectosilicate frameworks are composed of linked tetrahedra of SiO_4 or AlO_4. Accordingly three kinds of bond are possible:

$$\text{(i)}\quad \geqslant Si{-}O{-}Si \leqslant$$
$$\text{(ii)}\quad \geqslant Si{-}O{-}Al \leqslant$$
$$\text{(iii)}\quad \geqslant Al{-}O{-}Al \leqslant$$

We choose the $\geqslant Si{-}O{-}Si \leqslant$ bond as the reference state. If Al replaces Si in a given tetrahedron four such bonds are replaced by four $\geqslant Si{-}O{-}Al \leqslant$ bonds (with an appropriate interstitial cation to maintain neutrality) and an energy change ϵ is involved (excluding for the moment the bonding energy of the cation). If both Si atoms are so replaced giving an $\geqslant$Al—O—Al$\leqslant$ linkage then over and above the energy ϵ per Al there is assumed to be an extra energy per $\geqslant$Al—O—Al$\leqslant$ bond of $2w/\nu = \frac{1}{2}w$ ($\nu = 4 =$ coordination number of a tetrahedral site). According to Loewenstein's rule (Loewenstein 1954) the upper limit to the ratio Al/Si is 1 implying that $\frac{1}{2}w$ must be large and endothermal so that $\geqslant$Al—O—Al$\leqslant$ bonds are rare.

To estimate the contribution of $\geqslant$Al—O—Al$\leqslant$ bonds to the total free energy of the crystal for any value of $\frac{1}{2}w$ the treatment of adsorption with interaction given by Lacher (1937) and by Fowler & Guggenheim (1939) may be applied to the above situation. The SiO_4 tetrahedra of the framework correspond formally with bound unoccupied sites and the AlO_4 tetrahedra correspond with occupied sites. The energy ϵ corresponds formally with the energy of adsorption. If there are N_{Si} unoccupied sites (unreplaced SiO_4 tetrahedra), N_{Al} occupied sites (AlO_4 tetrahedra), the framework partition function is

$$\frac{N_\gamma!}{N_{Al}!\,N_{Si}!}\,J_{Si}^{N_{Si}}J'^{N_{Al}}_{Al}\exp\left(-\frac{\epsilon N_{Al}}{kT}\right)P_{Al}^{int}.$$

In this expression $N_\gamma = N_{Al}+N_{Si} =$ the total number of tetrahedra. P_{Al}^{int} allows for the contribution to the partition function arising from the extra energy $\frac{1}{2}w$ when a pair of AlO_4 tetrahedra occupy adjacent sites in the lattice. J_{Si} is the partition function of an SiO_4 tetrahedron for all internal degrees of freedom and the internal and bonding energy of this group. In Fowler & Guggenheim's treatment of adsorption the partition function for a vacant site was taken as unity. This would correspond with taking $J_{Si} = 1$. J'_{Al} is the corresponding function for the AlO_4 group excluding the extra terms due to ϵ and $\frac{1}{2}w$. We may incorporate the first of these, i.e. $\exp(-\epsilon N_{Al}/kT)$, into $J'^{N_{Al}}_{Al}$ to give $J_{Al}^{N_{Al}}$, and rewrite the partition function as

$$\frac{N_\gamma!}{N_{Al}!\,N_{Si}!}\,J_{Si}^{N_{Si}}J_{Al}^{N_{Al}}P_{Al}^{int}.$$

If $\frac{1}{2}w$ is sufficiently endothermal the number of linked AlO_4 tetrahedra tends to zero; in this case the limiting maximum ratio Al/Si → 1 (Loewenstein 1954). The actual distribution in space of the (Al, Si)O_4 tetrahedra can however reduce this limiting ratio. If the tectosilicate framework is composed only of rings of even numbers of linked (Al, Si)O_4 tetrahedra (e.g. sodalite, zeolite A, faujasite, chabazite) then for these compounds Al and Si can often alternate throughout the frameworks and so Al/Si can approach 1. If however 5-rings are present (e.g. yugawaralite, mordenite, stilbite) Al and Si cannot alternate everywhere throughout the framework and so the limiting composition must give Al/Si < 1, because although $\geqslant$Si—O—Si$\leqslant$ bonds are allowed $\geqslant$Al—O—Al$\leqslant$ bonds are, as noted above, very improbable.

(*c*) *Cations and guest molecules*

For simplicity a total of N identical crystallographic sites for cations is assumed. If cations A, B, ... are present in these sites in numbers N_A, N_B ... then the partition function for the cations, and also for the guest molecules, is

$$\frac{N!}{(N-N_A-N_B-\ldots)!\,N_A!\,N_B!\ldots}\,J_G^{N_G}J_A^{N_A}J_B^{N_B}\ldots.$$

As before J_A, J_B ... are the partition functions for individual ions A, B, ... and $J_G^{N_G}$ for the N_G guest molecules, as in §§ 1 and 2, includes a configurational term for these guest molecules. As before it is often the case that the number of cations needed to neutralise the framework charge is less than the total number of crystallographic sites so that the term $(N-N_A-N_B-\ldots)!$ is required.

