

Tests were made with a few solutes which showed that a week of shaking allowed the solution to become saturated. Solubility measurements were least precise for nearly insoluble substances. This was due to the small size of the sample of solid remaining from the evaporation of the solution. A one-mg. sample in one ml. of solvent corresponded to a solubility of 0.07 g. per 100 g. of acid. Since weighings were made estimating to the nearest 0.1 mg., large errors were made in low solubilities.

In Table II both the apparent composition of the solid and its solubility are given. The quantity following the  $\pm$  sign is the probable error calculated from the experimental data.

**Effect of Sodium Trifluoroacetate upon the Solubilities of Other Trifluoroacetates.**—A few tests were made to learn whether the presence of sodium trifluoroacetate had a marked effect upon the solubility of other metal trifluoroacetates. In each case, trifluoroacetic acid was saturated both with sodium trifluoroacetate and with the other trifluoroacetate. The amounts of the two metals in solution were determined by analysis of the residue remaining after evaporation of the solvent. Results are presented in Table III.

TABLE III  
SIMULTANEOUS SOLUBILITIES OF TWO SOLUTES AT 29.8°

Solution saturated with $\text{CF}_3\text{COONa}$ and	Concn. of $\text{CF}_3\text{COONa}$ g./100 g. trifluoroacetic acid	Concn. of other salt, g./100 g. solvent
$(\text{CF}_3\text{COO})_2\text{Zn}$	23.0	13.0
$(\text{CF}_3\text{COO})_2\text{Mg}$	13.2	0.59
$(\text{CF}_3\text{COO})_3\text{Al}$	13.0	Trace
$(\text{CF}_3\text{COO})_3\text{Nd}$	13.1	Trace

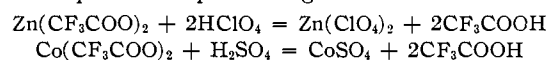
### Discussion

Trifluoroacetic acid acts as a highly acidic solvent. It reacts with the anions of many solutes to form volatile acids and the trifluoroacetates of many metals behave as bases in the sense that they are soluble in the solvent. It is of interest to compare their solubilities in the acid with the solubilities of the hydroxides of the same metals in water. In the larger families of groups 1, 2 and 3 of the periodic system one finds a close parallelism. The solubility of the base increases within a family with increasing atomic weight of the metal. The bases of

group 1 elements are more soluble than those of their neighbors in group 2 and the latter are in turn more soluble than those of group 3. Trifluoroacetates of cobalt and nickel and of the sub-group elements of groups 1 and 2 are much more soluble in trifluoroacetic acid than are the hydroxides of the same elements in water. The greater solubility of the trifluoroacetates is in keeping with the fact that trifluoroacetic acid is a more highly acidic solvent than water.

Zinc trifluoroacetate is amphoteric. Its solubility in trifluoroacetic acid is increased by the addition of the soluble base, sodium trifluoroacetate. By contrast, the solubility of magnesium trifluoroacetate is changed very little by the addition of sodium trifluoroacetate. It is not amphoteric and its solubility is apparently not decreased due to the common ion effect. This may be due in part to the low degree of ionization of the solutes.<sup>3</sup>

Both perchloric and sulfuric acids behave as acids when in trifluoroacetic acid. When a solution of perchloric acid is added to a solution of a trifluoroacetate, neutralization occurs and a precipitate of the perchlorate of the metal appears. In many cases a solution of sulfuric acid forms a precipitate of a sulfate. Equations representing such reactions are



Most of the trifluoroacetates used in this study were white solids and their solutions were colorless. Colors of the trifluoroacetates of certain metals and of their solutions in trifluoroacetic acid follow: Cu(II), blue green; Ni(II), green; Co(II), dark pink; Pr(III), pale green; Nd(III), pale pink. Cobalt(III) complex compounds had colors when dissolved in trifluoroacetic acid like those of aqueous solutions of the same substances.

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[CONTRIBUTION FROM THE CHEMICAL ENGINEERING DIVISION OF ARGONNE NATIONAL LABORATORY]

## Partial Molal Volumes and Molar Refractions of the System Bromine Trifluoride-Bromine Pentafluoride

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The refractive indices and densities of the system bromine trifluoride-bromine pentafluoride have been measured at 25°. Equations have been derived which express refractive index and density as functions of composition. The partial molal volumes are smaller than the molar volumes of the pure compounds, but the volume contraction upon mixing is always less than one per cent. The Lorentz-Lorenz molar refraction of the trifluoride is 13.22 cc. and that of the pentafluoride is 15.41 cc. The maximum deviation of the molar refraction from that of an ideal solution is -0.06 cc.

