U.D.C. 545.85

Mass-spectrometric Study of the Thermodynamic Properties of Binary Systems Comprising Sodium Fluoride and Scandium, Yttrium, and Lanthanum Trifluorides. II. The Composition–Pressure Diagram

L.N.Sidorov, V.P.Shcheredin, and P.A.Akishin

The experiments were performed by the method of isothermal evaporation. Composition–partial pressure diagrams are presented for NaF, Na_2F_2, Na_3F_3, ScF_3, and $NaScF_4$ at 1169°K. The variation of the activities of the initial components with composition in the systems NaF–YF_3 (1321°K) and NaF–LaF_3 (1276°K) has been obtained. It is suggested that systems of this type be characterised by a plot of the sum of the partial pressures of the initial components against composition and a table of equilibrium constants for the gas-phase reactions.

This paper describes the interpretation of the mass spectra of the saturated vapours in the systems NaF–MF_3 and the partial pressures of NaF, Na_2F_2, Na_3F_3, MF_3, and $NaMF_4$ at several temperatures and compositions of the condensate.

THE SYSTEM NaF–ScF_3

In order to plot the partial pressure–composition diagram, the experimental data were adjusted to 1169°K. Using the heats of evaporation of Na_2F_2 for different compositions, the pressure of Na_2F_2 was adjusted to 1169°K.

Partial vapour pressures.

[illegible]	$10^3 p_1$	$10^4 p_2$	$10^5 p_3$	$10^5 p_4$	$10^4 p_k$	Composition, mole % ScF_3	$10^3 p_1$	$10^4 p_2$	$10^5 p_3$	$10^5 p_4$	$10^4 p_k$
[illegible]	25.2	57.6	72,0	0	0	28.4	9.45	8.01	3.80	6.78	6.50
[illegible]	25.2	57.6	72.0	0.213	0.545	31.2	7.04	4.05	1.57	13.6	9.71
[illegible]	22.9	47.7	54.3	0.344	0.800	34.1	4.98	2.25	0.556	27.9	14.1
[illegible]	21.1	40.5	42.5	0.497	1.07	37.6	3.76	1.29	0.240	46.1	17.6
[illegible]	18.9	32.4	30.4	0.784	1.50	40.3	2.74	0.680	0.0923	76.0	21.1
[illegible]	15.4	21.6	16.5	1.63	2.55	41.4	2.24	0.454	0.0504	102	23.1
[illegible]	13.2	15.8	10.3	2.70	3.61	45.0	2.00	0.363	0.0360	118	24.0
[illegible]	12.6	14.4	9.00	3.09	3.95	100	0	0	0	118	0

The pressures of NaF (p_1) and Na_3F_3 (p_3) were calculated from the equilibrium constants of the gas-phase reactions

$$Na_2F_2 \rightleftharpoons 2NaF, \quad (1)$$

$$Na_3F_3 \rightleftharpoons 3NaF. \quad (2)$$

The pressures of ScF_3 (p_4) and $NaScF_4$ (p_k) were calculated from the Gibbs–Duhem equation[2,3] using the known values of ... for the entire range of compositions and the values of ... and p_k for 40 mole % ScF_3. The pressure p_4 was also calculated from the equilibrium constant for the reaction

$$NaScF_4 \rightleftharpoons NaF + ScF_3. \quad (3)$$

The partial pressures vary in accordance with the phase diagram[4]: for the heterogeneous regions melt–NaF (solid) and melt–ScF_3 (solid), the partial pressures p_1 and p_4 respectively agree with the data for the pure components[5-7]. The average partial pressures (mmHg) of the vapour components (1169°K) are presented in the Table and in Fig. 1. A total pressure–composition diagram was plotted on the basis of the tabulated data (Fig. 2). However, when the vapour contains complex molecules, this type of diagram provides no information about the molecular composition of the vapour. Therefore it is better to characterise systems of this kind by plots of the sum of the partial pressures of the initial components (p_1 and p_4) against composition and by the tabulated equilibrium constants for the gas-phase reactions. The K_p for reactions (1), (2), and (3) in the system NaF–ScF_3 (1169°K) are respectively 1.4×10^{-4} atm, 3.8×10^{-7} atm^2, and 1.3×10^{-7} atm.