(*d*) *The complete partition function*

The complete partition function is then

$$P = \frac{N_\gamma!}{N_{Al}!\,N_{Si}!}\cdot\frac{N!}{(N-N_A-N_B-\ldots)!\,N_A!\,N_B!}\,J_{Si}^{N_{Si}}J_{Al}^{N_{Al}}J_G^{N_G}J_A^{N_A}J_B^{N_B}\ldots P_{Al}^{int}. \tag{3.1}$$

We may further include the situation in which an extra change in the energy of the crystal also occurs whenever two cations A occupy adjacent crystal sites (see § 1 (*c*)). Let this energy change per pair be $2w_{AA}/\nu$ where w_{AA} is an energy and ν is the coordination number of a cationic site with respect to other nearest cation sites (not necessarily 4 as in the case of AlO_4 and SiO_4 tetrahedra). We assume further that there is no corresponding energy change whenever any other ionic pair occurs. In this case the above partition function for the tectosilicate crystal should be further multiplied by the term P^{int} (see § 1 (*c*)). A restriction of the extent of the replacement reaction

$$Si^{4+}\rightarrow Al^{3+}, A^{Z_A+}/Z_A$$

arises, even in the absence of interaction, if the total number of crystallographic sites available for the cations A is limited. The Al content cannot exceed the cation content. This limitation will be considered later.

For a mixed cationic population of ions A, B, ... on cation sites, P^{int} follows from the Fowler & Guggenheim treatment provided it is only the pairing AA which introduces any additional energy (§ 1). This energy is as noted above $2w_{AA}/\nu$. The properties of the partition function P can now be examined assuming for simplicity that there is only one type of cation, A, present and that J_{Si}, J_{Al}, J_A and J_G do not depend upon the extent of the replacement of Si by Al.

(*e*) *Free energy of the system*

The free energy, F, of the aluminosilicate with only one kind of exchange ion is

$$\begin{aligned}F = -kT\{&N_\gamma\ln N_\gamma - N_{Al}\ln N_{Al} - N_{Si}\ln N_{Si} + N\ln N - (N-N_A)\ln(N-N_A) - N_A\ln N_A\\ &+N_{Si}\ln J_{Si} + N_{Al}\ln J_{Al} + N_A\ln J_A + N_G\ln J_G\} + F_{Al}^{int} + F^{int},\end{aligned} \tag{3.2}$$

where

$$\left.\begin{aligned}F_{Al}^{int} &= 2kT\left[2N_{Al}\ln\frac{2X_{Si}}{D-2X_{Al}} + N_\gamma\ln\frac{D-2X_{Al}}{X_{Si}D}\right],\\ D &= [1-4X_{Al}X_{Si}\,\alpha]^{\frac{1}{2}}+1,\\ \alpha &= 1-\exp(-w/2kT),\end{aligned}\right\} \tag{3.3}$$

and where F^{int} has been defined in equation (1.16). We also use the following relations arising in part from stoichiometry and the electrical neutrality condition:

$$\left.\begin{aligned}N_{Al}+N_{Si} &= N_\gamma &\quad N_G/N_\gamma &= m_G\\ N_{Si}/N_\gamma &= X_{Si} & Z_A N_A &= N_{Al}\\ N_{Al}/N_\gamma &= X_{Al} & (N-N_A)/N_\gamma &= r_c - X_{Al}/Z_A\\ N/N_\gamma &= r_c & N_A/N_\gamma &= X_{Al}/Z_A.\end{aligned}\right\} \tag{3.4}$$

On dividing equation (3.2) by kTN_γ and using the relations (1.16), (3.3) and (3.4), one obtains:

$$\begin{aligned}\frac{F}{kTN_\gamma} = {} & X_{\mathrm{Al}} \ln X_{\mathrm{Al}} + X_{\mathrm{Si}} \ln X_{\mathrm{Si}} - r_{\mathrm{c}} \ln r_{\mathrm{c}} + \left(r_{\mathrm{c}} - \frac{X_{\mathrm{Al}}}{Z_{\mathrm{A}}}\right) \ln \left(r_{\mathrm{c}} - \frac{X_{\mathrm{Al}}}{Z_{\mathrm{A}}}\right) + \frac{X_{\mathrm{Al}}}{Z_{\mathrm{A}}} \ln \frac{X_{\mathrm{Al}}}{Z_{\mathrm{A}}} \\ & + X_{\mathrm{Al}} \ln \left[\frac{J_{\mathrm{Si}}}{J_{\mathrm{Al}} J_{\mathrm{A}}^{1/Z_{\mathrm{A}}}}\right] - \ln J_{\mathrm{Si}} - m_{\mathrm{G}} \ln J_{\mathrm{G}} + 2\left[2X_{\mathrm{Al}} \ln \frac{2X_{\mathrm{Si}}}{D - 2X_{\mathrm{Al}}} + \ln \frac{D - 2X_{\mathrm{Al}}}{X_{\mathrm{Si}} D}\right] \\ & + \nu \left[\frac{X_{\mathrm{Al}}}{Z_{\mathrm{A}}} \ln \frac{2(1-\theta_{\mathrm{A}})}{D_{\mathrm{AA}} - 2\theta_{\mathrm{A}}} + \tfrac{1}{2} r_{\mathrm{c}} \ln \frac{D_{\mathrm{AA}} - 2\theta_{\mathrm{A}}}{D_{\mathrm{AA}}(1-\theta_{\mathrm{A}})}\right]. \end{aligned} \tag{3.5}$$

