[CONTRIBUTION FROM THE RESEARCH LABORATORY OF INORGANIC CHEMISTRY, MASSACHUSETTS INSTITUTE OF TECHNOLOGY, NO. 27]

# Thermodynamic Properties of Fused Salt Solutions. VII. Zinc Bromide in Lead Bromide

BY EDWARD J. SALSTROM

The investigation herein described represents a continuation of a series of studies on the thermodynamics and free energies of fused salt solutions begun by Hildebrand.[1] Unlike this initial work, where the chlorine electrode was formed by a polarization method, the bromine electrode utilized by the author has been produced by bubbling electrolytic bromine vapor over a graphite rod dipping into the cell melt as previously described.[2]

The lead bromide used in the cells, and as a source of bromine, was prepared by precipitation with a slight excess of "C. P." hydrobromic acid from a lead acetate solution. The precipitate was repeatedly washed by decantation with a very dilute solution of the acid, then dried, first by suction and finally at 150° in a furnace for twenty-four hours. The zinc bromide, obtained from commercial sources of highest purity, was fused to partially free it from water. Final traces of moisture were removed from the cell by bubbling dry hydrogen bromide gas through the melt for an hour and a half. The lead used as the negative electrode was prepared by the electrolysis of lead bromide which had been similarly freed from moisture and hydrolysis products. The composition of the cell contents was determined after the run by converting the bromides to sulfates, in which form the lead was weighed.[3]

The results of the e. m. f. measurements are given in Table I and are shown graphically in Fig. 1. The values for pure lead bromide are the results of four separate cells, three of which are indicated in the figure by points of different type and were run at Berkeley.[2] The mean deviation of the points from a straight line in Fig. 1 is less than 0.2 mv. while the maximum deviation is 1.0 mv.

The fluctuations of these Pb(liq.), $PbBr_2$(liq.), $ZnBr_2$(liq.), $Br_2$(g.), cells were found to be more marked than those for any of the previous systems studied by the author. More than usual fluctuations were also found in the cell, Zn(liq.), $ZnBr_2$(liq.), $Br_2$(g.), while cells of Cd(liq.), $CdBr_2$(liq.), $Br_2$(g.) could not be measured due to metal fogs forming in sufficient amount to short the cell soon after the hydrogen bromide gas had been shut off and bromine bubbling begun. Thus it is likely that slight formation of metal fog by zinc may be responsible for this unsteadiness.

Reproducible cells for 0.9 mole fraction of zinc bromide in lead bromide

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[1] Hildebrand and Ruhle, THIS JOURNAL, **49**, 722 (1927).

[2] Salstrom and Hildebrand, *ibid.*, **52**, 4641 (1930).

[3] *Cf.* Treadwell-Hall, "Analytical Chemistry," Vol. II, John Wiley and Sons, Inc., New York, 1919, p. 174.

