general interpretation is clear: the shift in *g*-value for molecules in non-degenerate orbital ground states increases with the magnitude of the spin-orbit coupling and decreases with the separation between the ground and excited states.

The spin-orbit coupling in atoms increases rapidly with atomic number and thus the shift in *g*-value for sulfur radicals (0.022 unit) would be expected to be larger than the shift in radicals containing only first row elements (< 0.004 unit), as indeed is the case. The authors know of only two other systems that appear to involve sulfur radicals: ultramarine[55a] and sulfur in oleum.[55b] Both materials have *g*-values of about 2.02, and thus the data suggests the very tentative inference that all polyatomic free radicals in which the odd electron is primarily associated with a sulfur atom will have a *g*-value of about 2.02. When the odd electron is in a sulfur-containing compound but is not primarily localized on a sulfur atom, the *g*-value should be closer than this to the free electron value. Sulfur-containing free radicals have been observed in the presence of Lewis acids,[60,61] and the *g*-value obtained from the spectrum of a sulfuric acid solution of diphenyl disulfide was found to be 2.008.[24] It is also interesting to note that the black specks obtained from impure sulfur, corresponding to the empirical formula $C_2S$, have a *g*-value of 2.010.[43]

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(60) J. M. Hirshon, D. M. Gardner and G. K. Fraenkel, THIS JOURNAL, **75**, 4115 (1953).

(61) J. E. Wertz and J. L. Vivo, *J. Chem. Phys.*, **23**, 2193 (1955).

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# The Bromine Pentafluoride–Hydrogen Fluoride System. Solid–Liquid Equilibria, Vapor Pressures, Molar Volumes and Specific Conductances[1]

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Various physical properties of the bromine pentafluoride–hydrogen fluoride system have been investigated. The solid-liquid phase diagram shows a eutectic point at −85.61° and 95.2 mole per cent. hydrogen fluoride. The vapor pressure–composition diagram shows large positive deviations from Raoult's law. The deviations from ideality become larger at higher temperatures, and at 25° there is probably an azeotrope with maximum vapor pressure. Average molar volumes observed are lower than calculated for an ideal solution, the contraction on mixing being 2–3%. The specific conductance of a carefully purified sample of bromine pentafluoride was $9.1 \times 10^{-8}$ ohm$^{-1}$ cm.$^{-1}$. Conductances of bromine pentafluoride–hydrogen fluoride mixtures were studied over a range of temperatures and compositions.

## Introduction

The physical properties of bromine pentafluoride and of bromine pentafluoride–hydrogen fluoride mixtures have been little investigated. In order to extend the knowledge of these systems, we have measured freezing points, densities, vapor pressures and specific conductances of various mixtures of hydrogen fluoride and bromine pentafluoride.

## Experimental

**Materials.**—The method for purification, storage and handling of bromine pentafluoride and hydrogen fluoride has been described.[1,2]

**Cryoscopic Measurements.**—The freezing point cells for bromine pentafluoride–hydrogen fluoride solutions and the technique used have been described.[2] Difficulty was encountered with stirring pure bromine pentafluoride since the reciprocating stirrer froze in when less than half the liquid had frozen. A new cell was therefore constructed in which the liquid could be completely frozen. This cell was constructed entirely of fluorothene and was closed by a tapered plug held in place by a clamping device. A copper–constantan thermocouple was introduced through the plug and the leads were wound in a helix around a fluorothene rod which extended into the liquid. Materials could be introduced into the cell on the vacuum line by a connection through the plug. In use the cell was filled, closed and the entire assembly attached to a single-cylinder reciprocal-action air motor which provided very vigorous shaking of the contents.

**Density, Vapor Pressure and Conductance Measurements.**—The techniques were the same as used previously.[1] A new dipping-type conductance cell was employed which largely eliminated the use of fluorothene wax as a sealant around leads. This was important since the wax is dissolved by bromine pentafluoride. Measurements at −60° to −70° were made using a Dry Ice–acetone cooling bath; the cell was calibrated at low temperatures with solutions of salts in alcohol or acetone. The conductances of the latter were measured in a conventional glass cell fitted with platinized platinum electrodes.

