TABLE VI

COMPARISON OF RATIOS OF DIFFUSION CURRENTS AND OF THE SQUARE ROOTS OF DIFFUSION COEFFICIENTS OF ALKALI METAL IONS IN VARIOUS MEDIA

Medium	$\pi_{d.e.}$, volts	$m^{2/3}t^{1/6}$, mg.$^{2/3}$ sec.$^{-1/2}$	$i_d(K^+)/i_d(Na^+)$ Z. and K.[a]	P. and M.[b]	$(D_{K^+}/D_{Na^+})^{1/2}$	$i_d(K^+)/i_d(Li^+)$ Z. and K.[a]	P. and M.[b]	$(D_{K^+}/D_{Li^+})^{1/2}$
Water	−2.25	1.62	1.24	1.19	1.22	..	..	..
	−2.40	1.57	1.20					
50% Ethanol	−2.25	1.67	1.18					
	−2.25	2.05	1.21					
	−2.26	2.66	1.20	1.00	1.20			
	−2.37	1.63	1.18			1.48		1.40
	−2.37	1.98	1.21			1.52		
80% Ethanol	−2.41	1.63	1.16			1.35		
	−2.41	1.96	1.18	1.09	1.14	1.36	1.43	1.33
	−2.55	1.45	1.19			1.33		

[a] Zlotowski and Kolthoff. [b] Peracchio and Meloche.

sented the ratios calculated from the experimental data of Peracchio and Meloche.[14]

In general the experimental diffusion current ratios are in good agreement with the ratios of the square roots of the diffusion coefficients. The largest deviation of about 7% is found for the $i_d(K^+)/i_d(Li^+)$ ratio in 50% ethanol. The polarographic method seems suitable for rapid determination of diffusion coefficients of the alkali ions as well as of their mobilities at infinite dilution in water–ethanol mixtures.

Acknowledgment.—This work was started with the aid of a grant from the Carnegie Corporation of New York City and was concluded with the aid of a grant received by one of us (I. Z.) from the Rockefeller Foundation.

(14) It is to be noted that the diffusion wave heights given by these authors[18] under the heading "Sodium Chloride" apparently are for potassium chloride and those under "Potassium Chloride" for the sodium salt. The data given in their Table I probably represent but approximate values. As a matter of fact Peracchio and Meloche found the wave heights of potassium and sodium unchanged when the ethanol concentration was changed from 50 to 70%, while in 80% ethanol (compare Figs. 3 and 7 in their paper) the diffusion currents were from 10 to 15% smaller.

Summary

1. A satisfactory agreement is found between the experimentally determined diffusion currents of the alkali metals and the values calculated by means of the Ilkovič equation, provided that the initial drop time of the capillary be equal to or greater than three seconds.

2. The equation of the alkali metal waves corresponds to the reversible reduction of a univalent ion.

3. Half-wave potentials of potassium, sodium, and lithium in water and in water–ethanol mixtures were determined and found to be constant within the concentration range investigated.

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMICAL ENGINEERING OF THE UNIVERSITY OF WASHINGTON]

The System $Ca(NO_3)_2$–$Sr(NO_3)_2$–H_2O at 25 and 60°

BY KENNETH A. KOBE[1] AND PAUL B. STEWART

The chief use of strontium nitrate is in pyrotechnics, where the specifications of the technical salt call for substantial freedom from calcium nitrate, as this compound is extremely hygroscopic. Fractional crystallization has been considered as a means of producing strontium nitrate from the impure celestite–strontianite deposits in the State of Washington and elsewhere. Information as to the ternary system, $Ca(NO_3)_2$–$Sr(NO_3)_2$–H_2O necessary for an effective execution of this process, is not available in the literature, although both binary systems, $Ca(NO_3)_2$–H_2O and $Sr(NO_3)_2$–H_2O, have been mapped out completely.

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Experimental

Materials.—The calcium nitrate used in this work was Merck Reagent Grade chemical; the strontium nitrate Baker C. P. Grade. The analyses on the labels showed them to be essentially free from impurities. Qualitative tests substantially confirmed these claims.

