the following half-cell reaction

$$Am^{+++} + 2H_2O = AmO_2^{++} + 4H^+ + 3e^-$$

is in the range -1.8 ± 0.15 volts.

Acknowledgment.—The authors would like to express appreciation to E. Staritzky for the optical determinations, to F. H. Ellinger for the X-ray analysis, and to B. B. Cunningham of the University of California for his helpful suggestions.

LOS ALAMOS, NEW MEXICO RECEIVED JANUARY 17, 1951

[CONTRIBUTION FROM THE SCHOOL OF CHEMISTRY OF RUTGERS UNIVERSITY]

The Ternary System Potassium Bromide–Potassium Chloride–50% Aqueous Ethanol

BY EDWARD L. SIMONS[1] AND SAMUEL E. BLUM

The distribution of the isomorphous salts potassium bromide and potassium chloride in solubility equilibrium between liquid and solid solutions has been studied in 50% aqueous ethanol. As in water, the system belongs to Roozeboom Type II, but the solvent change shifts the crystallization end-point from 65.5 mole per cent. KBr to 83.5 mole per cent. The solvent change leaves unaltered the slope of the Hill, Durham and Ricci distribution plot. From the Yutzy and Kolthoff distribution equation heats of formation of the solid solutions have been calculated and compared with calorimetric and theoretical values.

The distribution of the isomorphous salts potassium bromide and potassium chloride in solubility equilibrium between solid and aqueous solutions has been studied at 25° by Amadori and Pampanini[2] and by Flatt and Burkhardt[3] and at 35° by Shlezinger and Zorkin.[4] All three reports are in qualitative agreement in classifying the distribution as Roozeboom Type II,[5] although the data of Amadori and Pampanini indicate a congruent crystallization end-point at 61.0 mole per cent. potassium bromide, while those of the latter two investigations indicate a value of 65.5%.

The data may also be compared in terms of the distribution equation 1[6] in which R_l and R_s represent

$$\log R_l = \log K + m \log R_s \qquad (1)$$

the mole ratios of bromide to chloride in the liquid and solid phases, K represents the ratio of the activity product constants of potassium bromide and chloride, and m is a constant assumed to be characteristic of the solid phase. In the range of $\log R_s$ values between $+1$ and -1, where equation 1 has previously been shown to be applicable,[6–9] all three sets of data can be represented by this equation with the following K and m values:

Investigators	m	log K (obsd.)	log K (calcd.)	Sat. solns. of pure salts molality mKBr	$\gamma_\pm$KBr[10]	molality mKCl	$\gamma_\pm$KCl[10]
Ref. 2	0.38	0.14_5	0.227	5.753	0.655	4.845	0.599
Ref. 3	.47	$.16_5$	.223	5.764	.655	4.869	.600
Ref. 4	.45	$.16_5$	.244	6.222[11]	.683	5.164[12]	.608

The discrepancy between the two investigations at 25° lies in the solid phase compositions, since the liquid phase solubility curves are identical over most of the composition range. In view of the special techniques employed by Flatt and Burkhardt to assure equilibrium it is felt that their data are the more reliable. The results of Shlezinger and Zorkin indicate that the distribution is essentially the same at 35° as at 25°.

It was the purpose of this investigation to observe the effect of solvent on the distribution by studying the ternary system potassium bromide–potassium chloride–50% aqueous ethanol at 35°.

Materials.—C.P. grade potassium bromide and potassium chloride were used without recrystallization. The potassium bromide was found to contain 0.10% potassium chloride, and this was taken into account in the preparation of complexes. After three days of drying at 190°, the salts were stored until used in a calcium chloride desiccator. The solvent was prepared from redistilled ethanol by dilution with distilled water. The resulting solution had a density of $0.91130\ ^{25}_{4}$, which corresponds to 49.35 weight per cent. ethanol.[13,14]

Solubility Determinations.—The solubility determinations were made according to the usual procedure described in similar investigations in so far as method of stirring, sampling, filtering and temperature control are concerned. The constant temperature bath was maintained at 34.95 ± 0.05°. The solid phases were determined by algebraic extrapolation[15] of the tie lines connecting the known complexes with the resulting saturated solutions. The constancy of successive analyses indicated that two weeks of stirring were sufficient for equilibration.

The analytical method used was that of Andrews,[16] which involves the Volhard determination of total halide on one sample and the Volhard determination of chloride on a second sample from which the bromide has been removed by oxidation to bromine with iodate followed by boiling. In applying Caldwell and Moyer's[17] Volhard procedure to the chloride determination, it was found necessary to add the indicator before adding the standard silver nitrate solution. When the order was reversed, unsatisfactory end-points were obtained.

