[CONTRIBUTION FROM THE INSTITUTE FOR THE STUDY OF METALS, THE UNIVERSITY OF CHICAGO]

A Thermodynamic Study of Liquid Metallic Solutions. V. The Systems Zinc–Bismuth and Zinc-Lead

BY O. J. KLEPPA

RECEIVED MARCH 22, 1952

The thermodynamic properties of the liquid systems zinc–bismuth and zinc–lead have been studied by the e.m.f. method. Both systems show a fairly large positive ΔH of mixing, and both systems have positive entropy deviations. The extent of the liquid miscibility gaps has been checked by equilibrium measurements. In the case of the system zinc–lead the results are in excellent agreement with the most reliable data available in the literature. For the system zinc–bismuth the present investigation gives a critical temperature of ~605° at 85 atomic per cent. zinc, while earlier work indicates a critical mixing temperature of about 750–800°. This discrepancy indicates that the earlier procedures did not provide full opportunity for the system to reach equilibrium.

Introduction

The present study forms a part of a systematic survey of the thermodynamic properties of binary liquid alloy systems. In earlier communications the author has presented data on and discussed the properties of the binary alloys of gold with such other components as bismuth, lead, thallium and tin.[1] In the accompanying paper[2] the liquid mixtures of copper with lead, bismuth and thallium have been discussed. The present investigation aimed at obtaining quantitative thermodynamic information on the binary alloys of zinc with the same three metals. Among these systems, zinc–lead has been investigated earlier by the vapor pressure method,[3] and, for zinc–lead and zinc–bismuth, calorimetric data are available in the literature.[4] For the system zinc–thallium no information beyond some data on the equilibrium phase diagram is available.

When it can be adopted, the e.m.f. method usually provides more accurate information than the vapor pressure method. In particular it is found that the e.m.f. data frequently allow a fairly reliable separation of the excess free energy of mixing into the appropriate heat and entropy terms. It was accordingly decided to adopt the e.m.f. method for the present investigation. It was found, however, that for the system zinc–thallium reproducible e.m.f. data could not be obtained. This is due to the small difference in electrochemical character between these two metals. In the present report, data will therefore be presented on the systems zinc–lead and zinc–bismuth only. For these systems the reversible galvanic cells take the form

$$\mathrm{Zn(l)/Zn^{++}/(Zn + Me)(l)}$$

Here Me designates Pb or Bi, respectively.

Experimental

Due to the volatile character of zinc (vapor pressure ~ 10 Tor at 600°) the measurements were all performed below 650°, where Pyrex and Duran glass cells could be used. The lower temperature limit was the melting point of pure zinc, 419°. The cell construction and experimental procedure was analogous to that adopted by the author for the system gold–tin.[1]

It is well known that the systems under consideration both show miscibility gaps in the liquid state.[5] In both cases the critical mixing temperatures reported in the literature are about 800°. It was therefore anticipated that only limited regions of homogeneous mixture could be investigated at and below 650°. It was found that for zinc–lead the homogeneous region at this temperature extended from 0 to about 21 and from about 98 to 100 atomic per cent. zinc. However, for zinc–bismuth a complete range of homogeneous mixtures was obtained above ~ 605°.

The measured electromotive forces were reproducible to between ±0.05 and ±0.3 mv., depending on the composition of the alloy. The lowest zinc content gave the highest temperature gradient of electromotive force, and also the largest scattering of the measured e.m.f.

After completion of each run the alloy and reference electrodes were removed from the cell as quantitatively as possible, and weighed. The alloy was then analyzed. It was found that the weight before and after the experiment never differed by more than a few milligrams. The chemical analysis showed no change in composition within the accuracy of the method.

The purity of the metals used for these experiments was tested spectrographically, and ranged from 99.8% (Zn) to better than 99.9%, as determined by semi-quantitative spectrographic analysis.