**Introduction.**—The partial molal volumes and molar refractions of the system bromine trifluoride-bromine pentafluoride have been determined, and the variations in these properties have been used to indicate the extent of molecular interactions. On the basis of their chemical similarity and apparent freedom from solvation effects, bromine trifluoride and bromine pentafluoride would be expected to form relatively ideal binary solutions. This investigation reveals some aspects of their behavior and points out the small magnitude of any effects

attributable to the ionic species which are present. The symbols to be used are defined as

- $M$  = molecular weight
- $N$  = mole fraction
- $d$  = density
- $n$  = index of refraction
- $\bar{V}$  = partial molal volume
- $R$  = molar refraction
- $\phi$  = prism angle
- $\delta$  = angle of deviation of light beam
- 1 =  $\text{BrF}_3$
- 2 =  $\text{BrF}_5$

### Experimental

**Purification of Bromine Fluorides.**—Technical grade bromine trifluoride and bromine pentafluoride obtained from the Harshaw Chemical Company were purified by distillation in an all-nickel still having a fractionating column 40 inches long and 1/2-inch in diameter, packed with 1/8-inch nickel helices. Center cuts of the trifluoride and pentafluoride fractions were collected in prefluorinated Monel vessels, which were then pressurized with helium. The physical properties of the purified materials were as follows: BrF<sub>3</sub>, pale yellow liquid, b.p. 125.8° (760 mm.), f.p. 8.8°,  $n_D^{25}$  1.4536,  $d_4^{25}$  2.8030 g./ml.; BrF<sub>5</sub>, colorless liquid, b.p. 41.3° (760 mm.), f.p. -61.3°,  $n_D^{25}$  1.3529,  $d_4^{25}$  2.4604 g./ml.

The above values for the boiling point and freezing point of bromine trifluoride are in excellent agreement with those reported by Oliver and Grisard.<sup>1</sup> Ruff and Menzel<sup>2</sup> reported 40.5° for the boiling point of bromine pentafluoride.

The binary solutions were made up by weight in fluorothene test-tubes from the purified materials. Since the two compounds differ greatly in volatility, the solutions were transferred by gravity-feed methods rather than vacuum methods, in order to avoid changes in composition.

**Refractive Index Measurements.**—The corrosive solutions could not be examined in a Pulfrich or Abbé refractometer without permanently damaging the optical parts, so the refractive index measurements were made with a hollow prism and spectrometer. The prism was made of nickel, with replaceable quartz windows and Teflon gaskets. It was prefluorinated with chlorine trifluoride vapor and swept out with helium before each filling. A Model 10025 Spencer spectrometer was used with sodium light from a General Electric Sodium Lab-Arc. Constant-temperature water was circulated through top and bottom jackets of the prism to provide temperature regulation to within ±0.05°.

The theory of the hollow prism method has been adequately described elsewhere.<sup>3,4</sup> In the present work the Fraunhofer Method<sup>3</sup> or Method of Minimum Deviation was used to determine the position of the emergent light beam, and the refractive index was computed from the equation

$$n = \frac{\sin\left(\frac{\phi + \delta}{2}\right)}{\sin\left(\frac{\phi}{2}\right)} \quad (1)$$

The phi and delta in the numerator are both divided by two.

**Density Measurements.**—The density measurements were made with 6-ml. Ostwald-Sprengel type Pyrex glass pycnometers and checked with similar pycnometers made of fluorothene. A carbon tetrachloride immersion bath controlled to ±0.1° was employed, since this was much less hazardous than water for use with the interhalogen compounds. The Pyrex pycnometers lost weight after each filling with interhalogen solution, but the milligram amounts of dissolved glass were retained in weighing the interhalogen contents, and it was found that correct results could be obtained by recalibrating the pycnometers with water prior to each use. The volume and weight of the fluorothene pycnometers were not affected by contact with the interhalogen solutions. Densities determined with both types of pycnometers agreed within the experimental error. ±0.0005 g./ml. The usual corrections for air buoyancy were applied.

**Discussion of Results.**—The refractive indices obtained for the binary solutions at 25.0° and given in Table I can be represented by equation 2<sup>5</sup>

$$n_D^{25} = 1.4536 - 0.1243N_2 + 0.0124N_2^2 + 0.0112N_2^3 \quad (2)$$

The probable error of a single point is ±0.0002. Since the refractive indices of the two fluorides dif-

(1) G. D. Oliver and J. W. Grisard, *THIS JOURNAL*, **74**, 2705 (1952).

(2) O. Ruff and W. Menzel, *Z. anorg. allgem. Chem.*, **202**, 49 (1931).

(3) H. Kessler, "Handbuch der Physik," Vol. XVIII, Springer, Berlin, 1927, pp. 632-682.

(4) A. Weissberger, "Physical Methods of Organic Chemistry," Part II, Second Edition, Interscience Publishers, Inc., New York, N. Y., 1949, p. 1217.

