

# THE SECONDARY ISOTOPE RATE EFFECT IN THE IODIDE DEBROMINATION OF *sym*-TETRABROMOETHANE AND *sym*-TETRABROMOETHANE-*d*<sub>2</sub><sup>1,2</sup>

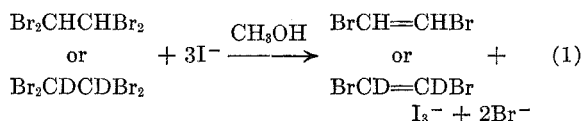
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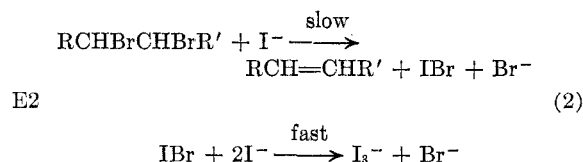
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For the iodide-promoted debromination of *sym*-tetrabromoethane and *sym*-tetrabromoethane-*d*<sub>2</sub>, the secondary isotope rate factor  $k_H/k_D \approx 1.28$  at 81–111°. Over this temperature range, a decrease in  $k_H/k_D$  of ca. 6% was observed. The activation energies and entropies for the hydrogen and deuterium tetrabromoethanes are, respectively,  $25.5 \pm 0.5$  and  $26.2 \pm 0.5$  kcal. mole<sup>-1</sup> and  $-12.7$  and  $-11.2$  cal. deg.<sup>-1</sup> mole<sup>-1</sup>. A negative kinetic salt effect was observed. Calculations suggest that the observed value of  $k_H/k_D$  is characteristic of an elimination (E2) rather than a displacement (S<sub>N</sub>2) path for debromination. The rate data also appear to be more consistent with those from comparable E2 rather than S<sub>N</sub>2 systems.

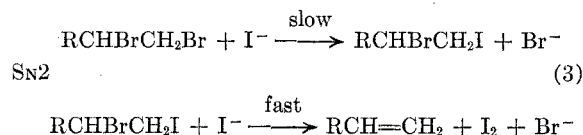
This paper is concerned with the secondary isotope effect and the reaction mechanism in the system



Because complete vibrational assignments for the reactants and products were available, we considered that calculations of  $k_H/k_D$  would be instructive: these are reported in another paper.<sup>3</sup> System 1 is an example of a large group of iodide ion debrominations of alkane dibromides.<sup>4</sup> This reaction has had synthetic utility.<sup>4,5</sup> It is perhaps more important theoretically as one of those early examples of stereospecific *trans* eliminations in which *D*-*L* or *threo*-dibromides generally yield *cis* products and *meso* or *erythro*-dibromides yield *trans* products. Originally, an E2 mechanism was accepted in which the bromine atoms were simultaneously removed in the *trans* sense



In 1955, Hine and Brader showed the S<sub>N</sub>2 mechanism applies to some terminal-type alkane dibromides.<sup>6</sup> These alternatives posed a mechanistic question which a kinetic isotope rate study could possibly resolve.



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## Experimental

**Materials.**—Reagent grade absolute methanol was further purified by the method of Lund and Bjerrum.<sup>7</sup> Sodium iodide was dried at 150° and stored in a desiccator; its purity was checked against standard silver nitrate. *sym*-Tetrabromoethane (500 g.) was washed, dried, and fractionated; a middle fraction (ca. 140 ml.) had b.p. 118° at 15 mm. and  $n_D^{20}$  1.6379 (lit.<sup>8</sup> b.p. 120° at 15 mm. and lit.<sup>9</sup>  $n_D^{20}$  1.6353). The preparation of *sym*-tetrabromoethane-*d*<sub>2</sub> has been described<sup>10</sup>; a middle fraction (ca. 50 ml.) had b.p. 52.8–53° (0.4 mm.) and  $n_D^{20}$  1.6356. An infrared spectrum of the deuteriated sample as well as that of the derived dibromoethenes showed no protonated material (<1%).<sup>11</sup>

**Rate Studies.**—Reaction 1 in the solvent methanol was studied in the range 75–110° by established procedures: the ampoule technique was used; 10<sup>-2</sup> mmole of iodine could be determined with standard thiosulfate to the “dead stop” end-point with an accuracy of 1%.<sup>12</sup> Apart from a few early ampoules in any given run for which the uncertainty in the time may be  $\pm 2$  min., this source of error was generally negligible. Calibrated thermometers were used in the thermostats: the temperature variation was ca.  $\pm 0.05^\circ$ .