Results

A total of 16 successful runs were performed on zinc–lead alloys and 19 runs on zinc–bismuth alloys. During each run 6–12 determinations of electromotive force and temperature were carried out. Each of these determinations represents the average of 5–15 separate measurements which were performed during a period of constant temperature (±1°) lasting for 1–3 hours.

The electromotive forces were plotted *versus* temperature in order to obtain for each alloy composition the following data: (1) the e.m.f. at a common reference temperature, 600° for Zn–Bi and 653° for Zn–Pb; (2) the temperature gradient of the e.m.f.; (3) the temperature of liquid–liquid phase separation (segregation curve).

Because of the limited temperature region experimentally available for some homogeneous mixtures, the temperature gradient of the e.m.f. could not in all cases be obtained. It was also found that for mixtures with compositions in the critical region it was not possible to determine the temperature of liquid–liquid phase separation.

The experimental results are recorded in Tables I(a) and I(b). In the same tables will be found the corresponding activities, "entropy fractions" and partial molal heat contents for zinc. For the system zinc–bismuth we have given in Table II, a summary of the thermodynamic data for both components at round figure atomic fractions. The data for bismuth have been calculated by use of the Gibbs–Duhem equation.

---

[1] O. J. Kleppa, THIS JOURNAL, **71**, 3275 (1949); O. J. Kleppa, *ibid.*, **72**, 3346 (1950); O. J. Kleppa, *ibid.*, **73**, 385 (1951).

[2] O. J. Kleppa, *ibid.*, **74**, 6047 (1952).

[3] K. Jellinek and H. A. Wannow, *Z. Elektrochem.*, **41**, 347 (1935).

[4] M. Kawakami, *Z. anorg. allgem. Chem.*, **167**, 345 (1927).

[5] M. Hansen, "Aufbau der Zweistofflegierungen," Berlin, 1936.

TABLE I

EXPERIMENTAL RESULTS, CALCULATED ACTIVITIES AND "ENTROPY FRACTIONS"

Run	Composition x_{Zn}	E at 653°, mv.	$\Delta E/\Delta T$, mv./100°	Phase separation, °C.	a_{Zn}, 653°	x'_{Zn}	$\bar{L}_{Zn}$, cal./g. atom
			(a) The system Zn(l)–Pb(l)				
8	0.0388	48.7	17.5	...	0.295	0.017	5240
4	.0730	26.0	14.1	471	.521	.038	4820
1	.0964	20.17	13.4	505	.603	.045	4775
3	.1229	11.6	11.4	555	.747	.071	4330
12	.1408	9.96	11.2	569	.779	.074	4330
14	.1560	7.00	10.3	591	.839	.091	4080
2	.1645	5.90	11.5	608	.862	.069	4640
16	.1816	4.20	9.8	615	.900	.103	4035
5	.2043	1.26	...	...	.970	...	..
17	.2613	0.90	...	...	.978	...	..
18	.5058	0.90	...	...	.978	...	..
11	.8986	0.80	...	...	.980	...	..
7	.9394	0.70	...	...	.983	...	..
6	.9684	0.75	...	...	.981	...	..
10	.9788	0.75	...	...	.981	...	..
9	.9894	0.48	0.12	510	.988	0.975	24
		E at 600°, mv.			a_{Zn}, 600°		
			(b) The system Zn(l)–Bi(l)				
5	0.0639	66.6	15.2	...	0.170	0.029	3040
6	.1284	42.8	11.8	...	.320	.065	2760
1	.2122	27.25	9.65	...	.484	.106	2640
7	.2560	21.2	8.1	...	.569	.153	2280
2	.2939	18.10	7.70	...	.618	.167	2270
3	.3945	11.05	5.90	<420	.745	.255	1860
4	.4655	6.87	4.95	475	.835	.317	1680
13	.4989	5.50	4.42	482	.864	.359	1530
14	.5523	3.12	3.30	520	.920	.465	1180
15	.6042	2.50	2.90	536	.936	.510	1060
21	.6533	1.76	2.42	556	.954	.570	895
19	.6961	1.38	1.88	567	.964	.646	695
18	.7642	1.01	1.46	595	.973	.713	540
23	.8018	0.99	1.10	597	.974	.775	400
17	.8437	0.98	...	...	.974	...	..
22	.8894	0.96	...	...	.975	...	..
12	.9439	0.85	...	~550	.978	...	..
10	.9463	0.87	...	~550	.977	...	..
11	.9741	0.55	0.17	500	.985	0.961	44