Results.—The solubility data are shown in Table I. The change in the distribution between

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(1) Research Laboratory, General Electric Co., Schenectady, N. Y.

(2) M. Amadori and G. Pampanini, *Atti accad. Lincei*, II **20**, 473 (1911).

(3) R. Flatt and G. Burkhardt, *Helv. Chim. Acta*, **27**, 1605 (1944).

(4) N. A. Shlezinger and F. P. Zorkin, *J. Phys. Chem.* (*U. S. S. R.*), **13**, 1502 (1939).

(5) B. Roozeboom, *Z. physik. Chem.*, **8**, 521 (1891).

(6) A. E. Hill, G. S. Durham and J. E. Ricci, THIS JOURNAL, **62**, 2723 (1940).

(7) J. E. Ricci and S. H. Smiley, *ibid.*, **66**, 1011 (1944).

(8) E. L. Simons and J. E. Ricci, *ibid.*, **68**, 2194 (1946).

(9) N. O. Smith and C. S. Lennox, *ibid.*, **70**, 1793 (1948).

(10) Obtained by extrapolation of data of H. S. Harned and M. A. Cook, *ibid.*, **61**, 495 (1939).

(11) A. Seidell, "Solubility of Inorganic and Metal Organic Compounds," Vol. I, 3d ed., D. Van Nostrand Co., Inc., New York, N. Y., 1940, p. 686.

(12) *Ibid.*, p. 747.

(13) We are indebted to Dr. K. C. Bachman, formerly of this Laboratory, for this preparation and assay.

(14) A. J. Berry, *Analyst*, **64**, 190 (1939).

(15) A. E. Hill and J. E. Ricci, THIS JOURNAL, **53**, 4305 (1931).

(16) L. W. Andrews, *ibid.*, **29**, 275 (1907).

(17) J. R. Caldwell and H. V. Moyer, *Ind. Eng. Chem., Anal. Ed.*, **7**, 38 (1935).

TABLE I

THE SYSTEM KBr–KCl–50% AQUEOUS ETHANOL AT 35°

Liquid solution			Original complex		Solid solution
Wt. % KCl	Wt. % KBr	Density	Wt. % KCl	Wt. % KBr	wt. % KBr
	17.21			100.0	100.0
0.75	16.28	1.010	0.99	27.13	99.01
1.02	15.96	1.006	1.46	26.72	95.70
1.51	15.34	1.004	2.28	25.92	92.82
1.76	15.00	1.001	2.99	25.16	89.25
2.27	14.22	0.998	4.02	23.06	83.91
2.56	13.81	1.001	5.03	21.08	76.22
3.00	12.95	0.995	6.02	19.09	69.27
3.18	12.65	.990	7.03	18.09	61.61
3.50	11.91	.993	8.04	17.09	57.01
3.80	11.27	.983	9.03	15.11	47.19
4.11	10.35	.978	10.08	13.08	37.17
4.70	8.47	.971	12.07	10.09	24.13
5.64	5.45	.958	14.06	6.05	11.34
6.69	2.09	.938	16.32	2.14	2.54
7.31			100.0		0.00

liquid and solid phases resulting from the change in solvent is clearly seen in Fig. 1 in which both the data of this investigation and those of Shlezinger and Zorkin[4] in pure water are plotted as the mole fraction of potassium bromide in the dissolved salts (y) against its mole fraction in the solid solution (x). The crystallization end-point has shifted from 65.5 mole per cent. potassium bromide to 83.5%.

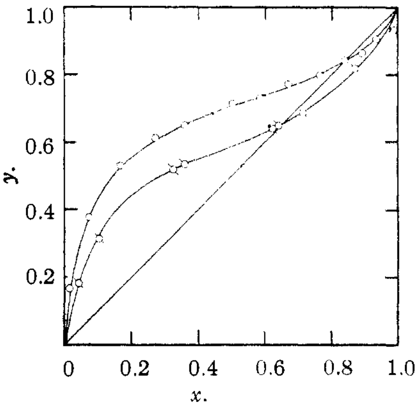

Fig. 1.—Distribution of KBr and KCl between liquid and solid solutions at 35°: O—O, 50% aqueous ethanol; ø—ø, H_2O.[4]

The effect of solvent change upon the distribution described by equation 1 is shown in Fig. 2, which also includes the data of Shlezinger and Zorkin[4] for comparison. Although the value of the intercept (log K) has changed from 0.165 to 0.385, the slope remains essentially unchanged with values of 0.45 and 0.44, respectively. In the absence of any data on the activity coefficients of the pure salts in 50% aqueous ethanol an independent determination of log K is impossible. The constancy of the slope with solvent change, however, would indicate that the actual log K is reasonably close to the value given by the intercept. This constancy of slope with solvent change may also be taken as evidence that the term m in equation 1 is indeed characteristic of the solid phase, and represents, as suggested by Hill, Durham and Ricci,[6] the effect of solid phase composition upon the solid phase activity coefficient ratio.