Methanol containing either sodium iodide or *sym*-tetrabromoethane produced no titratable iodine or bromide under the conditions of the experiments. However, within ca. 20 hr. at 110°, a methanol solution originally 1 mmole in iodine had lost 0.037 mmole of iodine and thereafter remained constant. As in previous studies,<sup>12,13</sup> a blank based on the temperature and reaction time was added to the iodine titer. The uncertainty in the rate constants due to this problem is smaller than the average deviation listed for the rate constants (Tables II and III).

A standard rate expression was used to treat the data<sup>12</sup>

$$kt = \frac{2.303}{(b-3a)} \log \frac{a}{b} \left( \frac{b-3x}{a-x} \right)$$

where  $a = [\text{C}_2\text{H}_5\text{Br}]_0$ ,  $b = [\text{NaI}]_0$ , and  $x = [\text{I}_3^-]$ , all in mole liter<sup>-1</sup>. The best value of  $k$  was determined by averaging the results of any one run and from  $kt$  vs.  $t$  plots. A typical run is given in Table I. The average rate constant was corrected to  $k_{\text{cor}}$  for the expansion of solvent.<sup>14</sup>

**Rate Study of 1,1-Dibromoethane and Sodium Iodide.**—One preliminary run of the following reaction was made at 101.1°



(7) H. Lund and J. Bjerrum, *Ber.*, **64**, 1210 (1931).

(8) T. E. Jordan, “Vapor Pressure of Organic Compounds,” Interscience Publishers, Inc., New York, N. Y., 1959, p. 35.

(9) A. I. Vogel, *J. Chem. Soc.*, 1850 (1948).

(10) S. I. Miller and W. G. Lee, *J. Am. Chem. Soc.*, **81**, 6313 (1959).

(11) J. M. Dowling, P. G. Puranik, A. G. Meister, and S. I. Miller, *J. Chem. Phys.*, **26**, 233 (1957).

(12) S. I. Miller and R. M. Noyes, *J. Am. Chem. Soc.*, **74**, 3403 (1952).

(13) R. T. Dillon, W. G. Young, and H. Lucas, *ibid.*, **52**, 1953 (1930).

(14) “Landolt-Bornstein Tabellen,” Julius Springer, Berlin, 1923, p. 278.

(1) (a) Presented in part at the 130th National Meeting of the American Chemical Society, Atlantic City, N. J., Sept., 1958. (b) Abstracted from a portion of the Ph.D. thesis of Warren G. Lee, Illinois Institute of Technology, 1961.

(2) Supported in part by the Research Corporation.

(3) S. I. Miller, *J. Phys. Chem.*, **66**, in press (1962).

(4) See W. G. Young, S. J. Cristol, and T. Skei, *J. Am. Chem. Soc.*, **65**, 2099 (1943), and S. Winstein, D. Pressman, and W. G. Young, *ibid.*, **61**, 1645 (1939), for earlier references.

(5) D. H. R. Barton and E. Miller, *ibid.*, **72**, 1066 (1950).

(6) J. Hine and W. H. Brader, *ibid.*, **77**, 361 (1955). See also W. M. Schubert, H. Steady, and B. S. Rabinovitch, *ibid.*, **77**, 5755 (1955).

TABLE I  
REACTION OF *sym*-TETRABROMOETHANE AND SODIUM IODIDE  
AT  $(76.37 \pm 0.17)^\circ$  IN METHANOL

$$a = 0.4160, b = 0.1028$$

Time, min.	(I <sub>2</sub> <sup>-</sup> )	$k \times 10^4$
399	0.00278	1.70
964	.00750	1.94
1275	.00890	1.92
2937	.01668	1.94
4230	.02165	1.95
5558	.02471	1.91

$$k_{av} = 1.89 \pm 0.07$$

$$k_{cor} = 2.03 \pm 0.07 \text{ l. mole}^{-1} \text{ min.}^{-1}$$

The ampoule technique was used and an analysis of iodide in the presence of bromide was carried out.<sup>15</sup> On the basis that the reaction is first order in each reactant, the rate constant was found to be  $(15.6 \pm 0.7) \text{ l. mole}^{-1} \text{ min.}^{-1}$  at  $101.1^\circ$ .