TABLE II

COMPUTED THERMODYNAMIC DATA FOR THE SYSTEM Zn(l)–Bi(l)

x_{Zn}	a_{Zn}, 600°	a_{Bi}, 600°	x'_{Zn}	x'_{Bi}	$\bar{L}_{Zn}$, cal./g. atom	$\bar{L}_{Bi}$, cal./g. atom	ΔH, cal./g. atom
1.000	1.000	0.000	1.000	0.000	0	6700	0
0.900	0.975	.508	0.88	.044	115	4400	540
.800	.974	.508	.765	.101	380	2880	880
.700	.966	.522	.635	.176	720	1850	1060
.600	.936	.551	.500	.276	1100	1140	1120
.500	.865	.606	.370	.398	1480	685	1080
.400	.760	.672	.260	.533	1860	390	980
.300	.627	.744	.175	.660	2210	195	800
.200	.463	.821	.105	.784	2560	74	520
.100	.260	.905	.048	.896	2900	17	305
.000	.000	1.000	.000	1.000	3200	0	0

Discussion

Thermodynamic Data.—In order to calculate the integral heat data given in Figs. 1 and 2 use has been made of the following procedures: For the

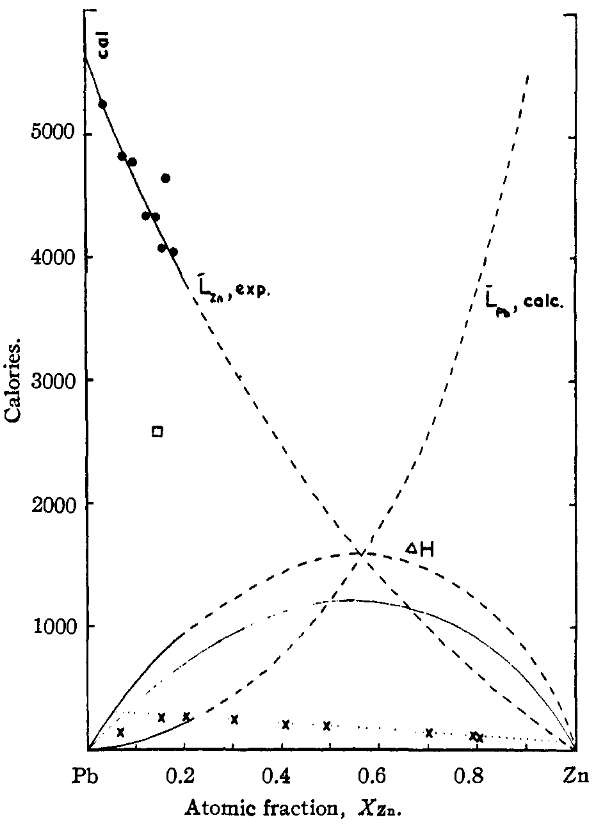

Fig. 1.—Relative partial molal heat contents and integral heats of mixing in the system Zn(l)–Pb(l): ●, $\bar{L}_{Zn}$, exptl.; □, $\bar{L}_{Zn}$, Jellinek and Wannow, exptl.; —, ΔH, Scheil, calcd.; ×, ΔH, Kawakami, exptl. (450°).