TABLE I

E. M. F. VALUES OF THE CELL, Pb(liq.), $PbBr_2$(liq.), $ZnBr_2$(liq.), $Br_2$(g.)

| Temp., °C. | E. m. f. obs., volts | Temp., °C. | E. m. f. obs., volts | Temp., °C. | E. m. f. obs., volts |
|---|---|---|---|---|---|
| Cell A($N_1$ = 1.000) | | Cell D($N_1$ = 0.704) | | Cell G($N_1$ = 0.392) | |
| 423.2 | 1.0788 | 395.1 | 1.1041 | 405.7 | 1.1123 |
| 438.3 | 1.0692 | 396.3 | 1.1040 | 406.2 | 1.1122 |
| 443.5 | 1.0665 | 426.5 | 1.0862 | 428.7 | 1.1000 |
| 450.5 | 1.0624 | 444.3 | 1.0759 | 456.8 | 1.0850 |
| 451.0 | 1.0615 | 469.2 | 1.0608 | 470.7 | 1.0771 |
| 453.0 | 1.0601 | 471.0 | 1.0607 | 496.1 | 1.0632 |
| 465.6 | 1.0525 | 497.4 | 1.0454 | 518.1 | 1.0516 |
| 468.0 | 1.0516 | 508.2 | 1.0389 | | |
| | | | | Cell H($N_1$ = 0.288) | |
| 478.1 | 1.0461 | | | | |
| 484.3 | 1.0416 | Cell E($N_1$ = 0.604) | | 403.5 | 1.1193 |
| 496.2 | 1.0330 | 402.6 | 1.1046 | 419.8 | 1.1107 |
| 501.1 | 1.0306 | 416.8 | 1.0959 | 420.0 | 1.1110 |
| 510.4 | 1.0265 | 417.1 | 1.0957 | 452.3 | 1.0946 |
| 517.1 | 1.0215 | 442.4 | 1.0817 | 475.3 | 1.0826 |
| 520.0 | 1.0200 | 442.6 | 1.0815 | 511.8 | 1.0639 |
| 527.6 | 1.0156 | 466.7 | 1.0674 | | |
| 530.6 | 1.0136 | 479.7 | 1.0603 | Cell I($N_1$ = 0.210) | |
| 532.5 | 1.0017 | 491.0 | 1.0532 | 392.1 | 1.1306 |
| | | 491.2 | 1.0530 | 408.7 | 1.1223 |
| Cell B($N_1$ = 0.902) | | 511.2 | 1.0424 | 418.7 | 1.1175 |
| 400.6 | 1.0945 | | | 437.1 | 1.1091 |
| 425.0 | 1.0798 | Cell F($N_1$ = 0.486) | | 438.6 | 1.1087 |
| 425.9 | 1.0792 | 401.9 | 1.1104 | 442.6 | 1.1072 |
| 452.6 | 1.0635 | 402.2 | 1.1101 | 445.9 | 1.1055 |
| 453.3 | 1.0632 | 424.0 | 1.0977 | 474.1 | 1.0917 |
| 475.4 | 1.0500 | 424.9 | 1.0974 | 501.9 | 1.0789 |
| 494.3 | 1.0384 | 450.4 | 1.0821 | | |
| 506.8 | 1.0311 | 450.7 | 1.0819 | Cell J($N_1$ = 0.200) | |
| | | 473.3 | 1.0697 | 429.1 | 1.1143 |
| Cell C($N_1$ = 0.794) | | 496.1 | 1.0571 | 429.3 | 1.1142 |
| 403.2 | 1.0971 | 513.8 | 1.0471 | 454.6 | 1.1022 |
| 433.7 | 1.0786 | 514.1 | 1.0470 | 475.6 | 1.0926 |
| 434.6 | 1.0783 | | | 505.3 | 1.0782 |
| 454.9 | 1.0662 | | | 516.6 | 1.0737 |
| 468.9 | 1.0580 | | | | |
| 478.7 | 1.0520 | | | | |

could not be obtained. Analysis of the lead electrode removed from these cells showed traces of zinc. In cells of 0.8 mole fraction of zinc bromide no such traces of zinc were found in the lead and reproducible results were obtained. The author has calculated the free energy of the reaction, Pb + $ZnBr_2$ = $PbBr_2$ + Zn, to be +10,990 cal. at 500° using an unpublished value of 1.2702 volts for the e. m. f. of the cell, Zn(liq.), $ZnBr_2$(liq.), $Br_2$(g.), obtained in this Laboratory. The analysis showed, and this value seems to indicate, that displacement of zinc from zinc bromide by lead does not take place at or below 0.8 mole fraction of zinc bromide.

To determine if the molal volume of the solution differs from additivity, density measurements were made upon pure zinc bromide and upon a half mole fraction solution of zinc bromide and lead bromide. The method was similar to that previously described.[4] The results are shown in Table II and the values for zinc bromide and the solution may be represented by the equations, $d^t = 3.776 - 0.000913t$ and $d^t = 5.086 - 0.001248t$, respectively.

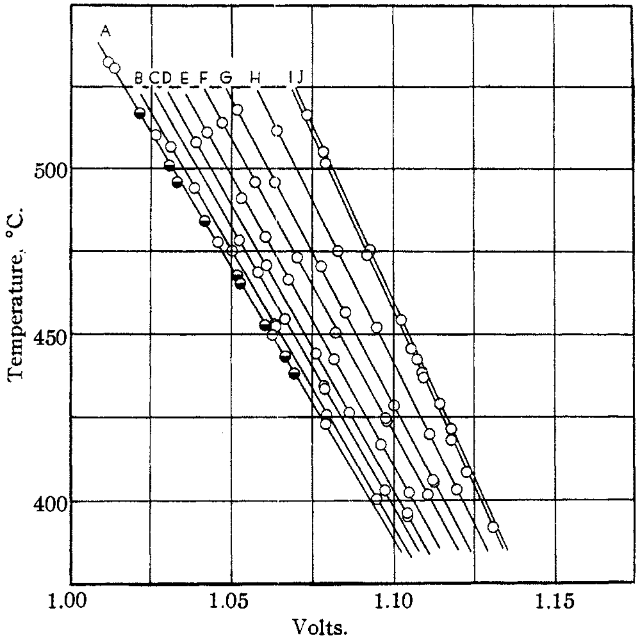

Fig. 1.—Temperature, e. m. f. and composition relations of the cells Pb, $PbBr_2$, $ZnBr_2$, $Br_2$. Mole fractions of lead bromide are shown in Table I.