Since the J are assumed to be independent of X_{Al}, so will be their combinations. It is convenient to introduce the following constants

$$\left.\begin{aligned} \ln \left[\frac{J_{\mathrm{Si}}}{J_{\mathrm{Al}} J_{\mathrm{A}}^{1/Z_{\mathrm{A}}}}\right] &= t_1, \\ \ln J_{\mathrm{Si}} + m_{\mathrm{G}} \ln J_{\mathrm{G}} &= t_2. \end{aligned}\right\} \tag{3.6}$$

We are dealing with a given total number, N_γ, of tetrahedra. The quantity $F/N_\gamma kT + t_2 \equiv f(F)$ will be plotted against the fraction, X_{Al}, of $\mathrm{AlO_4}$ tetrahedra. We have

$$\begin{aligned} f(F) = {} & X_{\mathrm{Al}} \ln X_{\mathrm{Al}} + X_{\mathrm{Si}} \ln X_{\mathrm{Si}} - r_{\mathrm{c}} \ln r_{\mathrm{c}} + \frac{X_{\mathrm{Al}}}{Z_{\mathrm{A}}} \ln \frac{X_{\mathrm{Al}}}{Z_{\mathrm{A}}} \\ & + \left(r_{\mathrm{c}} - \frac{X_{\mathrm{Al}}}{Z_{\mathrm{A}}}\right) \ln \left(r_{\mathrm{c}} - \frac{X_{\mathrm{Al}}}{Z_{\mathrm{A}}}\right) + X_{\mathrm{Al}} t_1 + 2\left[2X_{\mathrm{Al}} \ln \frac{2X_{\mathrm{Si}}}{D - 2X_{\mathrm{Al}}} + \ln \frac{D - 2X_{\mathrm{Al}}}{X_{\mathrm{Si}} D}\right] \\ & + \nu \left[\frac{X_{\mathrm{Al}}}{Z_{\mathrm{A}}} \ln \frac{2(1-\theta_{\mathrm{A}})}{D_{\mathrm{AA}} - 2\theta_{\mathrm{A}}} + \tfrac{1}{2} r_{\mathrm{c}} \ln \frac{D_{\mathrm{AA}} - 2\theta_{\mathrm{A}}}{D_{\mathrm{AA}}(1-\theta_{\mathrm{A}})}\right]. \end{aligned} \tag{3.7}$$

(*f*) *Properties of the function* $f(F)$

The equation for $f(F)$ contains X_{Al} as the independent variable and the constant quantities Z_{A}, r_{c}, t_1, w/kT and w_{AA}/kT. Z_{A} is the valency of the cation; r_{c} is the number of cationic sites in the aluminosilicate per tetrahedron of $\mathrm{SiO_4}$ or $\mathrm{AlO_4}$ and will depend on the type of structure considered. For $f(F)$ to exist one must have $(r_{\mathrm{c}} - X_{\mathrm{Al}}/Z_{\mathrm{A}}) > 0$, which is equivalent to restricting isomorphous replacement of Si by Al to $0 < X_{\mathrm{Al}} < Z_{\mathrm{A}} r_{\mathrm{c}}$, because once all the crystallographic cation sites are filled, no further replacement of Si by Al is possible. $f(F)$ contains the term $X_{\mathrm{Al}} t_1$ linearly dependent on t_1 and a strongly positive term in w/kT. In tectosilicates $\mathrm{AlO_4}$ tetrahedra avoid forming pairs and in the case of 4-coordination there would have to be such pairs for $X_{\mathrm{Al}} > 0.5$. It follows that $f(F)$ will increase rapidly above this value of X_{Al}. The term in w_{AA}/kT may be either positive or negative. $f(F)$ has been calculated as a function of X_{Al} using a computer program, and the results plotted. The influence of Z_{A}, r_{c}, t_1, w/kT and w_{AA}/kT has been explored. The following is a summary of the conclusions. Comments (i)–(vi) are for $w_{\mathrm{AA}}/kT = 0$; the role of this factor will be considered later, in comments (vii)–(ix).

(i) $f(F)$ tends to have a minimum, whose position and depth depend on the relative magnitudes of t_1 and w/kT (figure 15*a*). For sufficiently high values of w/kT this minimum becomes V-shaped (figure 15*b*). The minimum then lies very nearly at $X_{\mathrm{Al}} = 0.5$ and the rate of increase of $f(F)$ beyond this value is very rapid. Despite the very sharp minimum the curve of $f(F)$ against X_{Al} is of course always continuous. Since chemical systems tend towards the state of the lowest free energy, $X_{\mathrm{Al}} = 0.5$ will be the most probable composition of the tectosilicate. This situation appears in minerals such as nepheline, kalsilite or kaliophilite.