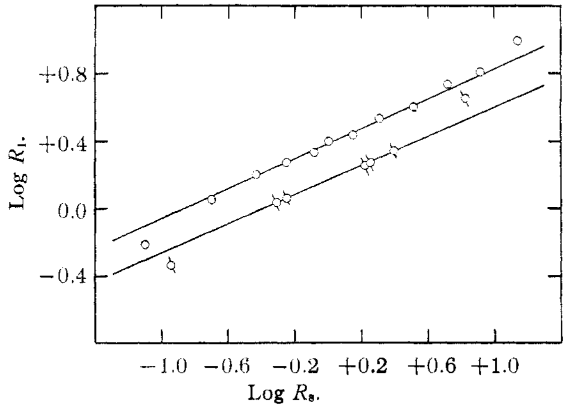

Fig. 2.—Distribution curve according to equation 1: O—O, 50% aqueous ethanol; ø—ø, H_2O.[4]

The distribution data may also be examined in the light of the equation (2) proposed for regular solutions[18] (random entropy of mixing) by Yutzy and Kolthoff[19] in which ΔH represents the enthalpy

$$\log R_l/R_s = \log K - [0.4343(\Delta H)/RTx(1 - x)](2x - 1) \quad (2)$$

of formation per mole of solid solution. The linear relationship between log R_l/R_s and x required by this equation is illustrated in Fig. 3 in which are plotted only the results of this investigation. The data of Shlezinger and Zorkin[4] yield a parallel plot with the same slope of −1.13. The K values obtained from equation 2 are identical with those from Fig. 2.

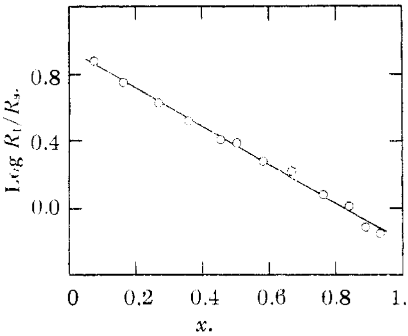

Fig. 3.—Test of "regularity" of the solid solution.

Assuming the validity of equation 2 (*i.e.*, that the liquid phase activity coefficient ratio is exactly unity at all concentrations and that the heat of formation of the solid solutions can be represented by the form: $\Delta H = bx(1 - x)$) enthalpy values for the solid solutions may be calculated from the slope of Fig. 3. These are listed in Table II, where they are seen to be consistently lower than the values obtained calorimetrically by Fontell[20] on solutions which had been prepared by fusion of the pure salts. This is

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(18) J. H. Hildebrand, THIS JOURNAL, **51**, 66 (1929).

(19) H. C. Yutzy and I. M. Kolthoff, *ibid.*, **59**, 916 (1937).

(20) N. Fontell, *Soc. Sci. Fennica Commentationes Phys.-Math.*, **10**, No. 6, 1 (1939).

in qualitative agreement with Fontell's subsequent observation[21] that the calorimetrically determined enthalpy of a 50 mole per cent. solution prepared by crystallization from water is 222 cal. per mole compared with a value of 232 cal. for the fused preparation.

TABLE II

HEATS OF FORMATION OF KBr–KCl SOLID SOLUTIONS

Mole fraction KBr	This study eq. 2	Fontell[a]	Durham and Hawkins	Hovi	Wallace
	ΔH_f(cal.-mole^{-1} solid solution)				
0.17	112	141	130	145	
.34	179	217	196	207	
.50	199	232	208	219	450
,66	179	201	179	201	
.83	112	121	107	134	

[a] Calculated from the equation fitted to Fontell's data by Wallace and Fineman, *Soc. Sci. Fennica Commentationes Phys.-Math.*, 14, No. 6, 1 (1948).

The lower enthalpy values obtained in this investigation are also in agreement with the calculations of Durham and Hawkins[22] who suggested that in the stable state the ions of the alkali halide solid solutions are displaced from their normal lattice sites to positions of minimum potential energy with respect to each other. The heats of formation obtained by them from calculated lattice energies are also listed in Table II, where they are seen to be lower than the calorimetric values though slightly higher than the values calculated from Fig. 3. These latter values, though subject to the previously mentioned assumptions, do indicate that the solid solutions obtained in this investigation are more nearly in a state of thermodynamic equilibrium at room temperature than those used by Fontell.[20] Presumably the ions of this solid solution can readily assume the positions of minimum potential energy characteristic of room temperature only if the lattice is built up isothermally by crystallization from a suitable solvent, and they persist in a structure of higher energy if cooled from the molten state to room temperature.