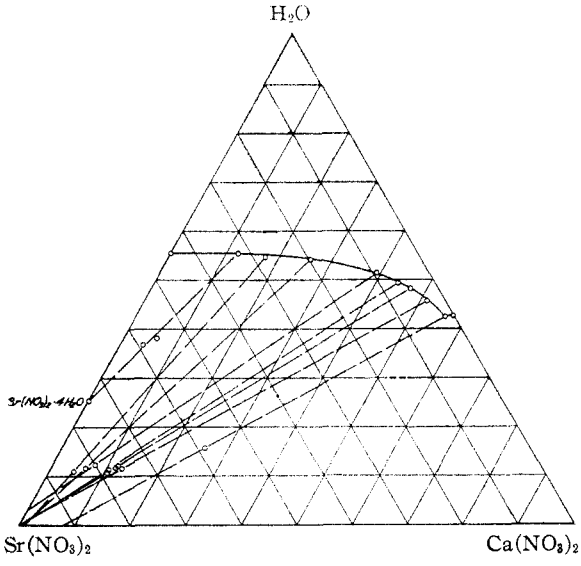

Fig. 1.—The system $Ca(NO_3)_2$–$Sr(NO_3)_2$–H_2O at 25°.

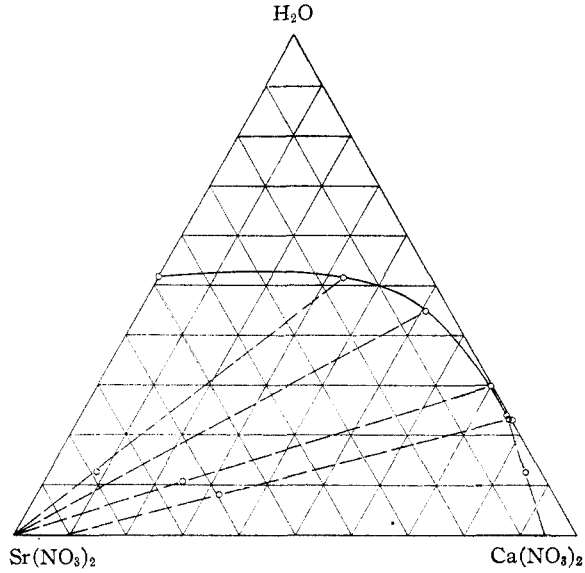

Fig. 2.—The system $Ca(NO_3)_2$–$Sr(NO_3)_2$–H_2O at 60°.

Procedure.—The solubilities were determined in the usual way in cork-stoppered Pyrex tubes. The temperatures were 25.08 ± 0.05° and 59.82 ± 0.10°. An unusually long time was required for equilibrium to be established, in some cases nearly two weeks, as proved by check analyses of the solution. This slowness presumably results from the high viscosity and density of the solutions. The samples were withdrawn from the solutions by pipets, the tips of which were covered with filter paper. At 60° the pipets were preheated to prevent crystallization of the salt from the sample in the pipet.

Total solids were determined by evaporation, the loss in weight giving the water present. The calcium nitrate was extracted from the dry residue with acetone and strontium nitrate determined by the method of Shreve and co-workers[2] as modified by the authors.[3]

The calcium nitrate was thus determined by difference. Solid phase compositions, for solutions containing both salts, were determined by Schreinemakers' wet residue method, using the same analytical procedure.

Results and Discussion

The data obtained for this system are collected in Table II and shown in Figs. 1 and 2.

With two exceptions, all values given for the solutions are the averages of three or more analyses. Those for the wet residue are from single analyses. The analytical values which were averaged agreed within 0.25% salt for the binary points, and within 0.5% salt for the ternary points, except at 60° for the extremely small amounts of strontium nitrate where the deviation from the average may be as high as 25%.

The solubilities of the pure salts are the only ones that can be compared with literature values. The weight percentage of salt was either the value obtained by direct determination or by interpolation on a solubility curve.

TABLE I

Temp., °C.	Workers	%
	Calcium Nitrate	
25	4	57.90% $Ca(NO_3)_2$
	5	57.98
	6 (interpol.)	57.3
	This work	57.20
60	5	78.2
	This work	77.15
	Strontium Nitrate	
25	6 (interpol.)	43.9% $Sr(NO_3)_2$
	7 (interpol.)	44.0
	8 (interpol.)	43.5
	9	44.22
	10	44.25
	This work	44.50
60	6	48.3
	7 (interpol.)	48.3
	8 (interpol.)	47.9
	This work	48.25

The 25° isotherm for this ternary system shows both strontium nitrate tetrahydrate and the an-

(2) Shreve, Watkins and Browning, *Ind. Eng. Chem., Anal. Ed.*, **11**, 215 (1939).

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(10) D'Ans and Siegler, *Z. physik. Chem.*, **82**, 35 (1912).