TABLE II

DENSITIES OF LIQUID ZINC BROMIDE AND OF ITS SOLUTION WITH LEAD BROMIDE

| 100% $ZnBr_2$ | | 100% $ZnBr_2$ | | 50% $ZnBr_2$, 50% $PbBr_2$ | | 50% $ZnBr_2$, 50% $PbBr_2$ | |
|---|---|---|---|---|---|---|---|
| Temp., °C. | Density | Temp., °C. | Density | Temp., °C. | Density | Temp., °C. | Density |
| 407.0 | 3.405 | 462.3 | 3.354 | 401.9 | 4.585 | 469.2 | 4.501 |
| 409.9 | 3.402 | 483.6 | 3.334 | 408.5 | 4.576 | 488.6 | 4.476 |
| 423.9 | 3.389 | 499.7 | 3.320 | 423.6 | 4.558 | 505.7 | 4.455 |
| 435.9 | 3.378 | 512.0 | 3.309 | 440.0 | 4.538 | 521.8 | 4.435 |
| 448.9 | 3.364 | | | 453.0 | 4.521 | | |

Using the density values for lead bromide previously obtained by the author,[2] the molal volumes of lead bromide and zinc bromide have been calculated to be 67.05 and 67.85 cc., respectively, at 500° while at 400°

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(4) Salstrom, THIS JOURNAL, 54, 2653 (1932).

their respective volumes are 65.60 cc. and 66.03 cc. The volumes of a mole of solution were found to be 66.36 cc. at 500° and 64.56 cc. at 400°. Thus the observed solution volumes differ from additivity by being 1.09 cc. less at 500° and 1.26 cc. less at 400°.

Since the chief interest lies in the relation of free energy to composition at constant temperature, Fig. 1 was made upon a large scale, and the values for the e. m. f.'s at each composition determined at the temperatures, 400, 450 and 500°. From these have been calculated the free energy of formation of lead bromide from molten lead and bromine vapor, $\Delta F_1$, the free energy of dilution or the partial molal free energy, $\bar{F}_1$, the temperature coefficient, $dE/dT$, the entropy change, $\Delta S_1$, the partial molal entropy, $\bar{S}_1$, the heat of formation, $\Delta H_1$, the partial molal heat, $\bar{H}_1$, the activity of lead bromide in the solutions, $a_1$, taking pure lead bromide as the standard state, and the activity coefficient of lead bromide, $\gamma$.

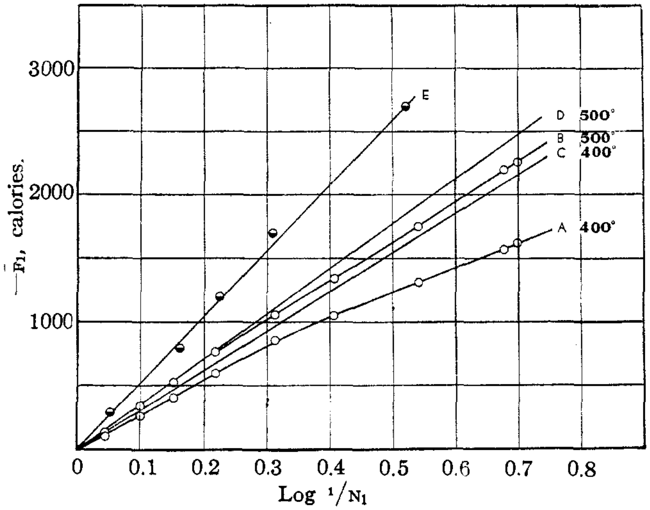

Fig. 2.—Variation of free energy of dilution of lead bromide with composition. Curve E is for $PbCl_2$–$ZnCl_2$ at 500°.

These values are given in Table III, and Fig. 2 curves A and B show the free energy of dilution of lead bromide, $-\bar{F}_1$, plotted against log $1/N_1$ at the temperatures of 400 and 500°, respectively, where $N_1$ is the mole fraction of lead bromide.