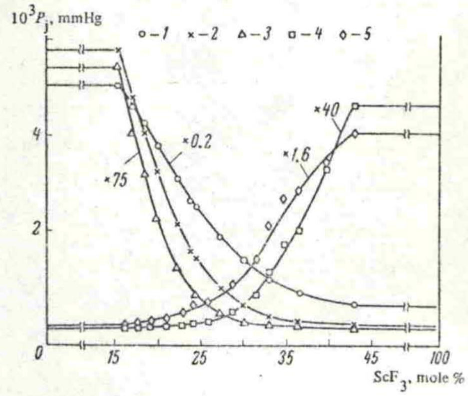


Figure 1. Partial pressure–composition diagram for the system NaF–ScF_3 at 1169°K: 1) NaF; 2) Na_2F_2; 3) Na_3F_3; 4) ScF_3; 5) $NaScF_4$.

Plots of selected sums of partial pressures against composition were constructed on the basis of the p_j data. Plots of $p_2 + p_k$ and of $p_2 + p_4 + p_k$ against composition have minima (Fig. 2) at which the following relations hold respectively[8]:

$$(2p_2 + p_k) / p_k = n_A / n_B;$$

$$(2p_2 + p_k) / (p_4 + p_k) = n_A / n_B,$$

where n_A and n_B are the mole fractions of NaF and ScF_3 in the melt respectively. On the other hand, there is no extremum in the total pressure, i.e. there is no azeotrope in the NaF–ScF_3 system at 1169°K.

THE SYSTEMS NaF–YF_3 AND NaF–LaF_3

In the construction of the pressure–composition diagrams for these systems it was assumed that the activity of NaF ($a_1 = p_1/p_1^\circ$) varies with composition (Fig. 3) in the same way as in the system NaF–ScF_3. The partial pressures of the remaining components were calculated from the Gibbs–Duhem equation and from the equilibrium constant for the reaction

$$NaMF_4 \rightleftharpoons NaF + MF_3. \quad (4)$$

The constants K_p (atm) for reaction (4) in the three systems are respectively 4.1×10^{-7} (1219°K), 2.0×10^{-6} (1321°K), and 6.2×10^{-6} (1276°K). According to the phase diagram for the system $NaF-LaF_3$,[9] in the region of 50 mole % LaF_3 (1276°K) the pressure of LaF_3 is the same as that of the pure trifluoride[6,7,10].

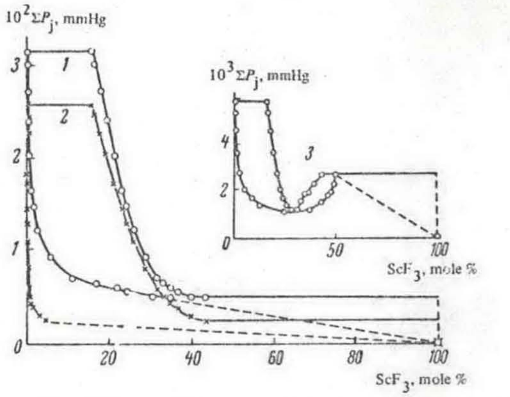


Figure 2. Variation of the sum of the partial pressures in the system $NaF-ScF_3$ (1169°K) with composition: 1) P_{tot}; 2) $p_1 + p_4$; 3) $p_2 + p_4 + p_k$.

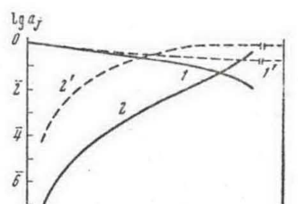


Figure 3. Variation of the activites of NaF and MF_3 with composition in the systems $NaF-YF_3$ (curves *1* and *2*) at 1321°K and $NaF-LaF_3$ (curves *1'* and *2'*) at 1276°K.

The experimental data show that the content of complex molecules in the vapours of the systems $NaF-YF_3$ and $NaF-LaF_3$ is much lower than in the vapour of the system $NaF-ScF_3$. This can be explained in the following way. Assuming that at the same temperature the K_p for reaction (4) in all the systems differ by not more than one power of 10, the content of complex molecules is largely determined by the partial pressure of MF_3: p_k increases with p_4. On the other hand, the pressure of ScF_3 at the same temperature is higher by almost two powers of 10 than those of YF_3 and LaF_3,[6,7,10] which leads to an appreciably higher content of $NaScF_4$ molecules in the vapour compared with $NaYF_4$ and $NaLaF_4$.