(ii) When t_1 is positive and increasing, the minimum in the curves of $f(F)$ against X_{Al} becomes shallower and moves towards lower values of X_{Al} (figure 15*c*). These values of X_{Al} for different t_1 were as follows:

t_1	2	4	6	8	10
$X_{\mathrm{Al}}^{\mathrm{min}}$	0.18	0.10	0.043	0.017	0.0065

Thus if t_1 were sufficiently positive it should be possible to prepare nearly pure porous crystalline silicas isostructural with and more stable than the aluminosilicate counterpart; while if t_1 is negative the porous silicas will be less stable than their aluminosilicate isostructures.

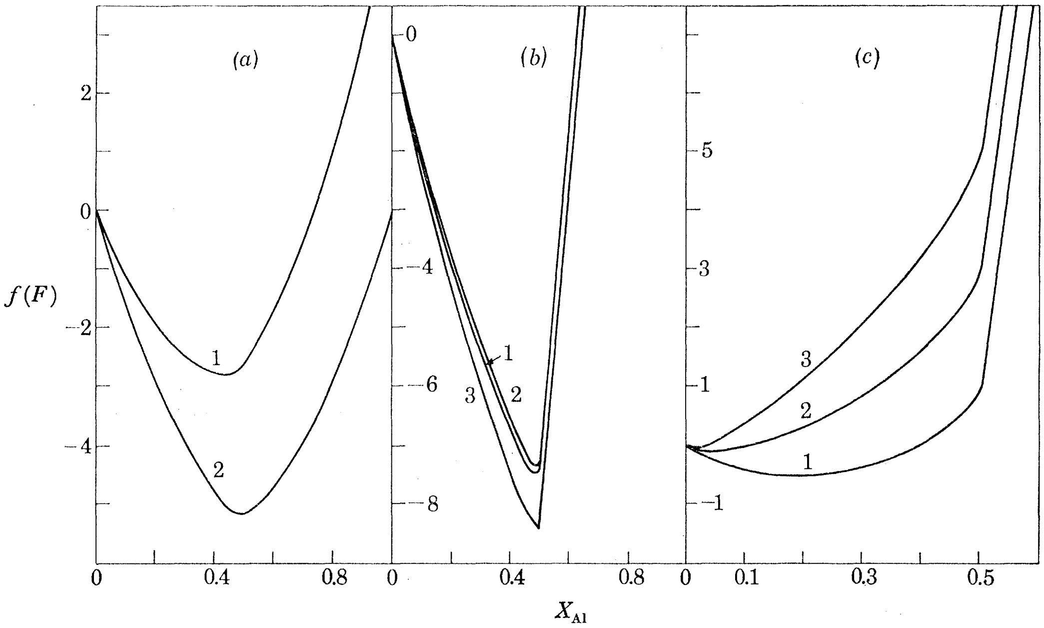

FIGURE 15. Plots of $f(F)$ against X_{Al} for $w_{\mathrm{AA}}/kT = 0$. For (*a*) $Z_{\mathrm{A}} = 1$, $r_{\mathrm{c}} = 1$, $w/kT = 10$; for curve 1 $t_1 = -5$; for curve 2 $t_1 = -10$. (*b*) $t_1 = -15$; $w/kT = 40$; for curve 1 $Z_{\mathrm{A}} = 1$ and $r_{\mathrm{c}} = 1$; for curve 2 $Z_{\mathrm{A}} = 2$ and $r_{\mathrm{c}} = 1$; for curve 3 $Z_{\mathrm{A}} = 1$ and $r_{\mathrm{c}} = 5$. (*c*) $Z_{\mathrm{A}} = 1$; $r_{\mathrm{c}} = 1$; $w/kT = 40$; for curve 1 $t_1 = 2$; curve 2 $t_1 = 6$; for curve 3 $t_1 = 10$.