### Results and Discussion

Most of the previous studies of the iodide-catalyzed debromination reaction were not concerned with salt effects. However, Van Duin found that the rate constants increased slightly with ionic strength in the system potassium iodide with sodium 2,3-dibromopropionate.<sup>16</sup> Dillon reported a slight decrease in rate when neutral salt was added to the system potassium iodide and 1,2-dibromoethane: for example, at  $40^\circ$  in 60% aqueous ethanol at ionic strengths = 0.22 (KI), 0.33 (0.22 KI + 0.11 KCl), and 0.44 (0.22 KI + 0.22 KBr), the second-order rate constants were 80, 77.9, and  $72.5 \times 10^3 \text{ liter mole}^{-1} \text{ min.}^{-1}$ , respectively. Dillon considered all of these to be Brönsted salt effects.<sup>17</sup>

Our data for reaction 1 are given in Tables II and III. The rate constants clearly decrease with increasing initial concentrations of sodium iodide. The present state of the theory on salt effects in

TABLE II  
KINETICS OF THE REACTION BETWEEN *sym*-TETRABROMOETHANE AND SODIUM IODIDE IN METHANOL

C <sub>2</sub> H <sub>2</sub> Br <sub>4</sub> , mole/l.	NaI, mole/l.	Temp., °C.	$k \times 10^4$ , l./mole min.
0.06249	0.06419	$76.25 \pm 0.17$	$2.24 \pm 0.04$
		$92.94 \pm .05$	$11.6 \pm .4$
		$108.98 \pm .09$	$57.2 \pm 1.2$
.4160	.1028	$76.37 \pm .17$	$2.03 \pm 0.07$
		$92.64 \pm .06$	$12.4 \pm .6$
		$108.81 \pm .07$	$59.0 \pm 1.2$
.1236	.2329	$76.21 \pm .10$	$1.83 \pm 0.03$
		$92.02 \pm .06$	$10.9 \pm .4$
		$108.96 \pm .04$	$50.0 \pm 1.0$
.3172	.3196	$76.21 \pm .10$	$1.87 \pm 0.05$
		$78.72 \pm .04$	$2.47 \pm .03$
		$92.11 \pm .06$	$10.1 \pm .4$
.05196	.6743	$108.92 \pm .06$	$51.6 \pm .6$
		$76.77 \pm .10$	$1.57 \pm .08$
		$92.72 \pm .07$	$9.00 \pm .37$
		$108.88 \pm .12$	$41.7 \pm 1.1$

(15) S. I. Miller and P. K. Yonan, *J. Am. Chem. Soc.*, **79**, 5931 (1957).

(16) C. F. Van Duin, *Rec. trav. chim.*, **43**, 341 (1924); **45**, 345 (1926); **47**, 715 (1928).

(17) R. T. Dillon, *J. Am. Chem. Soc.*, **54**, 952 (1932).

ion-molecule reactions is still inadequate. Even for solutions much more dilute than ours, opposing predictions have been made for the variations in  $k$  with ionic strength.<sup>18</sup> Therefore, we proceeded