## Results

**Solid–liquid Equilibria.**—Cooling curves obtained with various mixtures of bromine pentafluoride and hydrogen fluoride provided the initial and final freezing temperatures which are presented in Table I. The only definite feature is a eutectic point at −85.61° and 95.2 mole per cent. hydrogen fluoride. The freezing point of pure bromine pentafluoride calculated by the method of Witschonke[3] is −60.50 ± 0.10°, and the concentration of impurity in our starting material was about 0.02 molal. A slight discontinuity in the freezing point curve at 18 mole per cent. hydrogen fluoride does not seem to be a peritectic but might arise from a phase transition in the solid state.

The heat of fusion of bromine pentafluoride esti-

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(1) Physical Properties of the Halogen Fluorides. VIII. For the preceding article of this series see M. T. Rogers, J. L. Speirs, M. B. Panish and H. B. Thompson, THIS JOURNAL, **78**, 936 (1956).

(2) M. T. Rogers and J. L. Speirs, *J. Phys. Chem.*, in press.

(3) C. R. Witschonke, *Anal. Chem.*, **24**, 350 (1952).

TABLE I

CRYOSCOPIC DATA FOR BROMINE PENTAFLUORIDE–HYDROGEN FLUORIDE SOLUTIONS

| Mole % HF | F.P. (initial), °C. | Mole % HF | F.p. (initial), °C. |
|---|---|---|---|
| 0 | −60.63 ± 0.01 | 59.5 | −66.10 |
| 5.79 | −62.69 ± 0.02 | 67.0 | −66.70 |
| 12.9 | −63.50 | 81.9 | −68.40 |
| 17.9 | −63.75 | 89.3 | −72.7 ± 0.4 |
| 20.7 | −64.04 | 92.5[a] | −78.2 ± .4 |
| 25.8 | −64.43 | 94.5[a] | −84.5 ± .4 |
| 36.3 | −64.96 | 96.7 | −84.98 ± .03 |
| 49.3 | −64.62 | 98.6 | −83.94 ± .03 |

[a] A second halt in the cooling curve at −85.61° was observed; this is the eutectic temperature.

mated from the slope of the freezing point curve is 1.5 kcal./mole and the heat of fusion of hydrogen fluoride is similarly estimated to be 0.97 kcal./mole from the slope of the freezing point curve near 100 mole per cent. hydrogen fluoride. These values agree fairly well, considering the rather large experimental errors involved, with the values 1.76 kcal./mole for bromine pentafluoride[4] and 0.938 kcal./mole for hydrogen fluoride[5] obtained by more direct methods.

**Vapor Pressures of Solutions.**—The vapor pressures of bromine pentafluoride–hydrogen fluoride mixtures have been measured at 0 and 15° and are presented in Table II as a function of the composition of the solution. Rather large positive deviations from Raoult's law (calculations based on monomolecular species) are observed, and the deviations become larger at higher temperatures. There is no maximum in the curves at 0 or 15°, but we obtained some evidence of a maximum in the curve at 25°. An azeotrope with composition in the range 50–70 mole per cent. hydrogen fluoride probably is formed at 25°, but experimental difficulties prevented precise measurements being made at this temperature. It is likely that the degree of association of hydrogen fluoride is lowered in solution in bromine pentafluoride leading to an increase in volatility over that predicted for an ideal mixture.

TABLE II

VAPOR PRESSURES OF BROMINE PENTAFLUORIDE–HYDROGEN FLUORIDE SOLUTIONS

| 0° | | 15° | |
|---|---|---|---|
| Mole % HF | $p^a$, mm. | Mole % HF | $p$, mm. |
| 0 | 139 | 0 | 258 |
| 26.8 | 240 | 26.8 | 505 |
| 51.2 | 300 | 47.5 | 585 |
| 69.0 | 350 | 63.3 | 612 |
| 78.6 | 365 | 78.6 | 640 |
| 82.1 | 368 | 100 | 664 |
| 91.5 | 380 | | |
| 100 | 398 | | |

[a] The probable error in these measurements is about ±1%.