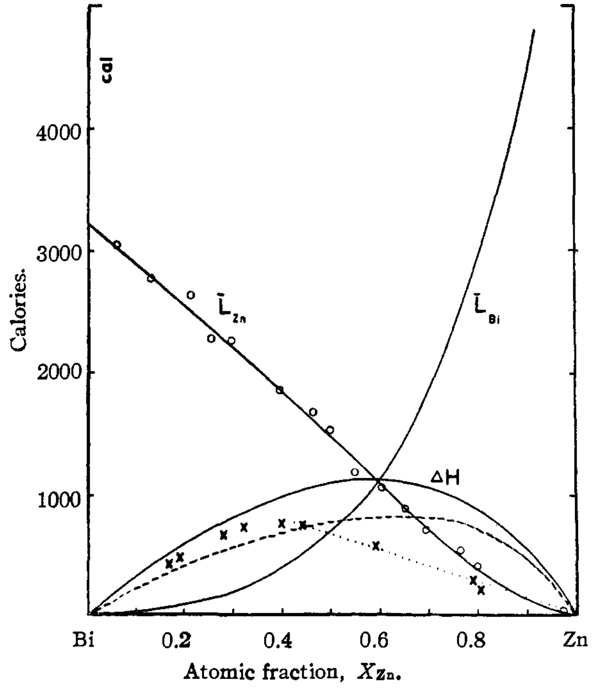

Fig. 2.—Relative partial molal heat contents and integral heats of mixing in the system Zn(l)–Bi(l): ○, $\bar{L}_{Zn}$, exptl.; —, $\bar{L}_{Zn}$, $\bar{L}_{Bi}$, ΔH, calcd.; - - -, ΔH, Scheil, calcd.; ×, ΔH, Kawakami, exptl. (450°).

system zinc–bismuth the curve which has been drawn through the experimental points is based on the volume fraction expression (Eq. 9a, b of Ref. 2)

$$\bar{L}_{Zn} = \bar{L}^0{}_{Zn}\vartheta^2{}_{Bi}$$

Here $\bar{L}^0{}_{Zn}$ is the relative partial molal heat content for zinc at high dilution (3200 cal.), and ϑ_{Bi} is the volume fraction of bismuth $x_{Bi}V_{Bi}/[x_{Bi}V_{Bi} + x_{Zn}V_{Zn}]$ in the mixture. The volume ratio V_{Bi}/V_{Zn} has been taken to be 2.1.

We find that the volume fraction expression used for zinc–bismuth fits the experimental points within the limits of error over the whole concentration range! This lends support to the use of such expressions for the heat of mixing of alloy systems. Among other systems for which it is found that the experimental heat data may be represented to a good approximation by the volume fraction expression are gold–bismuth,[1] zinc–tin and lead–cadmium.[6,7] For the system zinc–lead the volume-fraction expression does not fit the experimental points as well as is the case for zinc–bismuth. In order to obtain values for the partial molal heat content of zinc at other concentrations a simple graphical interpolation has therefore been carried out (broken line between 100 and 20 atomic per cent. zinc).

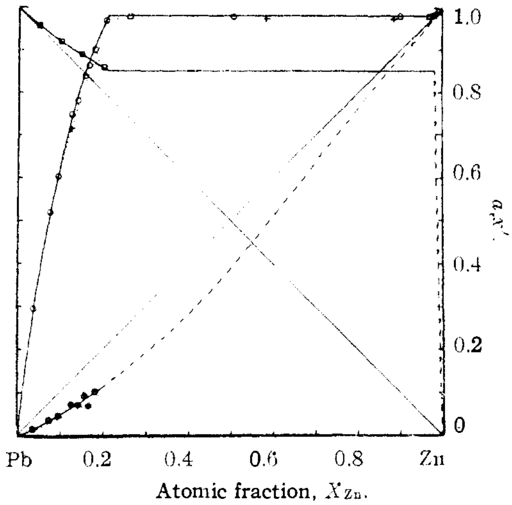

Fig. 3.—Activities and entropy fractions in the system Zn(l)-Pb(l): ○, a_{Zn}, 653°, exptl.; +, a_{Zn}, 653 °, Jellinek and Wannow, exptl.; ●, x'_{Zn}, exptl.; ...... a_{Zn}, 653° and x'_{Zn}, Lumsden, calcd.; □, a_{Pb}, 653°, calcd.