TABLE III  
REACTION BETWEEN *sym*-TETRABROMOETHANE-*d*<sub>2</sub> AND SODIUM IODIDE IN METHANOL

C <sub>2</sub> D <sub>2</sub> Br <sub>4</sub> , mole/l.	NaI, mole/l.	Temp., °C.	$k \times 10^4$ , l./mole min.
0.1336	0.1023	$78.92 \pm 0.05$	$2.16 \pm 0.03$
		$90.10 \pm .05$	$7.11 \pm 0.14$
		$108.78 \pm .05$	$45.9 \pm 1.3$
.2053	.1263	$79.09 \pm .10$	$2.23 \pm 0.04$
		$90.05 \pm .05$	$6.83 \pm 0.20$
		$108.93 \pm .05$	$49.7 \pm 1.6$
.07405	.1707	$76.37 \pm .07$	$1.56 \pm 0.03$
		$78.72 \pm .04$	$2.06 \pm .04$
		$90.24 \pm .02$	$6.69 \pm .21$
		$92.18 \pm .02$	$8.37 \pm .25$
		$108.96 \pm .04$	$42.9 \pm .7$
.03538	.2317	$78.72 \pm .04$	$2.00 \pm .05$
		$90.24 \pm .02$	$6.02 \pm .22$
		$108.96 \pm .04$	$39.4 \pm 1.3$
.1054	.2344	$80.39 \pm .02$	$2.29 \pm 0.06$
		$90.11 \pm .06$	$6.12 \pm 0.17$
		$109.86 \pm .10$	$45.4 \pm 1.1$
.07210	.7595	$80.52 \pm .09$	$2.00 \pm 0.05$
		$90.10 \pm .08$	$5.71 \pm .15$
		$109.86 \pm .10$	$40.1 \pm .6$

empirically and found  $\log k$  to be linear in  $b$ , the concentration of sodium iodide, *i.e.*

$$\log k = \log k^0 + mb \quad (4)$$

To treat the data, it was necessary to make Arrhenius plots at constant ionic strength. The rate data were normalized at 80.82, 90.48, and  $111.46^\circ$ .

These isothermal data were fitted to eq. 4 by least squares. The slopes obtained for the three temperatures were:  $m_H = -0.257$ ,  $m_D = -0.127$  at  $80.82^\circ$ ;  $m_H = -0.243$ ,  $m_D = -0.142$  at  $90.48^\circ$ ;  $m_H = -0.219$ ,  $m_D = -0.142$  at  $111.46^\circ$ . The rate constants at zero ionic strength, derived activation parameters, and isotope rate factors are given in Table IV under Method 1. A plot of  $\log k_H^0/k_D^0$  vs.  $1/T$  was linear.

The lack of parallelism between the hydrogen and deuterium salt plots is difficult to reconcile with any existing theory. Intuitively, it seems improbable that the presence of deuterium in a molecule would greatly alter its sensitivity to salt effects. We have, therefore, applied a second least squares treatment of the ionic strength effect. Here it was assumed that the slopes of  $\log k$  vs.  $b$  for the hydrogen and deuterium compounds at a given temperature were the same. The calculated slopes<sup>19</sup> at 80, 90, and  $111^\circ$  are  $-0.1556$ ,  $-0.1583$ , and  $-0.1551$  and essentially independent of temperature. This treatment reduced  $k_H/k_D$  and changed the activation parameters somewhat (see Table IV under Method 2).

Both methods of treating the data have their merits. By the first method  $k_H/k_D = 1.39$ – $1.28$ ;

(18) E. S. Amis, "Kinetics of Chemical Change in Solution," The Macmillan Co., New York, N. Y., 1949, Ch. 8.

(19) S. Ergun, *Ind. Eng. Chem.*, **48**, 11, 2063 (1956).

TABLE IV

REACTION OF DEUTERATED AND NORMAL *sym*-TETRABROMOETHANE WITH SODIUM IODIDE IN METHANOL

Temp., °C.	$k_H^0 \times 10^4,^a$ l./mole min.	$k_D^0 \times 10^4,^a$ l./mole min.	$k_H^0/k_D^0$	$\Delta\Delta F^*,^b$ cal./mole
Method 1 <sup>c</sup>				
80.82	3.641	2.621	1.389	-231
90.48	10.05	7.439	1.351	-216
111.46	65.32	51.17	1.277	-186
$\Delta E_H = 25.5 \pm 0.5$ kcal./mole				$\Delta S_H = -12.7$ cal./deg. mole
$\Delta E_D = 26.2 \pm 0.5$ kcal./mole				$\Delta S_D = -11.2$ cal./deg. mole
Method 2 <sup>d</sup>				
80.82	3.415	2.669	1.28	-173
90.48	9.517	7.518	1.27	-172
111.46	62.78	51.17	1.23	-158
$\Delta E_H = 25.6 \pm 0.5$ kcal./mole				$\Delta S_H = -12.3$ cal./deg. mole
$\Delta E_D = 26.0 \pm 0.5$ kcal./mole				$\Delta S_D = -11.6$ cal./deg. mole