REFERENCES

1. V. P. Shcheredin and L. N. Sidorov, Zhur. Fiz. Khim., 44, 514 (1970) [Russ. J. Phys. Chem., No. 2 (1970)].
2. L. N. Sidorov, Dokl. Akad. Nauk SSSR, 176, 1351 (1967).
3. L. N. Sidorov, V. I. Belousov, and P. A. Akishin, Zhur. Fiz. Khim., 43, 80 (1969) [Russ. J. Phys. Chem., No. 1 (1969)].
4. R. E. Thoma and R. H. Karraker, Inorg. Chem., 5, 1933 (1966).
5. L. N. Sidorov, P. A. Akishin, V. I. Belousov, and V. B. Shol'ts, Zhur. Fiz. Khim., 38, 146 (1964) [Russ. J. Phys. Chem., No. 1 (1964)].
6. R. A. Kent, K. F. Zmbov, A. S. Kana'an, G. Besenbruch, J. D. McDonald, and J. L. Margrave, J. Inorg. Nuclear Chem., 28, 1419 (1966).
7. Al. L. Suvorov and G. I. Novikov, Vestnik Leningrad. Univ., No. 4, 81 (1968).
8. L. N. Sidorov and V. B. Shol'ts, Zhur. Fiz. Khim., 41, 1960 (1967) [Russ. J. Phys. Chem., No. 8 (1967)].
9. R. E. Thoma, H. Insley, and G. M. Hebert, Inorg. Chem., 5, 1222 (1966).
10. R. W. Mar and A. W. Searcy, J. Phys. Chem., 71, 888 (1967).

Faculty of Chemistry,
Lomonosov Moscow State
University

Received 31st July 196

U. D. C. 541.121/.123

Temperature Variation of the Heat Capacity of Catenary Magnesium, Calcium, and Barium Metagermanates

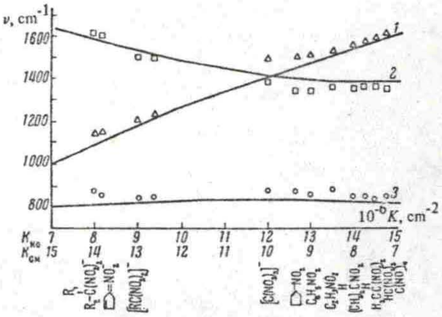
V.V.Tarasov (deceased) and P.A.Soboleva

Experimental data for the temperature variation of the heat capacities of the catenary alkaline earth metal metagermanates have been obtained for the first time. The experimental heat capacities and the theoretical values calculated from Tarasov's theory of the heat capacity of phonon chains have been compared and found to agree. A correlation has been observed between the characteristic temperatures determined from the heat capacity data and the values calculated from the infrared spectra.

The heat capacities of alkaline earth metal (magnesium, calcium, and barium) metagermanates were measured in the range 60–300°K. The heat capacities of alkali metal metagermanates were reported previously. The experimental results were compared with the theoretical values calculated from Tarasov's theory of the heat capacity of phonon chains[1], which has been frequently confirmed experimentally and which ensures good agreement with experiment. Rigorous mathematical calculations[2,3] confirm the findings based on the theory. It is therefore possible to obtain information about the nature of the chemical bond in the substance from the theoretical calculations.

The compounds indicated above were synthesised. Their principal physicochemical characteristics were quoted previously. As for alkali metal metagermanates, the heat capacities were measured on a KU-300 calorimetric apparatus, which ensures an accuracy of 0.3%. The method employed to calculate the heat capacities of the alkaline earth metal metagermanates was similar to that employed in the study of Li_2GeO_3.

frequencies for the compounds corresponding to the right-hand and left-hand parts of the curves agree well with the calculation. A similar satisfactory agreement is obtained for aromatic and unsaturated nitro-compounds. Since on passing from salts of mononitro-compounds to those of polynitro-compounds the negative charge at the oxygen atoms of the nitro-groups should diminish (in the anions of mononitro-compounds the charge of a single electron is distributed between two oxygen atoms, in *gem*-dinitro-compounds between four oxygen atoms, and in trinitro-compounds between six oxygen atoms), it is reasonable to suppose that the $C-NO_2$ vibration frequencies of polynitroalkane salts should occur in the region between those in unsaturated compounds and mononitroalkane salts. Preliminary data for the spectra of several polynitroalkane salts support this hypothesis.



Spectra of nitro-compounds.

It is noteworthy that in general the assignment of the stretching vibration frequencies ν_1, ν_2, and ν_3 is frequently difficult because of the splitting of the infrared absorption bands and the Raman lines. The problem of the assignment of ν_3 (ν_{CN}) is solved most simply: all the nitro-compounds which we investigated have an intense and polarised band in the 800–900 cm^{-1} region in Raman spectra (see below):

In-phase ν_3 vibration of the CNO_2 fragment in nitro-compounds.