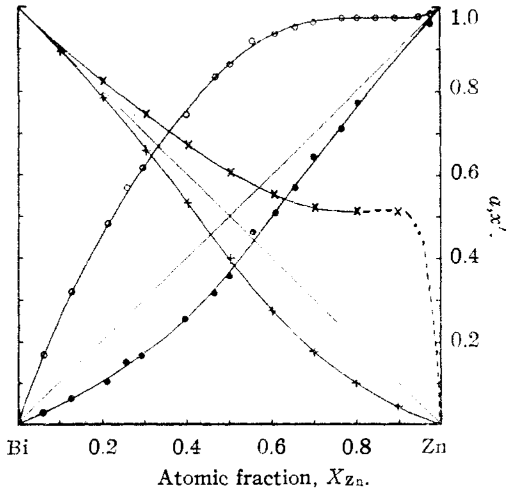

Fig. 4.—Activities and entropy fractions in the system Zn(l)-Bi(l): ○, a_{Zn}, 600°, exptl.; ●, x'_{Zn}, exptl.; ×, a_{Bi}, 600°, calcd.; +, x'_{Bi}, calcd.

The liquid systems zinc–lead and zinc–bismuth both show a relatively large positive ΔH of mixing. It is calculated that for zinc–lead ΔH is about 1.6 kcal./g. atom for equi-atomic mixtures; the corresponding figure for zinc–bismuth is 1.1 kcal./g. atom. We have included in the figures some older heat data for the two systems. It will be noticed that the agreement with the calorimetric data of Kawakami is not very good. It should be observed, however, that Kawakami's data for these two systems are referred to 450° at which temperature both systems have extensive miscibility gaps. In the figures the extent of the miscibility gap is indicated by a dotted line through the corresponding experimental points. The present results should be compared to those given by Kawakami in the region of homogeneous solutions only.

Curves for ΔH calculated by Scheil[8] from the equilibrium phase diagrams will also be found in Figs. 1 and 2.

In a previous communication[2] some comments have been presented on Scheil's method of calculation. In particular it is pointed out that Scheil's assumption of an ideal ("regular") entropy of mixing is likely to lead to incorrect values for the calculated heat of mixing. For the two systems under consideration Scheil's work is associated with an additional uncertainty. This is due to his use of the miscibility gap information reported by Haas and Jellinek[9] (see below).

Although Haas and Jellinek's data would tend to give too *high* values for ΔH, it is found that the net result obtained by Scheil is considerably *lower* than the experimental curves presented in this paper.

In Figs. 3 and 4 graphs are presented of the experimental activities and "entropy fractions" for the systems under consideration. Included in Fig. 3 (zinc–lead) are also the activity data at 653° reported by Jellinek and Wannow.[3] At this temperature the activities determined in the present investigation are only slightly different from theirs. However, on the basis of the temperature dependence of the activity these workers also calculated the partial molal heat content for zinc in an alloy containing 14.3 atomic per cent. zinc. The result is plotted in Fig. 1. As this point falls far below all other experimental points, the agreement for 653° must in part be considered as fortuitous.

The system zinc–lead has been discussed in con-

[6] N. W. Taylor, THIS JOURNAL, **45**, 2871 (1923).

[7] J. H. Hildebrand, "Solubility of Non-electrolytes," 1st ed., Reinhold Publ. Corp., New York, N. Y., 1924, long ago suggested the volume fraction representation for the excess free energy of liquid alloy mixtures. For "regular" solutions the excess free energy is of course equal to the heat of mixing.

[8] E. Scheil, *Z. Elektrochem.*, **49**, 242 (1943).