<sup>a</sup>  $k^0$ , rate constant at zero ionic strength. <sup>b</sup>  $\Delta\Delta F^* = -RT \ln k_H^0/k_D^0$ . <sup>c</sup>  $k^0$  from least squares treatment of 4. <sup>d</sup>  $k^0$  from least squares treatment of 4 in which a constant slope was required for the deuterated and normal tetrabromoethanes at a given temperature.

by the second  $k_H/k_D = 1.28$ –1.23. These experimental uncertainties render uncertain any estimates of the temperature dependent and independent parts of the isotope rate effect. We infer that these are limits on the isotope rate effect and that the true value lies between the two extremes, say  $k_H/k_D = 1.28$  in the range 80–111°. However, the trend in  $k_H/k_D$  with increasing temperature is clear: there is a decrease in  $k_H/k_D$  of ca. 4–8% over a 30° temperature interval.<sup>20</sup>

There is an alternative view of the medium effect, namely, that the sodium iodide is incompletely dissociated in methanol.



Accordingly

$$K = y^2/(b - y) \quad (6)$$

where no aggregates beyond dimers are assumed,  $y$  is the concentration of free iodide and only free iodide is effective in reaction 1.

Then

$$y/b = k/k^0 = m \quad (7)$$

Using  $k^0$  for the hydrogen compound at 80.82°, we calculate  $K = 1.7 \times 10^{-3}$  or  $2.5 \times 10^{-3}$  depending on the two methods of evaluating  $k^0$ . This is in the range of the dissociation constants of alkali iodides in similar solvents, e.g.,  $K = 5.3 \times 10^{-3}$  for sodium iodide in 1-propanol.<sup>21</sup> Although it would appear that association accounts nicely for the whole "medium" effect, it is probable that both a normal kinetic salt effect and ion aggregation diminish the effectiveness of added iodide in reaction 1.<sup>22</sup>

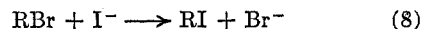
(20) The lower figure for the temperature coefficient is more probable.<sup>4</sup>

(21) M. B. Reynolds and C. A. Kraus, *J. Am. Chem. Soc.*, **70**, 1709 (1948); R. L. Kay, *ibid.*, **82**, 2099 (1960); T. A. Gover and P. G. Sears, *J. Phys. Chem.*, **60**, 330 (1956).

(22) S. Winstein, L. G. Savedoff, S. Smith, I. D. R. Stevens, and J. S. Gall, *Tetrahedron Letters*, 24 (1960).

**Debromination Mechanism.**—It is not obvious whether the E2 scheme in equation 2 or the SN2 scheme in 3 best represents the debromination process in tetrabromoethane. Three lines of argument, all favoring one of the mechanisms, will be developed.

Consider the displacement (SN2)<sup>6</sup>



The steric requirements of CH<sub>3</sub> and Br are closely similar—their Taft  $E_s$  parameters are identical—but CH<sub>3</sub> is electron-releasing compared with Br.<sup>23a</sup> In 8, the relative rates for different R groups are CH<sub>3</sub> (100), C<sub>2</sub>H<sub>5</sub> (1.65), *n*-C<sub>3</sub>H<sub>7</sub> (1.32), *i*-C<sub>4</sub>H<sub>9</sub> (0.059), and *i*-C<sub>3</sub>H<sub>7</sub> (0.022)<sup>23b</sup>; the important point is that alkyl substitution at the reacting center reduces the displacement rate sharply. This behavior is further illustrated for a series of known displacements: the rate constants per Br at 101.1° in l. mole<sup>-1</sup> min.<sup>-1</sup> follow the order, BrCH<sub>2</sub>CH<sub>2</sub>Br (1310),<sup>24</sup> Br<sub>2</sub>CHCH<sub>2</sub>Br (13.3),<sup>24</sup> CH<sub>3</sub>CHBrCH<sub>2</sub>Br (64),<sup>24</sup> and CH<sub>3</sub>CHBr<sub>2</sub> (7). If reaction 1 went through the displacement mechanism, one might predict Br<sub>2</sub>CHCHBr<sub>2</sub> (0.7–0.07) in this series. Since the observed rate constant is 7.5 on this scale, this argues against the displacement mechanism.