(5) The equation given earlier in report ANL-4941 of Argonne National Laboratory was based upon a less accurate value for the refractive index of BrF<sub>3</sub>.

fer by approximately 0.1, it should be possible to analyze the binary solutions to within ±0.2% by refractive index measurements. At 70.0°,  $n$  was found to be 1.4302 for bromine trifluoride and 1.3275 for bromine pentafluoride. The approximate temperature coefficients of  $n$  are therefore -0.00052 and -0.00056 unit/degree, respectively.

TABLE I  
REFRACTIVE INDICES OF BrF<sub>3</sub>-BrF<sub>5</sub> SOLUTIONS AT 25.0°  
WITH SODIUM D LIGHT

Mole fraction of BrF <sub>3</sub>	$n_D^{25}$	Mole fraction of BrF <sub>5</sub>	$n_D^{25}$
0.0000	1.4536	0.4784	1.3982
.1764	1.4321	.6608	1.3803
.3621	1.4109	.8199	1.3660
.3867	1.4078	1.0000	1.3529

The densities obtained at 25.0° are given in Table II. Those of the pure compounds differ slightly from earlier data.<sup>2,6,7</sup> The differences in densities and other physical properties indicate that the earlier work may have been done with compounds of lower purity.

TABLE II  
DENSITIES OF BrF<sub>3</sub>-BrF<sub>5</sub> SOLUTIONS AT 25.0°

Mole fraction of BrF <sub>3</sub>	$d_4^{25}$ , g./ml.	Mole fraction of BrF <sub>5</sub>	$d_4^{25}$ , g./ml.
0.0000	2.8030	0.5685	2.5990
.1009	2.7646	.6711	2.5648
.1610	2.7418	.6965	2.5560
.3074	2.6893	.7220	2.5495
.3868	2.6609	.8472	2.5102
.4532	2.6389	.8691	2.5025
.4618	2.6366	1.0000	2.4604

Equation 3 gives the density as a function of composition.

$$d_4^{25} = 2.8030 - 0.3884N_2 + 0.0641N_2^2 - 0.0183N_2^3 \quad (3)$$

Since the probable error of a single point is ±0.0005 g./ml. and the densities of the pure compounds differ by 0.3426 g./ml., it should be possible to analyze the binary solutions to within ±0.15% by density measurements.

The density of bromine trifluoride at 50.0° was found to be 2.7351 ± 0.0005 g./ml., and that of bromine pentafluoride at 0.0° was found to be 2.5475 ± 0.0005 g./ml. The approximate temperature coefficients of density are therefore -0.00272 g. ml.<sup>-1</sup> degree<sup>-1</sup> from 25 to 50° for the trifluoride and -0.00348 g. ml.<sup>-1</sup> degree<sup>-1</sup> from 0 to 25° for the pentafluoride.

Equation 3 leads to equations 4 and 5 for the partial molal volumes of BrF<sub>3</sub> and BrF<sub>5</sub>, respectively

$$\bar{V}_1 = \frac{M_1}{d} + N_2 \left[ \frac{(N_1 M_1 + N_2 M_2)(-0.3884 + 0.1282N_2 - 0.0549N_2^2)}{d^2} \right] \quad (4)$$

$$\bar{V}_2 = \frac{M_2}{d} - N_1 \left[ \frac{(N_1 M_1 + N_2 M_2)(-0.3884 + 0.1282N_2 - 0.0549N_2^2)}{d^2} \right] \quad (5)$$

(6) O. Ruff, A. Braid, O. Bretschneider, W. Menzel and H. Plaut, *Z. anorg. allgem. Chem.*, **206**, 59 (1932).

(7) O. Ruff and A. Braid, *ibid.*, **214**, 91 (1933).

The partial molal volumes computed from these equations and given in Table III with a probable error of  $\pm 0.05$  ml./mole decrease continuously with increasing dilution of each component. This decrease between the mole fractions 1.0 and 0.0 amounts to 4.7% for  $\text{BrF}_3$  and 2.7% for  $\text{BrF}_5$ . However, the volume contraction which occurs on mixing is always less than one per cent.

TABLE III

PARTIAL MOLAL VOLUMES OF  $\text{BrF}_3$  AND  $\text{BrF}_5$  AT  $25.0^\circ$ 

Mole fraction of $\text{BrF}_3$	$\bar{V}_{\text{BrF}_3}$ , ml./mole	$\bar{V}_{\text{BrF}_5}$ , ml./mole	Mole fraction of $\text{BrF}_3$	$\bar{V}_{\text{BrF}_3}$ , ml./mole	$\bar{V}_{\text{BrF}_5}$ , ml./mole
0.0	48.85	69.17	0.6	48.15	70.72
.1	48.83	69.50	.7	47.86	70.87
.2	48.78	69.80	.8	47.50	70.99
.3	48.69	70.07	.9	47.07	71.07
.4	48.56	70.31	1.0	46.54	71.09
.5	48.38	70.53			