[9] K. Haas and K. Jellinek, *Z. anorg. allgem. Chem.*, **12**, 356 (1933).

siderable detail by Lumsden,[10] who presents for this particular system an analytical expression for the free energy of mixing. His results both with respect to free energy (activity) and entropy (entropy fraction) are in good agreement with the experimental data presented in this paper (Fig. 3). Lumsden's expression, which is a four-constant equation, has been derived from the experimental miscibility gap (see below) by successive approximations.

The author has previously called attention to the correlation between positive entropy deviations for liquid alloy mixtures and the difference in size between the two components.[1] It is recalled that the excess entropies found in such systems frequently are very large. In many cases the entropies cannot be accounted for by the various formulas derived on a theoretical basis to correct the (athermal) entropy of mixing for a difference in size of the two components.[11] It is therefore believed that the excess entropy to a large extent arises from the non-validity of the Neumann–Kopp rule for the specific heat (vibrational entropy terms), and that the effect is related to the problem of packing atoms of different size in the mixture. In general agreement with this we find that the systems zinc–lead and zinc–bismuth both have fairly large positive entropy deviations. It may be pointed out, however, that mixtures of gold with lead and with bismuth show somewhat larger excess entropies than the corresponding mixtures involving zinc. As the atomic volume of gold is slightly larger than that of zinc, this is another indication that the excess entropy also arises from other factors than the difference in volume.

In earlier work the author has also pointed out how non-zero heats of mixing may be associated with short range order or clustering in the mixture and accordingly reduce somewhat the entropy of mixing.[1] In particular, it was pointed out that this reduction of the entropy per g. atom should be of the order of 0.1 entropy unit or less if $|\Delta H_{\max}| < {}^1/_2 RT$, while larger numerical values for ΔH should lead to larger deviations. It was actually possible to find a slight reduction in the partial molal entropy of zinc at temperatures just above the segregation curve in the zinc–lead system, at zinc concentrations of 10–20 atomic per cent. For zinc–bismuth, which has a smaller numerical value for ΔH, this effect could not be detected with certainty.

Liquid Miscibility Gap.—In Fig. 5 are plotted the temperatures of liquid–liquid phase separation for lead–zinc alloys obtained in the present investigation. (The point at 653° has been obtained from Fig. 4, the rest of the experimental points from Table I(a). Due to the restricted temperature region the results only refer to alloys with less than 21 atomic per cent. zinc. In the same figure will be found the segregation curve given by Waring and collaborators,[12] and the experimental points determined by Spring and Romanoff[13] and by Haas and Jellinek.[9] Waring, *et al.*, carried out a critical investigation of the extent of the miscibility gap, and their curve is the result of work involving four different experimental methods. It is interesting to note the excellent agreement between the results of the present investigation and the curve given by Waring.

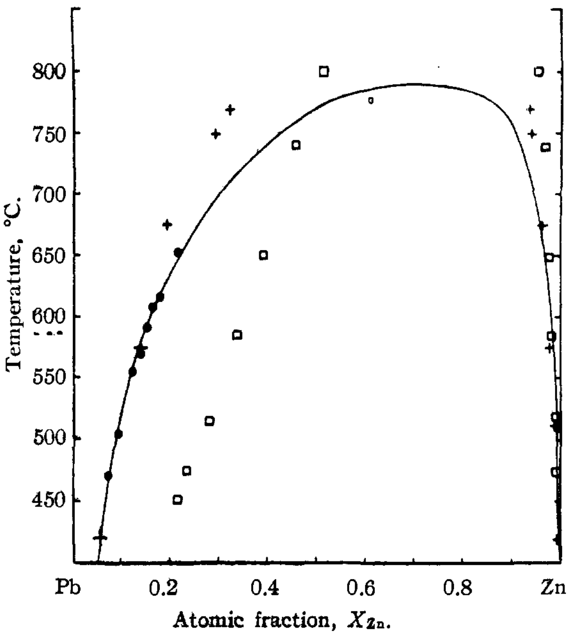

Fig. 5.—Liquid miscibility gap in the system Zn–Pb: ●, present work; +, Haas and Jellinek; □, Spring and Romanoff; —, Waring, *et al.*

Waring, *et al.*, also duplicated the experimental procedures adopted by Spring and Romanoff and by Haas and Jellinek. They stated that these workers had used procedures which did not provide adequate opportunity for the system to reach equilibrium.