These curves may be compared with those predicted by Raoult's law which assumes that $a_1 = N_1$. In this case, the assumption of no ionization, or of complete ionization of both salts with no change in the interionic forces, makes no difference since in the latter case dilution with zinc bromide would make no change in the proportion of the bromide ion, the only effect being a substitution of lead ion by zinc ion reducing the activity of the former and hence of lead bromide in proportion to $N_1$. Such calcu-

TABLE III

THERMODYNAMIC PROPERTIES OF LEAD BROMIDE DILUTED WITH ZINC BROMIDE

| $N_1$ | 1.000 | 0.902 | 0.794 | 0.704 | 0.604 | 0.486 | 0.392 | 0.288 | 0.210 | 0.200 |
|---|---|---|---|---|---|---|---|---|---|---|
| dE/dT, mv./deg | −0.607 | −0.599 | −0.590 | −0.580 | −0.571 | −0.564 | −0.542 | −0.511 | −0.470 | −0.469 |
| $\Delta S_1$, cal./deg. | −28.0 | −27.6 | −27.2 | −26.8 | −26.4 | −26.0 | −25.0 | −23.6 | −21.7 | −21.6 |
| $\bar{S}_1$, cal./deg. | 0 | 0.4 | 0.8 | 1.2 | 1.6 | 2.0 | 3.0 | 4.4 | 6.3 | 6.4 |
| 400° E | 1.0928 | 1.0951 | 1.0986 | 1.1016 | 1.1058 | 1.1114 | 1.1155 | 1.1211 | 1.1268 | 1.1279 |
| 400° $\Delta F_1$ | −50430 | −50540 | −50700 | −50840 | −51030 | −51290 | −51480 | −51740 | −52000 | −52050 |
| 400° $\bar{F}_1$ | 0 | −110 | −270 | −410 | −600 | −860 | −1050 | −1310 | −1570 | −1620 |
| 400° $\Delta H_1$ | −69270 | −69140 | −69020 | −68850 | −68800 | −68790 | −68310 | −67610 | −66600 | −66590 |
| 400° $\bar{H}_1$ | 0 | 130 | 250 | 420 | 470 | 480 | 960 | 1660 | 2670 | 2680 |
| 400° $a_1$ | 1.000 | 0.921 | 0.817 | 0.736 | 0.639 | 0.526 | 0.456 | 0.376 | 0.309 | 0.298 |
| 400° $\gamma$ | 1.00 | 1.02 | 1.03 | 1.05 | 1.06 | 1.08 | 1.16 | 1.30 | 1.47 | 1.49 |
| 450° E | 1.0624 | 1.0652 | 1.0691 | 1.0726 | 1.0772 | 1.0832 | 1.0884 | 1.0956 | 1.1033 | 1.1045 |
| 450° $\Delta F_1$ | −49030 | −49160 | −49340 | −49500 | −49710 | −49990 | −50230 | −50560 | −50910 | −50970 |
| 450° $\bar{F}_1$ | 0 | −130 | −310 | −470 | −680 | −960 | −1200 | −1530 | −1880 | −1940 |
| 450° $a_1$ | 1.000 | 0.914 | 0.806 | 0.721 | 0.623 | 0.513 | 0.434 | 0.345 | 0.270 | 0.259 |
| 450° $\gamma$ | 1.00 | 1.01 | 1.02 | 1.02 | 1.03 | 1.06 | 1.11 | 1.20 | 1.29 | 1.30 |
| 500° E | 1.0321 | 1.0352 | 1.0396 | 1.0436 | 1.0487 | 1.0550 | 1.0613 | 1.0700 | 1.0798 | 1.0810 |
| 500° $\Delta F_1$ | −47630 | −47770 | −47980 | −48160 | −48400 | −48690 | −48970 | −49380 | −49830 | −49890 |
| 500° $\bar{F}_1$ | 0 | −140 | −350 | −530 | −770 | −1060 | −1340 | −1750 | −2200 | −2260 |
| 500° $a_1$ | 1.000 | 0.913 | 0.796 | 0.708 | 0.606 | 0.502 | 0.418 | 0.320 | 0.239 | 0.230 |
| 500° $\gamma$ | 1.00 | 1.01 | 1.00 | 1.01 | 1.00 | 1.03 | 1.07 | 1.11 | 1.14 | 1.15 |

lations give at 400 and 500° curves C and D, respectively. Thus it is seen that at the higher temperature, curve B, agreement is very good up to 0.6 mole fraction of lead bromide. Beyond this point a small but increasingly positive deviation takes place. At the temperature of 400°, curve A, there is considerably greater positive deviation from Raoult's law which persists throughout the entire range of composition. This can be seen with equal readiness by noting the increase in the activity coefficients above unity in Table III on proceeding to lower temperatures.