Independently of Durham and Hawkins, Wasastjerna and Hovi[23-25] have suggested that the solid solution lattice is characterized not only by the geometrical displacements of the ions but by a certain degree of local order. Hovi's calculated enthalpies[25] are also listed in Table II. Calculations by Wallace,[26] based upon the Born–Mayer model, but assuming no ionic displacements, lead to enthalpies considerably higher than the calorimetric data.

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(21) N. Fontell, V. Hovi and A. Mikkola, *Ann. Acad. Sci. Fennica, Math.-Phys. Ser. A*, **54**, 1 (1949).

(22) G. S. Durham and J. A. Hawkins, *J. Chem. Phys.*, **19**, 149 (1951).

(23) J. A. Wasastjerna, *Soc. Sci. Fennica, Commentationes Phys.-Math.*, **13**, No. 5, 1 (1946).

(24) J. A. Wasastjerna, *ibid.*, **15**, No. 3, 1 (1949).

(25) V. Hovi, *ibid.*, **15**, No. 12, 1 (1950).

(26) W. E. Wallace, *J. Chem. Phys.*, **17**, 1095 (1949).

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[CONTRIBUTION FROM THE RESEARCH LABORATORIES, K-25 PLANT, CARBIDE AND CARBON CHEMICALS DIVISION, UNION CARBIDE AND CARBON CORPORATION]

Thermodynamic Properties and *P–V–T* Relations of Chlorotrifluoroethylene[1]

BY GEORGE D. OLIVER, J. W. GRISARD AND C. W. CUNNINGHAM

Thermal measurements made on chlorotrifluoroethylene include heat capacity from 16°K. to the boiling point, 244.80°K., and a heat of fusion, 1327.1 ± 1.3 cal./mole, at the triple point, 115.00 ± 0.05°K. Vapor pressure measurements which covered the temperature range of −67 to −11° and pressure range up to two atmospheres are represented by $\log_{10} P_{\mathrm{mm}} = 6.90199 - 850.649/(t + 239.91)$. Bubble point pressures from 25° to the t_c are represented by $\log_{10} P_{\mathrm{mm}} \times 7.75412 - 1392.82/(t + 319.70)$. The calculated heat of vaporization is 4965 cal./mole at the boiling point, −28.36 ± 0.05°. Entropy values calculated for the liquid and and ideal gas state at the boiling point are 52.74 ± 0.10 and 73.18 cal./deg. mole, respectively. Pressure–volume–temperature relations were measured at five isotherms between 25° and the critical point. The experimental critical constants are: t_c 105.8°; p_c 40.1 atm.; d_c 0.55 g./ml.

Introduction

Chlorotrifluoroethylene may be polymerized to form liquid polymers and a plastic known as Fluorothene.[2] The work of Gabbard and co-workers on the physical properties of the liquid polymers has been summarized and published.[3] Fluorothene has the usual properties attributed to plastics as well as the additional advantage of resisting attack by acids and other corrosive materials. In order to better understand the starting material for these plastics, some of the thermodynamic properties of the pure monomer have been investigated.

Experimental

Material.—The samples investigated were taken from a ten pound cylinder of material prepared at the K-25 Plant by dechlorinating Freon-113 with zinc in alcohol solution. In order to reduce the rate of polymerization, it has been refrigerated at −75° since preparation. In an attempt to obtain the best sample, the cylinder was placed in a Dry Ice-bath before and during transfer of the sample to apparatus, and the top vapors were pumped off each time before a vapor sample was taken. The material used for low temperature studies had a purity of 99.84 mole %, and since identical procedures were followed to obtain the other samples it is reasonable to assume a similar value for their purity.

Apparatus.—Since the vapor pressure of chlorotrifluoroethylene is about 5000 mm. at room temperature, a stronger calorimeter was needed. Therefore, a copper calorimeter of the previously described design,[4] except a wall thickness

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(1) This document is based on work performed for the Atomic Energy Commission by Carbide and Carbon Chemicals Division, Union Carbide and Carbon Corporation, Oak Ridge, Tennessee.

(2) J. D. Gibson, *et al.*, *Ind. Eng. Chem.*, **42**, 2314 (1950).

(3) W. H. Reysen and J. D. Gibson, *ibid.*, **42**, 2468 (1950).

(4) G. D. Oliver and J. W. Grisard, THIS JOURNAL, **73**, 1688 (1951).