The appendix shows how the sign of t_1 would be expected to depend on $(\epsilon_{\mathrm{A}}/Z_{\mathrm{A}} + \epsilon_{\mathrm{Al}})$, the overall energy of isomorphous replacement. Whether $(\epsilon_{\mathrm{A}}/Z_{\mathrm{A}} + \epsilon_{\mathrm{Al}})$ is endo- or exothermic is expected to depend largely upon the fit of the cation $\mathrm{A}^{Z_{\mathrm{A}}+}$ within a crystalline silica when the replacement $\mathrm{Si}^{4+} \rightarrow \mathrm{Al}^{3+}$, $\mathrm{A}^{Z_{\mathrm{A}}+}/Z_{\mathrm{A}}$ occurs. If the crystalline silica is compact, e.g. quartz, only the smallest cation Li^{+} can be inserted. β-eucryptite ($\mathrm{LiAlSiO_4}$) has indeed the same framework topology as β-quartz (Buerger 1948) so that for $\mathrm{Si}^{4+} \rightarrow \mathrm{Al}^{3+}$, Li^{+} in the quartz framework $(\epsilon_{\mathrm{A}}/Z_{\mathrm{A}} + \epsilon_{\mathrm{Al}})$ and t_1 are presumably negative. For larger interstitial ions (e.g. Na^{+}, K^{+}) significant isomorphous substitution is not found in the quartz structure and so t_1 is presumably positive. As the tectosilicate becomes more open these larger cations can be accommodated with negative values of t_1. Thus α-carnegeite, $\mathrm{NaAlSiO_4}$, has the framework topology of α-cristobalite (Buerger 1948), which is more open than quartz. As $(\epsilon_{\mathrm{A}}/Z_{\mathrm{A}} + \epsilon_{\mathrm{Al}})$ and therefore t_1 become more negative the substituted aluminosilicate frameworks become progressively more stable than their pure silica counterparts, so that, in accord with chemical experience, porous crystalline silicas having the framework topologies of zeolites, for example, have not been synthesized directly. The one very open crystalline silica, melanophlogite (Zak 1972) has not been synthesized in the laboratory and may exist because it is stabilized by included organic molecules, just as guest species such as water help to stabilise zeolites (Barrer 1960).

(iii) The shape of the plot of $f(F)$ against X_{Al} depends only slightly on the valency of the cation, Z_{A} (curves 1 and 2 in figure 15 *b*).

(iv) If the entire range of X_{Al} is potentially realizable (that is if there are enough crystallographic sites to accommodate the cations needed to reach the theoretical purely aluminous system with $X_{\mathrm{Al}} = 1$) the value of r_{c} does not have much influence on the *shape* of the plot of $f(F)$ or on the position of the minimum. The actual *value* of the function does however depend on r_{c} due mostly to the term $r_{\mathrm{c}} \ln r_{\mathrm{c}}$ (compare curves 1 and 3 in figure 15 *b*).

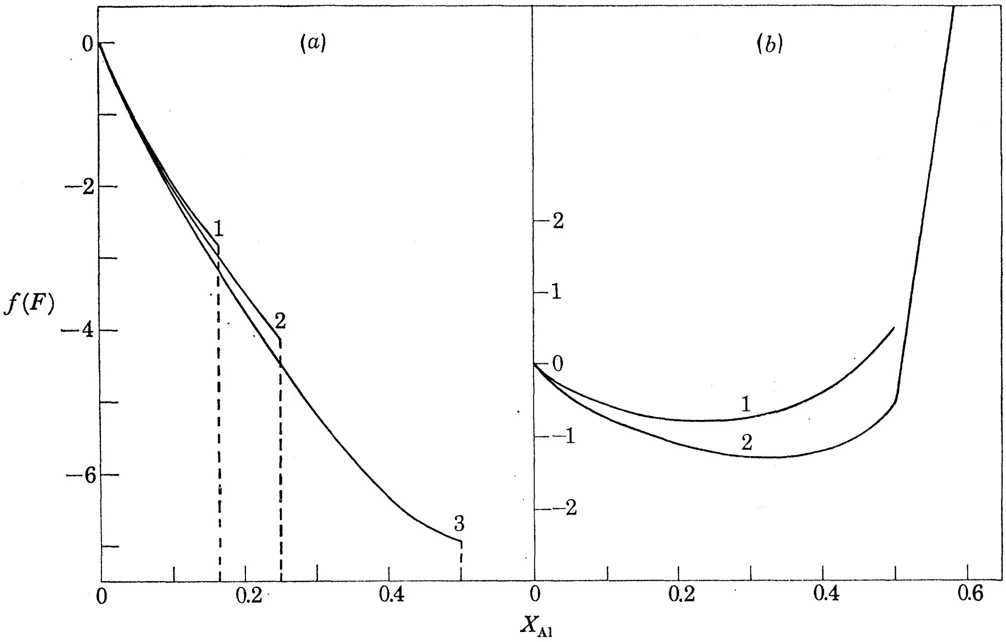

FIGURE 16. Plots of $f(F)$ against X_{Al} drawn for $Z_{\mathrm{A}} = 1$, $w/kT = 40$ and $w_{\mathrm{AA}}/kT = 0$. (*a*) $t_1 = -15$. For curve 1 $r_{\mathrm{c}} = \frac{1}{6}$; for curve 2 $r_{\mathrm{c}} = \frac{1}{4}$; for curve 3 $r_{\mathrm{c}} = \frac{1}{2}$. (*b*) For curve 1 $t_1 = -0.2$ and $r_{\mathrm{c}} = \frac{1}{2}$; for curve 2 $t_1 = -1.1$ and $r_{\mathrm{c}} = 1$.