This observation is of particular interest in view

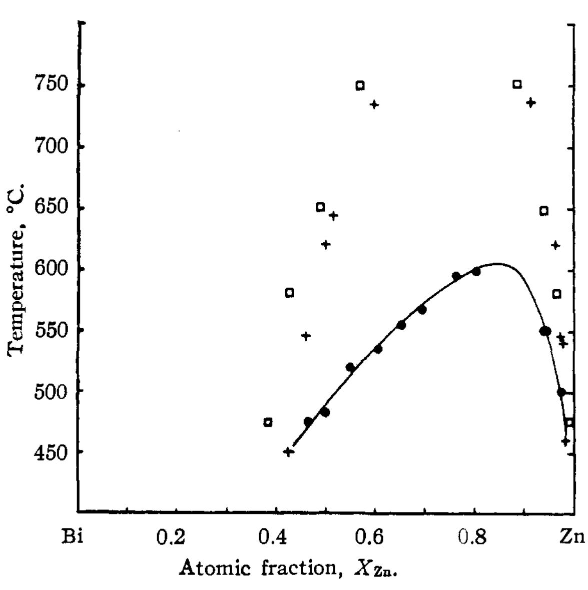

Fig. 6.—Liquid miscibility gap in the system Zn–Bi: ●, present work; +, Haas and Jellinek; □, Spring and Romanoff.

---

[10] J. Lumsden, *Disc. Faraday Soc.*, **4**, 60 (1948).

[11] J. H. Hildebrand and R. L. Scott, "Solubility of Non-electrolytes," 3rd ed., New York, N. Y., 1950, pp. 106–118.

[12] R. K. Waring, E. A. Anderson, R. D. Springer and R. L. Wilcox, *Trans. A.I.M.E.*, **111**, 255 (1934).

[13] N. Spring and L. Romanoff, *Z. anorg. allgem. Chem.*, **13**, 29 (1897).

of the results obtained in the present investigation for the system zinc–bismuth. Reference is here made to Fig. 6, which contains these results as well as the experimental points given by Spring and Romanoff and by Haas and Jellinek. It will be noticed that there is a very large difference between our results and those of the earlier workers. Thus we find here a critical temperature of about 605°, while the value accepted previously is between 750 and 800°.

Acknowledgments.—The experimental part of the present paper was carried out while the author was associated with the Norwegian Defense Research Establishment, Lillestrom, Norway. The author is indebted to Miss E. Aamodt for assistance in carrying out the measurements and for analytical work. He also wishes to acknowledge the help offered by Messrs. L. J. Howell and Th. Holager in checking the purity of the metals used.

CHICAGO, ILLINOIS

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, GEORGE WASHINGTON UNIVERSITY]

Evidence for Preferential One-Step Divalent Changes in the Molybdate-Catalyzed Reduction of Perchlorate by Stannous Ion in Sulfuric Acid Solution

BY G. P. HAIGHT, JR.,* AND W. F. SAGER

RECEIVED MARCH 12, 1952

The study of kinetics of the molybdenum-catalyzed reduction of perchlorate ion by stannous ion in sulfuric acid solution follows the law given in equation (1). A reaction mechanism which fits this law is proposed and scrutinized. Evidence for direct bivalent reduction of molybdate is presented and its bearing on current controversy concerning one- and two-electron reductions is discussed. Other possible molybdenum-catalyzed reductions are mentioned.