Compound	ν, см⁻¹	Compound	ν, см⁻¹
$(CH_3)_2CHNO_2$	852	$[(CH_3)_2CNO_2]^-Na^+$	833
$HC(NO_2)_3$	837	$[HC(NO_2)_2]^-K^+$	{1014 783
$ClC(NO_2)_3$	841	$[C(NO_2)_3]^-Na^+$	875
$BrC(NO_2)_3$	841	$[ClC(NO_2)_2]^-Na^+$	830*
sym-$C_6H_3(NO_2)_3$	833	$[BrC(NO_2)_2]^-Na^+$	824*
$C_2H_3NO_2$	885	$[C_2H_3C(NO_2)_2]^-Na^+$	853*

*Data of Mel'nikov et al.[9]; spectra recorded in aqueous solutions.

Thus the agreement between the experimental frequencies and the calculated curves [$\nu_{str} = f(K_{NO}, K_{CN})$] suggests a linear relation between the force constants of the NO and CN bonds: $K_{NO} = A - BK_{CN}$. Nitro-compounds and their salts may be represented by a series with a successive change in the force parameters of the NO and CN bonds.

The authors are sincerely grateful to P. P. Shorygin for valuable comments and discussion.

REFERENCES

1. E. M. Popov and V. A. Shlyapochnikov, Optika i Spektrosk., Collection No. 2, 1963, p. 115.
2. K. R. Loos and H. H. Günthard, J. Chem. Phys., 46, 1200 (1967).
3. S. Pinchas, D. Samuel, and B. L. Silver, Spectrochim. Acta, 20, 179 (1964).
4. N. Jonathan, J. Mol. Spectroscopy, 7, 105 (1961).
5. V. A. Shlyapochnikov and V. G. Osipov, Zhur. Prikl. Spektr., 8, 1003 (1968).
6. V. A. Shlyapochnikov and V. G. Osipov, Izv. Akad. Nauk SSSR, Otd. Khim. Nauk, 8, 1870 (1968).
7. V. A. Konshev and G. I. Oleneva, Zhur. Prikl. Spektr., 10, 653 (1969).
8. E. M. Popov and V. A. Shlyapochnikov, Optika i Spektrosk., 14, 779 (1963).
9. V. V. Mel'nikov, I. V. Nel'son, I. N. Shokhor, and I. V. Tselinskii, Zhur. Org. Khim., 4, 349 (1968).

Zelinskii Institute of Organic Chemistry, USSR Academy of Sciences, Moscow

Received 12th September 1968

U. D. C. 545.83

A Mass-spectrometric Study of the Thermodynamic Properties of the Sodium Fluoride–Vanadium Trifluoride System. III. Composition and Pressure

L.N.Sidorov, V.B.Shol'ts, and Yu.M.Korenev

The partial pressures of the gas phase components of the $NaF-VF_3$ system have been determined over the entire composition range. The experimental ratios of the ionisation cross-sections of the NaF, VF_3, $NaVF_4$, and NaV_2F_7 molecules have been found to differ from the values calculated on the assumption of additivity using the atomic ionisation cross-sections.

It has been shown[1] that the gas phase of the system contains the molecules NaF, Na_2F_2, VF_3, V_2F_6, $NaVF_4$, and NaV_2F_7 and the mass spectrum has been fully resolved. To determine the partial pressures of the components p_j from the resolved ionic currents I_{ij}, we employed the generally accepted equation

$$p_j = k_{ij} I_{ij} T, \tag{1}$$

where the subscript i indicating the type of ion, assumes the following values:

$0 - Na^+$, $1 - NaF^+$, $2 - Na_2F^+$, $3 - VF_2^+$, $4 - VF_3^+$, $k - NaVF_3^+$;

and the subscript j, indicating the type of molecule, is:

$1 - NaF$, $2 - Na_2F_2$, $3 - VF_3$, $D - V_2F_6$, $m - NaVF_4$, $n - NaV_2F_7$.

The problem consists in the determination of the coefficients $k_{ij} = k/\sigma_{ij}$, where k is the sensitivity of the mass spectrometer and σ_{ij} is the ionisation cross-section of the molecule j with formation of an ion i.