The elimination mechanism has been established in the reaction of iodide with the 2,3-dibromobutanes.<sup>6</sup> At 59.7°, relative rates are as follows: *meso*-CH<sub>3</sub>CHBrCHBrCH<sub>3</sub> (1.5),<sup>4</sup> *racemic*-CH<sub>3</sub>CHBrCHBrCH<sub>3</sub> (0.78),<sup>4</sup> and Br<sub>2</sub>CHCHBr<sub>2</sub> (0.37). Since the inductive effect of bromine is bond strengthening on a *gem*-bromine and opposite to that of methyl, this order is at least consistent for an elimination series.

In another paper, calculations for secondary isotope-effects have been presented.<sup>3</sup> These suggest that  $k_H/k_D < 1$  for SN2 processes and  $k_H/k_D > 1$  for E2 processes. Data from the literature are consistent with these predictions.<sup>25,26</sup> The calculations also indicate that for an E2 process  $k_H/k_D$  should decrease as the temperature increases. This temperature dependence was found (see Table IV). This and the finding that  $k_H/k_D \approx 1.28$  for the debromination constitute the strongest argument for an E2 process in equation 1.<sup>3</sup>

Finally, addition reactions of alkenes are the reverse of E2 processes. The calculations<sup>3</sup> indicate that additions should have both a reverse secondary isotope effect, that is  $k_H/k_D < 1$ , and a reverse temperature dependence, i.e.,  $k_H/k_D$  should increase as  $T$  increases. The thiocyanate-catalyzed isomerization of maleic acid<sup>27</sup> or the bromine addition to stilbene<sup>28</sup> exhibit the expected behavior.<sup>29</sup> These authentic addition mechanisms provide

(23) (a) R. W. Taft, Jr., "Steric Effects in Organic Chemistry," M. S. Newman, Editor, John Wiley and Sons, New York, N. Y., 1956, p. 650; (b) E. L. Eliel, *ibid.*, pp. 73–77.

(24) D. Pressman and W. G. Young, *J. Am. Chem. Soc.*, **66**, 705 (1944).

(25) R. R. Johnson and E. S. Lewis, *Proc. Chem. Soc.*, 52 (1958).

(26) V. J. Shiner, *J. Am. Chem. Soc.*, **82**, 2655 (1960).

(27) S. Seltzer, *ibid.*, **83**, 1861 (1961).

(28) D. B. Denny and N. Tunkel, *Chem. & Ind. (London)*, 1383 (1959).

(29) The symmetry of elimination-addition processes is beautifully illustrated by these isotope effects.

another argument in favor of an E2 process for the debromination of tetrabromoethane.

**Acknowledgment.**—We wish to thank the Research Corporation for its financial support.

## THE THERMODYNAMIC PROPERTIES OF LIQUID TERNARY ZINC, INDIUM, AND GALLIUM SOLUTIONS

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The ternary system zinc-indium-gallium and the binary systems zinc-indium and zinc-gallium have been investigated by electrode-potential methods over the temperature range of 420 to 520°. The properties,  $\Delta F^\circ$ ,  $\Delta H^\circ$ ,  $\Delta S^\circ$ ,  $\Delta \bar{F}_i^\circ$ ,  $L$ , and activities were calculated from the experimental data for the systems at 470°. The corresponding properties of the gallium-indium binary system were obtained by calculation by means of Darken's procedure utilizing the experimental data.

### Introduction

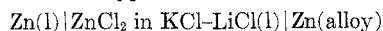
At the time this research was started, thermodynamic studies of liquid alloys involving more than two components were limited. The studies on the cadmium-lead-bismuth, cadmium-lead-tin, and the cadmium-lead-antimony systems had been reported by Elliott and Chipman<sup>2</sup> and the cadmium-bismuth-tin system by Mellgren.<sup>3</sup> Both papers made use of Darken's equations<sup>4</sup> developed for a single phase ternary system in which the composition of the third component is varied in a constant ratio mixture of the other two components.