TABLE II

Solution % Sr-$(NO_3)_2$	Solution % Ca-$(NO_3)_2$	Wet solid % Sr-$(NO_3)_2$	Wet solid % Ca-$(NO_3)_2$	Solid phase
		25° Isotherm		
44.50	...	...	...	$Sr(NO_3)_2 \cdot 4H_2O$
32.30	12.23	58.90	4.21	$Sr(NO_3)_2 \cdot 4H_2O$
		55.80	6.00	
27.70	17.60	84.40	4.53	$Sr(NO_3)_2$
19.90	25.90	82.80	6.09	$Sr(NO_3)_2$
9.25	39.15	80.00	8.70	$Sr(NO_3)_2$
6.54	44.00	78.05	10.56	$Sr(NO_3)_2$
4.85	46.80	76.55	11.46	$Sr(NO_3)_2$
4.71	47.05	78.10	10.76	$Sr(NO_3)_2$
4.58	48.10	77.80	11.06	$Sr(NO_3)_2$
3.15	51.00	75.40	12.85	$Sr(NO_3)_2$
1.55	56.10	58.50	28.80	$Ca(NO_3)_2 \cdot 4H_2O + Sr(NO_3)_2$
		66.20	20.60	
..	57.20			$Ca(NO_3)_2 \cdot 4H_2O$
		60° Isotherm		
48.25	...			$Sr(NO_3)_2$
15.42	33.04	78.50	8.69	$Sr(NO_3)_2$
4.20	51.00			
0.14	70.20	64.45	24.85	$Sr(NO_3)_2$
0.084	76.00			
0.07	76.98	59.70	32.10	$Ca(NO_3)_2 + Sr(NO_3)_2$
		2.60	84.80	
..	77.15			$Ca(NO_3)_2$

hydrous salt as solid phases in equilibrium with the solutions. The appearance of anhydrous salt was checked by obtaining it in each of two tubes, one prepared at room temperature and the other at 100°. The composition of the solution in equilibrium with both forms was not determined. The 60° isotherm shows only the anhydrous salts present as solid phases. The calcium nitrate branch of the curve is so short that no investigation was made and the solid phase is considered to be that reported by the previous workers.

Summary

The 25° and 60° isotherms for the system $Ca(NO_3)_2$–$Sr(NO_3)_2$–H_2O have been determined. From these it follows that the solid phases at 25° are: $Sr(NO_3)_2 \cdot 4H_2O$, $Sr(NO_3)_2$ and $Ca(NO_3)_2 \cdot 4H_2O$; at 60°, $Sr(NO_3)_2$ and $Ca(NO_3)_2$.

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF PURDUE UNIVERSITY]

The Dropping Mercury Electrode in Acetic Acid. I. Discontinuous Current–Voltage Curves[1]

BY G. BRYANT BACHMAN AND MELVIN J. ASTLE[2]

Phenomena associated with the dropping mercury electrode have been investigated extensively in aqueous solutions, but not much has been published concerning this electrode in non-aqueous solvents. This is not surprising since analytical conditions in such solvents are not ideal and do not compare favorably in most respects with those in water. Current–voltage curves in organic solvents are generally smaller in amplitude. This follows from Ilkovic's equation[3] for the diffusion current, $i_d = 0.627nFD^{1/2}Cm^{2/3}t^{1/6}$, where i is the diffusion current, n the number of electrons involved in the reduction, F the faraday, D the diffusion coefficient of the ion or molecule being reduced, C its concentration, and m and t are the rate (in g. sec.$^{-1}$) and time of formation, respectively, of the mercury drop. Kolthoff and Lingane[4] have shown that for a given capillary, at a given pressure on the dropping mercury, and at a constant temperature, m is practically independent of the medium. Since the drop time is proportional to the interfacial tension, t will vary with the medium, but since i_d is proportional only to the sixth root of t, large variations in the drop time will produce only small changes in the magnitude of the diffusion current. It follows, therefore, that in going from aqueous to non-aqueous systems, variations in current will result almost entirely from changes in the diffusion coefficient D. The diffusion coefficients for reducible ions are, in general, smaller in non-aqueous systems than in water, and therefore the wave heights are also smaller in non-aqueous systems. This has been established experimentally on a qualitative basis by Perachio and Meloche,[5] who studied the diffusion currents of various alkali ions in alcohol–water, ethylene glycol–water and glycerol–water mixtures and found them to be smaller in these systems than in water. At present there are not sufficient data on diffusion coefficients to make possible quantitative predictions concerning wave heights in non-aqueous systems.

(1) Presented before the Physical and Inorganic Division at the St. Louis meeting of the American Chemical Society, April 8–12, 1941. From the Ph.D. thesis of Melvin J. Astle.

(2) Present address, University of Kentucky, Lexington, Kentucky.

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(4) Kolthoff and Lingane, *Chem. Rev.*, **24**, 1 (1939).

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