(v) As already mentioned, a limit to isomorphous substitution is $X_{\mathrm{Al}}^{\mathrm{max}} = Z_{\mathrm{A}} r_{\mathrm{c}}$ or $X_{\mathrm{Al}}^{\mathrm{max}} = \frac{1}{2}$, whichever is the less. When $Z_{\mathrm{A}} r_{\mathrm{c}} < \frac{1}{2}$ only part of the curve of $f(F)$ against X_{Al} is realizable. Two examples will be considered.

In felspars there is one cation site per four tetrahedra. Accordingly $r_{\mathrm{c}} = 0.25$, so that the function $f(F)$ terminates at the limiting compositions $(\mathrm{K,Na})\mathrm{AlSi_3O_8}$ (for which $X_{\mathrm{Al}} = 0.25$) or $(\mathrm{Ca,Ba})\mathrm{Al_2Si_2O_8}$ ($X_{\mathrm{Al}} = 0.5$) respectively for uni- or divalent cations. If t_1 is sufficiently negative, as in figure 16 *a*, felspar compositions poorer in Al and so with some vacant cation sites would not be expected. In this case homoionic Na-, K-, Ca- or Ba-felspars would, as found in nature, have virtually fixed compositions. Thus the function $f(F)$ is able to account for minerals of fixed Al/Si ratios which are one or less than one.

In TMA-sodalite the unit cell composition is (Baerlocher & Meier 1969) $(\mathrm{TMA})_2[\mathrm{Al_2Si_{10}O_{24}}]$, where TMA denotes tetramethylammonium ion. Here, because of the size of the TMA ion there is room for only one cationic site per 14-hedral sodalite cage. This corresponds with $r_{\mathrm{c}}^{\mathrm{TMA}} = \frac{1}{6}$, so that $X_{\mathrm{Al}} = \frac{1}{6}$ is the maximum value possible in TMA-sodalite. $X_{\mathrm{Al}}^{\mathrm{max}} = \frac{1}{6}$ corresponds also with the lowest value of $f(F)$ in the allowed range (curve 1 in figure 16*a*) and will thus be the most probable composition. On the other hand, in Na-sodalite hydrate there are four times as many cation sites as in TMA-sodalite, so that $r_c = \frac{2}{3}$. This means that X_{Al}^{max} is governed in this case not by the value of r_c but by the magnitude of $\frac{1}{2}w$ giving $X_{Al}^{max} \simeq 0.5$ for large endothermal $\frac{1}{2}w$ in accord with Loewenstein's rule. This is the composition found in naturally occurring sodalites. In solid solutions of Na- with TMA-sodalites where both cations are present and the equivalent fraction of the sodium sodalite is Na_c^{sod} we expect

$$X_{Al} = \tfrac{1}{6}(1+2Na_c^{sod}).$$

(vi) If the minimum of the free energy curve is not very pronounced, it is expected that a considerable range of X_{Al} contents would be realizable by varying the conditions of synthesis. Thus curve 1 of figure 16 *b* represents the most favoured aluminium content as one in which $X_{Al} \simeq 0.25$, although other compositions in the range $0 < X_{Al} < 0.5$ might, from the shape of the curve, be achieved in synthesis under suitably varied conditions. Curve 2 of figure 16 *b* shows another possibility of a variable Al/Si ratio, with a shallow minimum at Al/(Al+Si) = 0.33. This minimum corresponds with normal analcime compositions, but as curve 2 suggests other compositions have indeed been observed in syntheses of this zeolite (see, for example, Saha 1959).

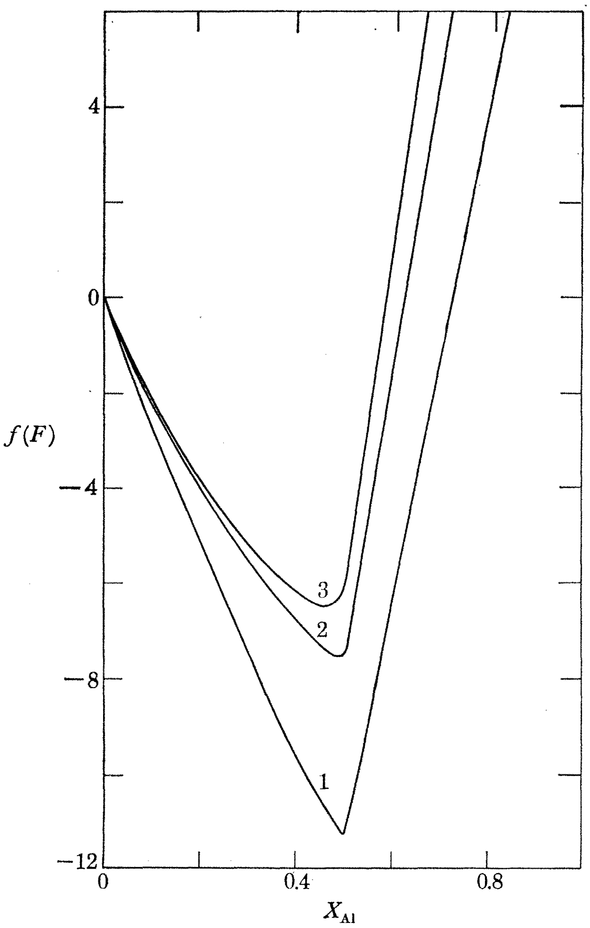

FIGURE 17. Plots of $f(F)$ against X_{Al} drawn for $Z_A = 1$, $t_1 = -15$, $r_c = 1$, $w/kT = 40$ and $\nu = 4$. For curve 1 $w_{AA}/kT = -10$; for curve 2 $w_{AA}/kT = 0$; for curve 3 $w_{AA}/kT = 10$.