**Molar Volumes.**—The average molar volumes $V$ observed (Table III) are slightly less than calculated assuming an ideal solution ($V°$). The percentage contraction on mixing ($100\,\Delta V/V°$) is 2–3%; this is considerably smaller than the decrease observed in the iodine pentafluoride–hydrogen fluoride system.[1]

TABLE III

DENSITIES AND AVERAGE MOLAL VOLUMES OF BROMINE PENTAFLUORIDE–HYDROGEN FLUORIDE SOLUTIONS AT 25°

| Mole % HF | $d^{25}{}_4$, g./cc. | $V°$, ideal | $V$, obsd. | $100\,\Delta V/V°$ |
|---|---|---|---|---|
| 100.0 | 0.945 | 21.2 | .. | ... |
| 97.4 | 1.13 | 22.7 | 22.1 | −3.0 |
| 76.1 | 1.79 | 33.1 | 32.1 | −3.1 |
| 62.9 | 1.97 | 39.7 | 39.0 | −1.8 |
| 49.8 | 2.15 | 46.2 | 45.1 | −2.3 |
| 0 | 2.465 | .. | 71.0 | ... |

**Conductance Measurements.**—The specific conductance of specially purified bromine pentafluoride and of various mixtures of bromine pentafluoride and hydrogen fluoride are reported in Table IV. Values have been corrected for polarization at the smooth platinum electrodes as described previously.[6] Measurements at −60° have a rather larger probable error (±5%) than measurements at higher temperatures. The lowest value observed for the specific conductance $L$ of purified bromine pentafluoride at 25° was $9.1 \times 10^{-8}$ ohm$^{-1}$ cm.$^{-1}$; however, the material used in the measurements recorded here had a somewhat higher conductance ($9.9 \times 10^{-8}$ ohm$^{-1}$ cm.$^{-1}$ at 25°).

TABLE IV

THE SPECIFIC AND MOLAR CONDUCTANCES OF BROMINE PENTAFLUORIDE–HYDROGEN FLUORIDE SOLUTIONS AT VARIOUS TEMPERATURES

| $C$(moles HF/l.) (at 25°) | $L$, ohm$^{-1}$ cm.$^{-1}$ × $10^7$ | | | $\Lambda \times 10^3$ (at 25°) |
|---|---|---|---|---|
| | −60° | 0° | 25° | |
| 0 | 0.78 | 0.884 | 0.991 | ... |
| 0.43 | 5.8 | 5.41 | 5.99 | 1.18 |
| 0.60 | .... | 9.54 | 10.2 | 1.54 |
| 0.83 | .... | 18.8 | 18.0 | 2.05 |
| 1.47 | 175 | 44 | 45 | 3.0 |
| 3.20 | 500 | 206 | 190 | 6.0 |
| 5.94 | 710 | 635 | 739 | 12.5 |
| 8.84 | 780 | 1080 | 1250 | 15.4 |

The only value reported previously for the specific conductance of bromine pentafluoride was somewhat higher.[7] We observe a small positive temperature coefficient (about 0.5% per degree) for the pure liquid. The temperature coefficients of conductance of the solutions are positive for dilute and concentrated solutions but become negative over an intermediate concentration range. The molar conductances (Λ) are very low indicating that hydrogen fluoride is not a strong electrolyte in bromine pentafluoride solutions at these (rather high) concentrations.

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(4) O. Ruff, *Z. angew. Chem.*, **41**, 1289 (1929).

(5) J. Hu, D. White and H. L. Johnston, THIS JOURNAL, **75**, 1232 (1953).

(6) H. B. Thompson and M. T. Rogers, *Rev. Sci. Instr.*, **27**, in press (1956).

(7) H. H. Hyman, H. Andrews and J. J. Katz, Abstracts of the 118th National Meeting of the American Chemical Society, Chicago, Ill., September, 1950.