This positive deviation of the results from Raoult's law is contrary to that found for the free energy of dilution of lead chloride by zinc chloride investigated by Wachter and Hildebrand,[5] where a marked negative deviation was found. Their observed results at 500° are shown in Fig. 2 by curve E. If an explanation of the deviation of $a_1$ from $N_1$ is sought in the difference of dissociation of the zinc and lead salts, it is found that it leads in the correct direction for lead chloride, but in the wrong direction for lead bromide. Positive deviations from Raoult's law are frequently accompanied by an expansion on mixing, and *vice versa*, since a respective weakening and strengthening of the internal forces might be expected. Such an explanation would seem plausible in accounting for the negative deviation found for lead chloride where contraction on mixing zinc and lead chlorides amounting to a little over one per cent. was found. However, such an explanation is not applicable to this system where a positive deviation is shown by lead bromide at 400° in spite of almost a two per cent. contraction on mixing. The very much better agreement of this salt with Raoult's law at 500° indicates that the partial molal entropy differs from that of an ideal solution, indicating that the randomness of the arrangement in the solutions differs at the two temperatures. A more searching treatment of this system will be attempted later when data for other systems now being investigated will be at hand.

By graphical integration of the equation given by the Duhem relationship

$$\log a_2/N_2 = -\int_0^{N_2} N_1/N_2 \, d \log a_1/N_1$$

the activities, $a_2$, and activity coefficients, $\gamma$, of zinc bromide in the solutions have been obtained. In performing this integration the difficulty is encountered that $N_1/N_2$ rapidly approaches infinity as $\log a_1/N_1$ approaches zero. This will not, however, produce any change in the ratio between two values of $a_2/N_2$ regardless of what method of extrapolation may be chosen. It thus becomes more convenient to evaluate the activity of the solute by choosing the standard state of zinc bromide as the pure salt, rather than the customary state of infinite dilution. With the aid of the equation $\bar{F}_2 = RT \ln a_2$ the partial molal free energy of zinc bromide also was obtained. These values when added to the free energy of formation of

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(5) Wachter and Hildebrand, THIS JOURNAL, **52**, 4655 (1930).

zinc bromide from molten zinc and bromine vapor, $\Delta F_2°$, given above, yield $\Delta F_2$. These values are given in Table IV, while Fig. 3 shows the activities of lead bromide and zinc bromide at 400° plotted against their mole fractions.

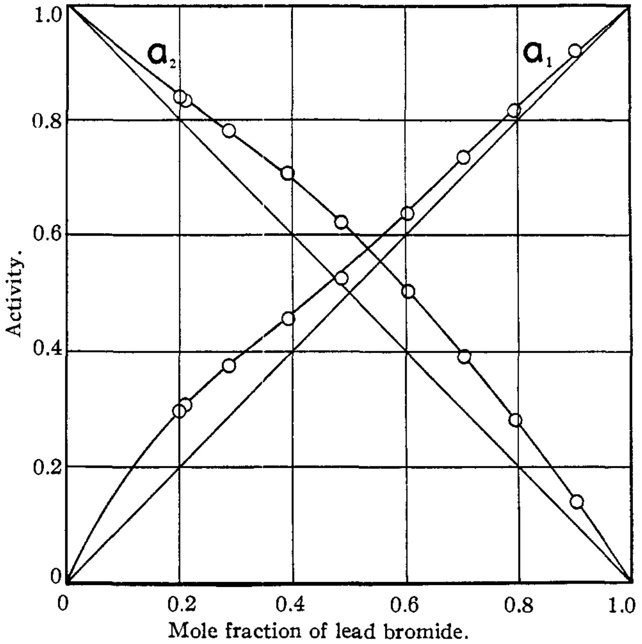

Fig. 3.—Relation of the activities of lead bromide and zinc bromide to their compositions at 400°.