Partial Pressures of the Vapour Components in the Range 0–26.6 mole % VF_3

To determine the coefficients k_{ij}, we shall formulate Knudsen's equation for the evaporation of sodium fluoride and vanadium trifluoride bearing in mind that in the above concentration range sodium fluoride evaporates in the form of the molecules NaF, Na_2F_2, and $NaVF_4$ and vanadium trifluoride in the form of the molecules VF_3 and $NaVF_4$:[1]

$$q_1^0 = \sum_T [B_1 k_{01}(S_{01} + 1/2^{1/2} S_{22}) + (M_1/M_m) B_m k_{om} S_{om}] T^{1/2}, \quad (2)$$

$$q_3^0 = \sum_T [B_3 k_{33} S_{33} + (M_3/M_m) B_m k_{om} S_{om}] T^{1/2}, \quad (3)$$

where $B_j = La(M_j/2\pi R)^{1/2}$, L is the Clausing coefficient, a the area of the effusion aperture, M_j the molecular weight, R the gas constant, $S_{ij} = \int_0^t I_{ij} dt$ the area under the ionic current I_{ij} line, t_k the time required for the complete evaporation of the substance, q_1^0 and q_3^0 are the contents of NaF and VF_3 in the initial sample (mg), and T is the temperature (°K).

Table 1*.

Composition of condensed phase, mole % VF_3	$p_i \times 10^3$ mmHg			
	p_1	** p_2	p_3	p_M
1113° K				
0–19.9	8.00	2.08	—	—
21.0	8.00	2.08	—	—
22.3	7.68	1.95	—	—
23.1	6.95	1.68	—	—
23.8	5.72	1.22	—	—
24.8	4.14	0.55	0.03	0.15
25.7	2.08	0.13	0.15	1.08
26.3	1.82	0.10	0.21	1.22
1153° K				
26.6	5.05	0.35	0.68	4.61

*The Clausing coefficient $L = 0.8$ was employed in the calculations.

**$p_2 = \frac{1}{2} k_{01} I_{22}/T$.

Bearing in mind that the ions VF_3^+, VF_2^+, VF^+, and V^+ are formed from VF_3 molecules, while NaF molecules yield essentially Na^+ ions, we have

$$k_{01} \Big/ \sum_i k_{i3} = \sigma_3/\sigma_1 = 1.63, \quad (4)$$

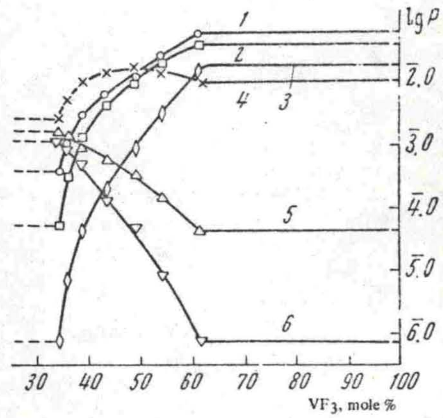
where σ_1 and σ_3 are the ionisation cross-sections of NaF and VF_3 calculated assuming additivity and using the atomic ionisation cross-sections[2]; $\sum_i k_{i3} = 1.65\, k_{33}$ according to the VF_3 mass spectrum which we obtained[3]. By solving Eqns. (2), (3), and (4), we find the unknown coefficients k_{01}, k_{om}, and k_{33} and from Eqn. (1) we obtain the partial pressures of NaF, Na_2F_2, $NaVF_4$, and VF_3. Table 1 lists the results of the determination of the partial pressures for the isotherm with the initial composition corresponding to 19.95 mole % VF_3 in the range between 0 and 26.6 mole % VF_3. The composition of the condensed phase (Table 1) was calculated by the integral method from Eqn. (13) of Ref. 4.

Partial Pressures of the Vapour Components in the Range 36.6–100 mole % VF_3

Bearing in mind that in the above concentration range the gas phase of this system contains the molecules NaF, Na_2F_2, VF_3, $NaVF_4$, and NaV_2F_7,[1] the Knudsen equations are formulated in the following form:

$$q_1^0 = \sum_T [B_1 k_{01}(S_{01} + 1/2^{1/2} S_{22}) + (M_1/M_m) B_m k_{om} S_{om} + (M_1/M_n) B_n k_{on} S_{on}] T^{1/2}, \quad (5)$$

$$q_3^0 = \sum_T [B_3 k_{33} S_{33} + (M_3/M_m) B_m k_{om} S_{om} + (M_3/M_n) B_n k_{on} S_{on}] T^{1/2}. \quad (6)$$



Variation of the partial pressures of the components of the gas phase in the NaF–VF_3 system with composition at 1141°K: 1) VF_3; 2) NaV_2F_7; 3) V_2F_6 ($p_d \times 100$); 4) $NaVF_4$; 5) NaF; 6) Na_2F_2 ($p_2 \times 10$). The dashed curves represent the pressures in the heterogeneous region adjoining the compound 3NaF.VF_3.