In our Laboratory, attempts had been made to study the gallium-indium binary system directly by use of the electrode-potential method. We were not successful. However, values of this binary may be calculated<sup>4</sup> from experimental measurements on a ternary system involving gallium, indium, and some other more electropositive metal, for example, zinc.

Consequently, the present research was undertaken in order to determine: (1) the thermodynamic properties of the zinc-indium-gallium system; (2) the thermodynamic properties of the gallium-indium binary system.

**Materials.**—The sources of indium,<sup>5</sup> zinc, and gallium<sup>6</sup> already have been described. However, gallium of 99.99% purity, obtained from the Aluminum Co. of America, also was used in some of the runs. Spectrographic analyses indicated the complete absence of foreign elements in all three metals.

**Apparatus.**—The apparatus was essentially the same as before.<sup>5</sup> Cells of the type



were used. Details concerning the preparation of the cells already have been described.<sup>5</sup>

### Experimental

A series of measurements of the e.m.f. of cells of the above type were made over a temperature range of 420 to 520° using zinc-gallium, zinc-indium, and zinc-indium-gallium alloys. In the latter series, the measurements were performed on alloys having constant atomic ratios of  $N_{\text{Ga}}/N_{\text{In}}$

equal to 3/17, 1/3, 1/1, and 3/1. The mole fraction of zinc was varied from 0.100 to 0.900 in each of the binary and ternary systems.

The experimental e.m.f. for each alloy was plotted against the temperature. Linear plots were obtained. The temperature gradient and the e.m.f. for each alloy at the arbitrarily selected temperature of 470° were determined from the plots. These data are given in Table I.

TABLE I  
CELL COMPOSITION AND POTENTIALS AT 470°

NZn	E.m.f. (mv.)	dE/dT mv./de- gree	NZn	E.m.f. (mv.)	dE/dT mv./de- gree
Zinc-gallium series			Zinc-indium-gallium series		
			$N_{\text{Ga}}/N_{\text{In}} = 1/3$		
0.100	61.45	0.11532	0.100	47.75	0.11333
.200	41.25	.08188	.200	29.63	.08275
.300	30.26	.06400	.300	20.37	.06133
.370	24.97	.05425	.400	15.05	.04762
.400	22.76	.04888	.500	11.04	.03538
.500	17.45	.03838	.600	8.29	.02434
.600	12.91	.02722	.700	6.42	.01750
.700	9.26	.01916	.800	4.45	.00974
.800	6.08	.01195	.900	2.44	.00403
.900	2.89	.00505	$N_{\text{Ga}}/N_{\text{In}} = 1/1$		
Zinc-indium series			0.100	54.11	0.11300
0.100	38.92	0.11600	.200	35.23	.08000
.200	21.91	.08333	.300	25.18	.06300
.350	11.90	.05525	.400	18.84	.04938
.500	7.54	.03573	.500	13.99	.03644
.548	6.74	.0308	.600	10.45	.02663
.600	6.06	.02669	.700	7.48	.01815
.700	4.92	.01961	.800	5.06	.01030
.749	4.18	.01331	.900	2.74	.00425
.800	3.70	.01013	$N_{\text{Ga}}/N_{\text{In}} = 3/1$		
.900	2.26	.00386	0.100	58.43	0.11375
Zinc-indium-gallium series			.200	39.47	.08289
$N_{\text{Ga}}/N_{\text{In}} = 3/17$			.300	28.63	.06257
0.100	43.28	0.11422	.400	21.32	.04863
.200	26.88	.0838	.500	15.99	.03675
.300	18.93	.06371	.600	12.12	.02738
.400	13.19	.04788	.700	9.08	.01976
.500	10.0	.0361	.800	5.96	.01254
.600	7.49	.02556	.900	2.98	.00504
.700	5.90	.01825			
.800	4.09	.01044			
.900	2.50	.00454			

When an alloy of a particular composition was chosen for analysis, part of the original sample was saved. After completion of a run, appropriate amounts of the used alloy

(1) Abstracted in part from a thesis submitted by Shirley M. Read to the Graduate School of the University of Maryland in partial fulfillment of the requirements for the degree of Doctor of Philosophy.

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