TABLE IV

THERMODYNAMIC PROPERTIES OF ZINC BROMIDE IN THE SOLUTIONS

| $N_2$ | $a_2$ | $\gamma$ | $\bar{F}_2$ | $\Delta F_2$ | $N_2$ | $a_2$ | $\gamma$ | $\bar{F}_2$ | $\Delta F_2$ |
|---|---|---|---|---|---|---|---|---|---|
| | | At 400 °C. | | | | | At 500 °C. | | |
| 1.000 | 1.000 | 1.00 | 0 | −61760 | 1.000 | 1.000 | 1.00 | 0 | −58620 |
| 0.800 | 0.852 | 1.06 | − 210 | −61970 | 0.800 | 0.812 | 1.01 | − 320 | −58940 |
| .790 | .844 | 1.07 | − 230 | −61990 | .790 | .803 | 1.02 | − 340 | −58960 |
| .712 | .792 | 1.11 | − 310 | −62070 | .712 | .730 | 1.03 | − 480 | −59100 |
| .608 | .717 | 1.18 | − 440 | −62200 | .608 | .637 | 1.05 | − 690 | −59310 |
| .514 | .630 | 1.23 | − 620 | −62380 | .514 | .564 | 1.10 | − 880 | −59500 |
| .396 | .509 | 1.29 | − 900 | −62660 | .396 | .443 | 1.12 | −1250 | −59870 |
| .296 | .397 | 1.34 | −1240 | −63000 | .296 | .331 | 1.12 | −1700 | −60320 |
| .206 | .283 | 1.38 | −1690 | −63450 | .206 | .230 | 1.12 | −2260 | −60880 |
| .098 | .140 | 1.43 | −2630 | −64390 | .098 | .110 | 1.12 | −3390 | −62010 |

## Summary

E. m. f. measurements of the cells, Pb(liq.), $PbBr_2$(liq.), $ZnBr_2$(liq.), $Br_2$(g.), have been made at mole fractions of lead bromide varying between 1.00 and 0.20 at temperatures from 390 to 520°.

Calculations have been made of the activities, activity coefficients, free energies of formation, and partial molal free energies of lead and zinc bromides.

Density measurements have been made upon zinc bromide and a fifty mole per cent. solution of zinc bromide and lead bromide which may be expressed by the equations: $d^t = 3.776 - 0.000913t$ for the salt, and $d^t = 5.086 - 0.001248t$ for the solution.

The positive deviation of the results from Raoult's law has been briefly discussed.

CAMBRIDGE, MASSACHUSETTS

RECEIVED OCTOBER 14, 1932
PUBLISHED MARCH 7, 1933

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[CONTRIBUTION FROM THE SCHOOL OF CHEMISTRY OF THE UNIVERSITY OF MINNESOTA]

# The Photochemical Polymerization of Methylacetylene and Allene

BY S. C. LIND AND ROBERT LIVINGSTON

The photochemical polymerization of acetylene has been studied quantitatively by Lind and Livingston,[1] who compared the quantum yield with the ion pair yield[2] of the radiochemical reaction. The radiochemical work has been extended by Heisig[3] to include the polymerization of a number of the simpler unsaturated hydrocarbons. The following deals with the photochemical polymerization of two of the compounds studied by Heisig, methylacetylene and its double-bonded isomer, allene.

## Rate of Polymerization as a Function of Pressure

**Apparatus.**—In these experiments a hot mercury arc was used, and particular care was taken to prevent the contamination of the reactants by mercury vapor. The details of the reaction system and the method of operation are described in an earlier paper.[4]

The gases used were highly purified samples,[3] kindly furnished by Dr. G. B. Heisig. They were further purified by low temperature distillation before use.

**Reaction Products.**—All of the gases studied (except ethylene) were polymerized by the action of ultraviolet light to solid (or viscous liquid) products of low vapor pressure.

The allene polymer precipitated on the walls as a smooth white film, which was either a solid or a very viscous liquid. In one experiment allene at 685 mm. pressure was radiated until the pressure had been reduced by 15.5 mm. The remaining allene was then frozen in a side tube with the aid of liquid air, and the residual pressure was found to be less than 0.2 mm. (the limit of accuracy of the manometer). This may be taken as evidence that the reaction consists of simple polymerization and that not more than 1% of the reaction involves the formation of hydrogen or methane. The polymer apparently has a higher vapor pressure than cuprene, since it can be sublimed in high vacuum by heating the reaction vessel with a direct flame (probably between 200 and

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[1] Lind and Livingston, THIS JOURNAL, **54**, 94 (1932).

[2] Lind and Bardwell, *ibid.*, **48**, 1556 (1926); Mund and Koch, *J. Phys. Chem.*, **30**, 292 (1926).

[3] Heisig, THIS JOURNAL, **53**, 3245 (1931).

[4] Ref. 1, pp. 95–96 and Fig. 1.