We have two equations with the four unknowns k_{01}, k_{om}, k_{on}, and k_{33}. The experimental ratio of the coefficients

$$k_{01}/k_{om} = 1.50 \pm 0.15, \quad (7)$$

determined in experiments with 5.0 and 19.95 mole % VF_3, is used as the third equation. To obtain a fourth equation, we employ the integral form of Eqn. (18) of Ref. 4 formulated for the composition with 50 mole % VF_3:

$$-\frac{d \ln I_{13}}{d \ln I_{11}} = \frac{n_1^0 - D_m k_{om} \int_0^t I_{om}\, dt - D_n k_{on} \int_0^t I_{on}\, dt}{n_3^0 - D_3 k_{33} \int_0^t I_{33} dt - D_m k_{om} \int_0^t I_{om} dt - 2D_n k_{on} \int_0^t I_{on} dt} = \frac{n_1(t)}{n_3(t)} = 1. \quad (8)$$

where n_1^0 and n_3^0 are the numbers of moles of NaF and VF_3 in the initial sample, $n_1(t)$ and $n_3(t)$ are the numbers of moles of NaF and VF_3 at time t corresponding to 50 mole % of VF_3, and $D_j = B_j T^{1/2}/M_j$.

After simple algebraic rearrangement, we obtain

$$n_3^{\circ} - n_1^{\circ} = D_3 k_{33} \int_0^t I_{33} dt + D_n k_{on} \int_0^t I_{on} dt. \qquad (8')$$

By solving Eqns. (5), (6), (7), and (8), we find that unknown coefficients k_{01}, k_{33}, k_{om}, and k_{on}, and from Eqn. (1) we obtain the partial pressures of NaF, Na_2F_2, VF_3, $NaVF_4$, and NaV_2F_7. The Figure presents a plot of the partial pressure against the composition of the condensed phase for one of the isotherms with the initial composition corresponding to 72.5 mole % VF_3. Table 2 lists the results of the determination of the partial pressures in the range 36.6–100 mole % VF_3 calculated as averages from several experiments. The composition of the condensed phase was determined by integral and differential methods[5].

Table 2.

Composition of condensed phase, mole % VF_3		$10^3 p_j$, mmHg					
integral method	differential method	p_1	p_2	p_3	$^*p_d$	p_m	p_n
		1154° K					
100–63.0	—	—	—	88.7	0.15	14.7	36.5
62.6	—	—	—	85.7	0.12	14.7	34.7
60.0	60.1±2	—	—	57.3	0.07	17.9	29.0
55.9	54.1±2	—	—	37.9	0.03	21.2	22.5
53.0	—	—	—	31.8	—	21.4	19.1
50.0	50.0±0.5	—	—	23.4	—	21.6	14.2
47.2	47.1±2	—	—	13.0	—	20.4	7.34
44.0	—	0.44	0.02	11.2	—	18.4	5.63
40.5	—	1.25	0.05	6.97	—	14.4	2.80
35.7	32.7±4	2.25	0.15	0.85	—	3.68	0.09
		1182° K					
35.9	—	4.07	0.29	1.68	—	6.99	0.20
		1218° K					
35.6	—	9.31	0.79	3.89	—	15.3	0.44

$$^*p_d = \tfrac{1}{2}\sum_i k_{i3} I_{4d} T.$$

To calculate the composition by the differential method, the Gibbs–Duhem equation was formulated for the system $NaF-VF_3$ in terms of the ionic currents I_{33} and $I_{on}(I_{om})$:

$$\frac{d \ln I_{on}}{d \ln I_{33}} = \frac{2N_1 - N_3}{N_1}, \qquad \frac{d \ln I_{om}}{d \ln I_{33}} = \frac{N_1 - N_3}{N_1}, \qquad (9)$$

where $N_1(N_3)$ is the mole fraction of NaF (VF_3) in the melt. The derivative $d \ln I_{on}/d \ln I_{33}$ $(d \ln I_{om}/d \ln I_{33})$ was found by the graphical differential of the function $\lg I_{on} = f(\lg I_{33})$ $[\lg I_{om} = f'(\lg I_{33})]$.

DISCUSSION

A general equation permitting the determination of the partial pressures of the vapour components in experiments by the isothermal evaporation method without recourse to any estimates of ionisation cross-sections was given in a previous communication[4]. The equation contains as many unknown k_{ij} as there are types of molecules present in the gas phase of the system. When n types of molecules are present, the equation is formulated for n times and the solution of the equations yields the unknown coefficients k_{ij}. When the initial sample evaporates completely in experiments with two-component systems, it is sufficient to formulate a general equation for $n - 2$ times because one can reasonably include among the equations the Knudsen equation describing the process of the total isothermal evaporation of the first and second component [see Eqns. (5) and (6) of this paper].