The experimental molar refractions were computed from the Lorenz-Lorentz expression 6, using values of  $n$  and  $d$  obtained from equations 2 and 3

$$R_{\text{exp}} = \frac{n^2 - 1}{n^2 + 2} \left( \frac{N_1 M_1 + N_2 M_2}{d} \right) \quad (6)$$

The  $R$  values are given in Table IV with a probable error of  $\pm 0.02$  cc. In an ideal system,  $R$  would be a linear function of  $N_2$ ; in the present system,  $R$  is linear within experimental error for  $N_2$  between 0.0 and 0.4, then exhibits a negative deviation from linearity which is greatest (0.06 cc.) at  $N_2 = 0.75$ . This maximum deviation is no larger than that commonly found in a mixture of neutral molecules, such as carbon tetrachloride and benzene.<sup>4</sup> Although bromine trifluoride is known to contain ( $\text{BrF}_2^+$ ) and ( $\text{BrF}_4^-$ ) ions,<sup>8</sup> its equivalent conductance decreases upon dilution with bromine pentafluoride, and the effect of the ions becomes progressively less important. The molar refractions of the binary solutions are therefore chiefly characteristic of the undissociated molecules.

(8) A. A. Banks, H. J. Emeleus and A. A. Woolf, *J. Chem. Soc.*, 2861 (1949).

tions of the binary solutions are therefore chiefly characteristic of the undissociated molecules.

TABLE IV

MOLAR REFRACTIONS OF  $\text{BrF}_3$ - $\text{BrF}_5$  SOLUTIONS

Mole fraction of $\text{BrF}_3$	$d^{25}_D$ , g./ml.	$n^{25}_D$	$R_{\text{exp}}$ , cc./mole	$R_{\text{ideal}}$ , cc./mole
0.0	2.8030	1.4536	13.22	13.22
.1	2.7648	1.4413	13.45	13.44
.2	2.7277	1.4293	13.67	13.66
.3	2.6918	1.4177	13.87	13.88
.4	2.6567	1.4066	14.08	14.10
.5	2.6225	1.3959	14.28	14.32
.6	2.5891	1.3859	14.48	14.53
.7	2.5562	1.3765	14.69	14.75
.8	2.5239	1.3677	14.91	14.97
.9	2.4920	1.3599	15.15	15.19
1.0	2.4604	1.3529	15.41	15.41

The atomic refractions of fluorine and bromine cannot be computed with any certainty from the above data. Bromine in particular must have different  $R$  values in the two compounds, since it has two more unshared electrons in the trifluoride than in the pentafluoride. Any  $R$  value ascribed to fluorine may be expected to vary also, but to a lesser extent. The interaction between bromine and fluorine probably has an effect upon the molar refractions of these compounds analogous to that which occurs in the alkali fluorides.<sup>9,10</sup> The molar refractions of the alkali fluorides are larger in the solid state than in solution, due to the loosening of the cation electronic system by the intense force field of the fluoride ion. Although in the bromine fluorides the bonding is largely covalent, similar loosening of the bromine electronic system by fluorine can be expected.

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(9) K. Fajans and G. Joos, *Z. Physik*, **23**, 26 (1924).

(10) N. Bauer and K. Fajans, *THIS JOURNAL*, **64**, 3023 (1942).

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, THE UNIVERSITY OF MANITOBA]

## Heat of Neutralization Studies at High Acid-Base Concentration. II. Sodium Hydroxide-Hydrobromic Acid<sup>1,2</sup>

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The heats of neutralization of sodium hydroxide and hydrobromic acid solutions have been measured at  $25^\circ$  for reactant concentrations from 3 to 16 molal, with an accuracy of 0.1%. The results have been used to calculate the relative enthalpies of hydrobromic acid solutions from 3 to 16 molal.

The chemical similarity between hydrochloric acid and hydrobromic acid makes it desirable that some studies be made of the thermodynamic properties of hydrobromic acid for comparison with the established properties of hydrochloric acid. The relative enthalpies of hydrobromic acid solutions can be determined by heat of neutralization measurements of the system hydrobromic acid-sodium

hydroxide since all supplementary data are available and reasonably reliable.

### Experimental Details

The apparatus was very similar to that described in a previous paper.<sup>3</sup> A second stirrer was placed in the calorimeter can to reduce the time required for equilibration, and the hollow lid of the calorimeter well was eliminated because of the mechanical difficulties in maintaining water-tightness. Instead, the well was closed with a brass plate which seated

(1) Aided by a grant from the National Research Council, Canada.

(2) Paper I, ref. (3).

(3) P. Bender and W. J. Biermann, *THIS JOURNAL*, **74**, 322 (1952).