(vii) One may consider the case for which $w_{AA}/kT \neq 0$. When w_{AA}/kT is large and negative there is a tendency for the cations A to cluster together and F^{int} has appreciable values. The last term in the expression for $f(F)$ (equation (3.7)) is negative and, as figure 17 shows, moves the curve of $f(F)$ against X_{Al} down, but without greatly changing its shape. For positive values of w_{AA}/kT cations A avoid each other and F^{int} in the region $0 < X_{Al} < 0.5$ is small. Neither the shape nor the numerical values for the plot of $f(F)$ against X_{Al} is significantly affected by the term in w_{AA}/kT in this case (figure 17).

(viii) Two parameters, t_1 and w/kT, have the dominant influence on the shape and the position of the minimum in the curve of $f(F)$ against X_{Al}. In addition, a low value of r_c restricts the allowed extent of Si → Al replacement.

(ix) The plots in figures 15–17 were drawn for the situation when there is only one kind of entering cation. If there are n kinds of cation, the fuller expression for the partition function must be used, and the plot will require $n+1$ dimensions. However, if there are two entering cations, A and B, the situation can be considered in terms of two sections of the 3-dimensional surface with planes $B_c = 0$ and variable X_{Al} (this part); or X_{Al} = constant and B_c variable. This second cross section represents an A ⇄ B cation exchange and is considered in § 1. B_c denotes the equivalent cation fraction of cation B.

Two further comments may be made. Firstly, although the foregoing considerations provide an evaluation of the conditions necessary for the validity of Loewenstein's rule, they do not preclude the possibility of a tectoaluminate structure. In this context it is of interest that tetracalcium trialuminate is reported to be the aluminate analogue of sodalite (Ponomarev, Kheiker & Belov 1971). Secondly, the above considerations treat all positions in the tectosilicate frameworks as equivalent. From the structures of zeolites (e.g. Meier & Olson 1971), for instance, one can see that there may be several geometrically distinguishable positions in which AlO_4 and SiO_4 tetrahedra can be found. However, this does not mean that, for example, the J_{Al} for the AlO_4 tetrahedra in this distinguishable positions are significantly different from each other.

The treatment given in § 3 can be extended in a straightforward manner to include replacements of the kinds Si ⇄ Ge, Ga ⇄ Al. Replacements such as Na, Ga ⇄ Si or Na, Ga ⇄ Ge are already included in the analogous formulations for Al and Si.

APPENDIX

In order to obtain an estimate of t_1 one makes the following assumptions:

(i) $J_{Si}/J_{Al} = \exp(-\epsilon_{Al}/kT)$;

(ii) cations A behave as isotropic three dimensional oscillators;

(iii) J_G is independent of composition of the crystal or there is no guest molecule in the structure.

With the above assumptions we obtain

$$t_1 = -\frac{1}{Z_A}\ln J_A - \frac{\epsilon_{Al}}{kT},$$

where (Rushbrooke 1949)

$$J_A = \left[2\sinh\left(\frac{h\omega}{2kT}\right)\right]^{-3}\exp\left(\frac{\epsilon_A}{kT}\right).$$

Thus

$$t_1 = \frac{3}{Z_A}\ln\left[2\sinh\left(\frac{h\omega}{2kT}\right)\right] - \frac{\epsilon_A}{Z_A kT} - \frac{\epsilon_{Al}}{kT},$$

where ϵ_A is the bonding energy of the cation in the lattice.

For $\omega = 10^{13}\,\mathrm{s}^{-1}$ and $T = 300\,\mathrm{K}$ we have

$$t_1 = \frac{1.7265}{Z_\mathrm{A}} - 0.401\left(\frac{\epsilon_\mathrm{A}}{Z_\mathrm{A}} + \epsilon_\mathrm{A1}\right),$$

where ϵ_A and ϵ_A1 are in $\mathrm{kJ\,mol^{-1}}$. To have $t_1 > 0$ it is necessary that $(\epsilon_\mathrm{A} + Z_\mathrm{A}\,\epsilon_\mathrm{A1}) < 4.306\,\mathrm{kJ\,mol^{-1}}$. To have $t_1 < 0$ the sign of the above inequality is reversed.