Disregarding dimeric species, the gas phase of the $NaF-VF_3$ system contains four types of molecules: NaF, VF_3, $NaVF_4$, and NaV_2F_7. As before, for the dimeric molecules Na_2F_2 and V_2F_6 we assume that $k_{22} = \frac{1}{2}k_{01}$ and $k_{4d} = \frac{1}{2}\Sigma k_{i3}$, i.e. $n = 4$. Since the experiments were carried out by the total isothermal evaporation method, the problem reduced to finding two additional equations. For the first additional equation, we employed the general equation formulated in the integral form for the time corresponding to the maximum ionic current I_{om} [Eqn. (8)]. Instead of employing as the second additional equation the same general equation referred to another time, we reduced the system of four equations essentially to only three using the ionisation cross-section ratio $\sigma_m/\sigma_1 = k_{01}/k_{om}$ determined in experiments with 5.0 and 19.95 mole % VF_3.

The experiments with 5.0 mole % VF_3 [6] and 19.95 mole % VF_3 [1] permitted a direct determination of the ionisation cross-section ratio for the $NaVF_4$ and NaF molecules. The introduction into the calculation of the quantity $\sigma_3/\sigma_1 = 1.63$ calculated using the atomic ionisation cross-sections[2] does not have a significant influence on the resulting ratios σ_m/σ_1, because the area under the ionic current I_{33} line is smaller by a factor of about 10–12 than the area under the ionic current I_{om} line, which is evidence of a small relative content of VF_3 in the gas phase. Calculations for the experiment with 5.0 mole % VF_3 [6] on the assumption that the entire VF_3 has evaporated in the form of $NaVF_4$ molecules gave $k_{01}/k_{om} = \sigma_m/\sigma_1 = 1.37$ and the value obtained for the experiment with 19.95 mole % VF_3 was 1.32. Both values constitute the lower limit of the required σ_m/σ_1 ratio. From an analysis of experimental data, a value of 1.50 ± 0.15 is recommended for the ratio σ_m/σ_1.

The relative ionisation cross-sections of NaF, VF_3, $NaVF_4$, and NaV_2F_7 determined experimentally and calculated assuming additivity using the atomic ionisation cross-sections quoted by Mann[2] and Otvos and Stevenson[7] are quoted below:

Data	σ_1'	σ_3'	σ_M'	σ_n'
Experimental	1.00	1.46	1.50	1.80
Calculated[2]	1.00	1.63	2.63	4.27
Calculated[7]	1.00	2.49	3.49	5.97

The experimental ionisation cross-sections of the complex molecules $NaVF_4$ and NaV_2F_7 were found to be smaller by a factor of 2–3 than the calculated value. This difference is probably to a considerable degree caused by the incomplete recording of Na^+ formed in the dissociative ionisation of the complex molecules with a high kinetic energy.

The experimental data obtained in the experiment with 19.95 mole % VF_3, the study of the temperature variation of the ionic currents, and also the preliminary data on the fusion diagram for the $NaF-VF_3$ system made it possible to revise the results quoted in an earlier communication[6]. The change in the mass spectrum in the experiment with an initial composition corresponding to 5.0 mole % VF_3, occurring during the isothermal evaporation process and attributed to fusion[6], in fact corresponds to the region of the solid solution adjoining the compound $3NaF.VF_3$. According to the revised data, the composition of the solid solution evaporating congruently under the conditions of molecular flow is 26.6 mole % VF_3.

REFERENCES

1. V. B. Shol'ts, L. N. Sidorov, and Yu. M. Korenev, Zhur. Fiz. Khim., 44, 2164 (1970) [Russ. J. Phys. Chem., No. 9 (1970)].
2. J. Mann, J. Chem. Phys., 46, 1646 (1967).
3. L. N. Sidorov, N. Ya. Denisov, P. A. Akishin, and V. B. Shol'ts, Zhur. Fiz. Khim., 40, 1151 (1966) [Russ. J. Phys. Chem., No. 5 (1966)].
4. L. N. Sidorov, Dokl. Akad. Nauk SSSR, 184, 889 (1969).
5. L. N. Sidorov, V. I. Belousov, and P. A. Akishin, Zhur. Fiz. Khim., 43, 80 (1969) [Russ. J. Phys. Chem., No. 1 (1969)].
6. L. N. Sidorov, Yu. M. Kornev, V. B. Shol'ts, P. A. Akishin, and V. P. Frolov, Zhur. Fiz. Khim., 41, 718 (1967) [Russ. J. Phys. Chem., No. 3 (1967)].
7. J. W. Otvos and D. P. Stevenson, J. Amer. Chem. Soc., 78, 546 (1956).