Introduction

It is well known that the perchlorate ion, although potentially a strong oxidant is reduced only with difficulty under usual conditions. A recent polarographic study has disclosed the powerful catalytic activity of molybdate and pentavalent molybdenum toward reduction of perchlorate at a mercury electrode.[1] An extension of this work, the subject of this paper, has now demonstrated that molybdate maintains its catalytic activity in the reduction of perchlorate by stannous ion. Inquiry into mechanism gives strong indication that the catalytic species is tetravalent molybdenum, a valence state which is unstable in solution. Moreover our evidence leads to the interesting conclusion that hexavalent molybdenum (molybdate) is reduced to the tetravalent state by stannous ion through a process which bypasses the easily accessible valence of five.

This last observation directly contradicts the theory of compulsory univalent oxidation of Michaelis[2] and of Haber and Weiss.[3]

So many violations of this principle may be found, violations which are most frequently encountered in oxidation–reduction reactions of covalent compounds, that only a few representative illustrations may be given here. For example electrophilic displacement of hydrogen of one carbonium ion by another as in hydrogen–halogen exchange, the nucleophilic displacement on halogen of one carbanion by another, and the exchange of oxygen between sulfate and sulfite are quite apparently oxidation–reduction reactions. Nevertheless they are closely analogous to other displacement processes such as the solvolysis of alkyl halides which are not normally regarded as oxidations. Whereas such illustrations in no way rule out simple electron transfer as a possible route for an oxidation–reduction process it must be borne in mind that most inorganic ions, especially those which participate in such processes, possess covalently bound structures. We are of the opinion that the process involved in our study is an oxidation–reduction reaction of the displacement type.

Procedure.—Analytical grade reagents were employed in all experiments. Stannous solutions were standardized with potassium permanganate immediately before use. The reaction was carried out in 2.5 *M* sulfuric acid in a round-bottom flask suspended in a thermostat at 25°. The reaction was started by adding a few milliliters of molybdate solution to a solution of stannous ion (as chloride) and perchloric acid in sulfuric acid. No perceptible reaction took place in the absence of molybdate in agreement with a report from Dr. R. Rivest.[4] Air was removed from reagents and again at the start of the reaction by bubbling nitrogen through the solutions. Continuous bubbling through the course of the reaction proved unnecessary. At various intervals samples of the reacting mixture were removed and titrated with standard permanganate solution to determine the amount of stannous ion remaining. This titration also included the reduced molybdenum, but this was for the most part insignificant and was ignored.

Experimental Observations and Results.—The reaction mixture at the beginning turns dark blue and becomes pale yellow as the reaction proceeds when the molybdate concentration is as high as 10^{-3} *M*. When the molybdate concentration is lower by tenfold the initial color is yellow and the solution becomes colorless to the eye as the reaction proceeds. Spectrophotometric studies showed that the concentration of pentavalent molybdenum during the latter part of the reaction was less than half the total molybdenum concentration. The intense initial coloration made spectrophotometric studies of the change in pentavalent molybdenum impossible to interpret because of lack of knowledge of interference of other valences of molybdenum. Two such studies are reproduced in Fig. 1. Perchlorate ion is reduced to chloride ion and stannous tin is oxidized to stannic tin.

Analysis of a variety of runs with equivalent concentrations of Sn^{++} and ClO_4^- and excess quantities

---

[*] Chemistry Department, University of Kansas, Lawrence, Kansas.

[1] G. P. Haight, Jr., *Anal. Chem.*, **23**, 1505 (1951).

[2] L. Michaelis, *Trans. Electrochem. Soc.*, **71**, 107 (1937); *Ann. Rev. Biochem.*, **7**, 1 (1938).

[3] Haber and Weiss, *Naturwissenschaften*, **20**, 948 (1932); *Proc. Roy. Soc. (London)*, **A142**, 332 (1934); *Nature*, **133**, 648 (1934); *Naturwissenschaften*, **23**, 64 (1935).

[4] Private communication from Dr. R. Rivest, University of California.