REFERENCES

Baerlocher, C. & Meier, W. M. 1969 *Helv. Chim. Acta.* **52**, 1853.
Barrer, R. M. 1960 *J. Phys. Chem. Solids* **16**, 84.
Barrer, R. M. & Baynham, J. W. 1956 *J. Chem. Soc.* 2882.
Barrer, R. M. & Brummer, K. 1963 *Trans. Faraday Soc.* **59**, 959.
Barrer, R. M., Buser, W. & Grütter, W. F. 1956 *Helv. Chim. Acta* **39**, 518.
Barrer, R. M. & Cole, J. F. 1970 *J. Chem. Soc.* A 1516.
Barrer, R. M., Davies, J. A. & Rees, L. V. C. 1969 *J. inorg. nucl. Chem.* **31**, 2599.
Barrer, R. M. & Falconer, J. D. 1956 *Proc. R. Soc. Lond.* A **236**, 227.
Barrer, R. M. & Gibbons, R. M. 1963 *Trans. Faraday Soc.* **59**, 2569.
Barrer, R. M. & Hinds, L. 1953 *J. Chem. Soc.* 1879.
Barrer, R. M. & Jones, D. L. 1971 *J. Chem. Soc.* A 503.
Barrer, R. M. & Klinowski, J. 1972 *J. Chem. Soc., Faraday I* **68**, 73.
Barrer, R. M. & Klinowski, J. 1974*a* *J. Chem. Soc., Faraday I* **70**, 2080.
Barrer, R. M. & Klinowski, J. 1974*b* *J. Chem. Soc., Faraday I* **70**, 2362.
Barrer, R. M., Klinowski, J. & Sherry, H. S. 1973 *J. Chem. Soc., Faraday II* **69**, 1669.
Barrer, R. M. & Mainwaring, D. E. 1972 *J. Chem. Soc., Dalton Trans.* 1259.
Barrer, R. M. & McCallum, N. 1953 *J. Chem. Soc.* 4035.
Barrer, R. M. & Munday, B. M. 1971 *J. Chem. Soc.* A 2904, 2909 and 2914.
Barrer, R. M., Papadopoulos, R. & Rees, L. V. C. 1967 *J. inorg. nucl. Chem.* **29**, 2047.
Barrer, R. M. & Townsend, R. P. 1976 *J. Chem. Soc., Faraday I* **72**, 2650.
Bonnin, D. & Legrand, A. P. 1975 *Chem. Phys. Lett.* **30**, 296.
Bragg, W. L. & Claringbull, G. F. 1965 *Atomic structure of minerals*, p. 299. London: G. Bell and Sons.
Breck, D. W. 1974*a* *Zeolite molecular sieves*, p. 93. New York: Wiley.
Breck, D. W. 1974*b* *Zeolite molecular sieves*, chs 3 and 4. New York: Wiley.
Breck, D. W. & Flanigen, E. M. 1968 In *Molecular sieves*, p. 58. London: Society of Chemical Industry.
Buerger, M. J. 1948 *Am. Mineralog.* **33**, 751.
Dempsey, E. 1968 In *Molecular sieves*, p. 293. London: Society of Chemical Industry.
Fowler, R. H. & Guggenheim, E. A. 1939 *Statistical thermodynamics*, p. 441. Cambridge University Press.
Gaines, G. L. & Thomas, H. C. 1953 *J. chem. Phys.* **21**, 714.
Gude, A. J. III & Sheppard, R. A. 1966 *Am. Mineralog.* **51**, 909.
Iiyama, J. T. 1974 *Bull. Soc. fr. Minéral. Cristallogr.* **97**, 143.
Kielland, J. 1935 *J. Soc. Chem. Ind.* **54**, 232T.
Lacher, J. R. 1937 *Proc. Camb. Phil. Soc.* **33**, 518.
Loewenstein, W. 1954 *Am. Mineralog.* **39**, 92.
Meier, W. M. & Olson, D. H. 1971 In *Molecular sieve zeolites*–I. *Advances in chemistry series*, No. 101, p. 155. Am. Chem. Soc.
Olson, D. H. & Sherry, H. S. 1968 *J. Phys. Chem.* **72**, 4095.
Orville, P. M. 1963 *Am. J. Sci.* **261**, 201.
Ponomarev, V. I., Kheiker, D. M. & Belov, N. V. 1971 *Sov. Phys., Crystallography*, **15**, 799.
Rushbrooke, G. S. 1949*a* *Introduction to statistical mechanics*, p. 32. Oxford University Press.
Rushbrooke, G. S. 1949*b* *Introduction to statistical mechanics*, p. 329. Oxford University Press.
Saha, P. 1959 *Am. Mineralog.* **44**, 300.
Sawhney, B. L. 1967 In *Clays and clay minerals* (ed. E. Ingerson), Proc. 15th National Conference, p. 75. Oxford: Pergamon.
Schoonheydt, R. 1975 Thesis, Catholic University of Leuven, p. 4. (Reproduced with permission.)
Sherry, H. S. 1971 In *Molecular sieve zeolites*–I. *Advances in chemistry series*, No. 101, p. 350. Am. Chem. Soc.
Smith, J. V. 1971 In *Molecular sieve zeolites*–I. *Advances in chemistry series*, No. 101, p. 171. Am. Chem. Soc.
Zak, L. 1972 *Am. Mineralog.* **57**, 779.