Faculty of Chemistry,
Lomonosov Moscow State
University

Received 2nd October 1968

U. D. C. 541.11"762"

Application of the Gyarmati Variational Principle to Isothermal Diffusion

J. Sandor

A complete independent system of equations of the Fick type has been derived for isothermal diffusion from the universal form of the Gyarmati variational principle. The relation between the universal and partial forms is discussed. It has been shown that only the universal form of the Gyarmati principle constitutes the variational principle for quasilinear equations. It has been demonstrated that the Gyarmati theorem, developed for thermal conductivity as an example, is applicable also to diffusion processes. The method proposed by the author supports the generality of the Gyarmati theorem.

In 1957 Gyarmati expressed the principle of minimum dissipation of Onsager energy[1] in terms of forces[2]. On the basis of this principle, he derived in 1965 his variational principle[3,4], which can be widely employed in the study of various irreversible processes[5-11]. The special form of this principle is clearly variational only when the coefficients of the linear laws are constant. Therefore the quasilinear equations for transport processes, which are important from the practical point of view, cannot be derived from the special form of the principle. Recently Gyarmati formulated the integral thermodynamic principle in a general form[2]. This form is a global representation of the local universal form of a principle of the Gaussian type[3,4,12]. From the universal integral principle, Gyarmati derived the Fourier thermal conductivity equation[13]. At the same time, with the aid of a new, additional theorem, he showed that the universal form of the principle constitutes an explicit variational thermodynamic principle for quasilinear differential equations, which has many advantages over the previously employed special form. The aim of the present study is to demonstrate the applicability of the Gyarmati principle to multicomponent diffusion in isothermal systems.

FUNDAMENTAL EQUATIONS

Our model is an isothermal continuum consisting of K locally superimposed continuous components. We shall assume that chemical reactions do not occur between the substances comprising the continuous components, i. e. isothermal diffusion is investigated. In our system the material balance equations are expressed as follows in terms of continuity equations:

$$\rho \dot{c}_i + \nabla \mathbf{J}_i = 0 \quad (i = 1, 2, \ldots, K), \tag{1}$$

where ρ is the density of total continuity, c_i the concentration of the ith component expressed in weight fractions (i.e. $\sum_{i=1}^{K} c_i = 1$), $\dot{c}_i$ the derivative of the concentration of the ith component with respect to time, and $\mathbf{J}_i$ the diffusion flux defined by the relation[12,14]

$$\mathbf{J}_i = \rho_i (\mathbf{v}_i - \mathbf{v}) \quad (i = 1.2, \ldots, K) \tag{2}$$

(here ρ_i is the density of the ith component and $\mathbf{v}_i$ its velocity).

With the aid of this relation, the velocity of the centre of gravity is expressed by

$$\mathbf{v} = \frac{\sum_{i=1}^{K} \rho_i \mathbf{v}_i}{\rho}. \tag{3}$$

It follows from Eqns. (2) and (3) that the fluxes of the components $\mathbf{J}_i$ are not independent and therefore by summation of Eqn. (2) with respect to i we obtain

$$\sum_{i=1}^{K} \mathbf{J}_i = \sum_{i=1}^{K} \rho_i (\mathbf{v}_i - \mathbf{v}) = 0. \tag{4}$$

Eqn. (4) shows that the number of independent fluxes diminishes by $K - 1$.

The entropy balance plays a central role in the thermodynamics of irreversible processes. In our case this balance is obtained from the Gibbs thermostatic relation:

$$T\,ds = \sum_{i=1}^{K} \mu_i\,dc_i = \sum_{i=1}^{K-1} (\mu_i - \mu_K)\,dc_i, \tag{5}$$

where T is the absolute temperature, s the specific entropy, and μ_i the chemical potential of the ith component. In Eqn. (5) account was taken of the dependence of the fluxes on one another and of the property of weight fractions. Having evaluated the substantial derivative of Eqn. (5), we obtain

$$\rho \dot{s} = \sum_{i=1}^{K-1} \rho \dot{c}_i \frac{\mu_i - \mu_K}{T}. \tag{6}$$

With the aid of the material balance equation (1) we obtain from this expression the substantial form of the entropy balance equation[12,14]:

$$\rho \dot{s} + \nabla \mathbf{J}_s = \sigma = \sum_{i=1}^{K-1} \mathbf{J}_i \nabla ((\mu_i - \mu_K)/T), \tag{7}$$

where

$$\mathbf{J}_s = \sum_{i=1}^{K-1} \mathbf{J}_i ((\mu_i - \mu_K)/T) \tag{8}$$