TABLE II

EQUILIBRIUM DATA FOR THE REACTION BETWEEN SODIUM AND BIPHENYL IN TETRAHYDROFURAN AT 25°

Run	N_B	N_T	N_S
1	0.002774	0.06050	0.0008408
2	.003940	.06033	.0011735
3	.003291	.06057	.0009897

Since the monovalent biphenyl anion is monomeric in solution, we may assume that the following two equilibria are involved.

$$Na(s) + C_{12}H_{10} \longrightarrow NaC_{12}H_{10} \quad (1)$$

$$NaC_{12}H_{10} \longrightarrow Na^+ + C_{12}H_{10}^- \quad (2)$$

Taking the standard state for sodium as the metal at 25° and assuming the activity of other molecules or ions equal to the mole fraction, the equilibrium constants, expressed in terms of mole fractions, for equations 1 and 2 may be written as

$$K_1 = \frac{N_S - x}{N_B - N_S}$$

$$K_2 = \frac{x^2}{(N_B + N_T + x)(N_S - x)} \approx \frac{x^2}{(N_B + N_T)(N_S - x)}$$

where x is the number of moles of sodium ion or biphenyl ion present at equilibrium. Eliminating x, we obtain

$$K_1K_2 = \frac{(N_S - K_1N_B + K_1N_S)^2}{K_1(N_B + N_T)(N_B - N_S)}$$

K_1 and K_2 can be evaluated from N_S, N_B and N_T of two different runs. Runs 1 and 2 give $K_1 = 0.367$ and $K_2 = 3.9 \times 10^{-4}$; runs 2 and 3 give $K_1 = 0.360$ and $K_2 = 4.8 \times 10^{-4}$; runs 1 and 3 give $K_1 = 0.370$ and $K_2 = 3.6 \times 10^{-4}$. The average values of K_1 and K_2 at 25° are 0.366 and 4.1×10^{-4}, respectively.

The reaction between sodium and aromatic hydrocarbons in tetrahydrofuran is reversible as indicated by the fact that the intense color of hydrocarbon anion solutions disappears almost completely on shaking with mercury and is restored again by shaking with sodium. Because of the nearly complete removal of sodium by mercury, it was not possible to obtain accurate data by approaching the equilibrium from the other side.

Acknowledgment.—The financial assistance of Research Corporation in carrying out this research is gratefully acknowledged.

PITTSBURGH, PA.

[CONTRIBUTION NO. 1179 FROM THE DEPARTMENT OF CHEMISTRY, YALE UNIVERSITY]

The Thermoelectric Properties of Metal–Ammonia Solutions. I. The Thermoelectric Power of Sodium and Potassium at $-33°$

BY JACOB F. DEWALD[1] AND GERARD LEPOUTRE[2]

RECEIVED DECEMBER 10, 1953

The thermoelectric properties of sodium and potassium solutions in liquid ammonia at −33° have been studied over the concentration range from 0.002 *M* to saturation. Experimental procedures are outlined, with particular emphasis on methods of preparing solutions of maximum stability. The data for the concentrated solutions are shown to be in strikingly good accord with the predictions based on a degenerate electron gas model. In the dilute range of concentration, where one ordinarily expects the best agreement between theory and experiment, a marked anomaly is observed. The thermoelectric power increases with dilution almost exactly twice as rapidly as theory predicts it should.

Introduction

Investigations of the thermoelectric properties of matter have in the past been primarily concerned with metals and alloys and with electrolytes. In this and subsequent papers we report on our investigations of the thermoelectric properties of metal–ammonia solutions. Such solutions have been extensively investigated in the past and previous work has been reviewed recently.[3,4] Metal–ammonia solutions are unique in allowing one to study the behavior of electrons over an extremely wide range of concentration. Many theories have been presented to account for the observed behavior. The data which we present in this and following papers are in some ways quite anomalous; an understanding of the anomalies should afford additional evidence for a choice between the several models which have been proposed for these solutions.

Experimental

Elimination of Decomposition.—The greatest single difficulty encountered in previous physical measurements on metal–ammonia solutions has been the chemical reactivity of the solute metal with the solvent ammonia. The solutions are thermodynamically quite unstable, decomposing to yield hydrogen and metal amide. In our early work this instability proved troublesome, as it has for others in the past. This was especially true in dilute solution, and since particularly anomalous thermoelectric behavior was observed in this concentration range, considerable time was spent in attempting to minimize the rate of decomposition. Our experience in this regard is worth repeating in detail. Even in our early experiments elementary care was taken. The cells were cleaned with chromic acid solution in standard fashion. The sodium was distilled into the preparation cell under a vacuum of less than 10^{-5} mm.; subsequently sodium-dried ammonia was passed through glass wool and condensed onto the sodium. Although the general trends of the thermoelectric data were apparent (and were subsequently verified by more careful experiments) the scatter of the data was considerable.

To determine the extent of the decomposition reaction and its effect on our data, we then started making conductance measurements immediately before and after the thermoelectric measurements. The kinetics of the decomposition reaction were notably irreproducible at concentrations below 0.1 *M*. One solution would show a change of less than 0.1% per hour and the very next one might be as high as 10% per hour. The largest conductance changes were observed for potassium solutions; for a time we abandoned measurements on these. The figures quoted above represent true bulk decomposition rates, the solutions having been thoroughly mixed just prior to the conductance measurement. The measured resistance was invariably higher

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[3] C. A. Kraus, *J. Chem. Ed.*, **30**, 83 (1953).

[4] W. Bingel, *Ann. Phys.*, **12**, 57 (1953).

before mixing than after, indicating that the bright platinum electrodes were acting catalytically. This is in accord with the previous experience of others.

It has now been fairly conclusively demonstrated by us that the decomposition reaction is strongly catalyzed by even minute traces of impurities. This had previously been strongly suspected by others. We have not established the nature of the active impurities (this would make an interesting kinetic study) but we have determined methods for their apparent exclusion. These include: 1. The vacuum system must be thoroughly outgassed.

2. Carbon dioxide must be rigorously excluded from the vacuum system once ammonia has ever been present in the system.[5]

3. The attainment of pressure lower than 10^{-6} mm. of mercury seems to be essential. In a complicated vacuum system with many stopcocks this is a very stringent requirement, but only by working with true "stick-vacs" could we be assured of satisfactory stability.

4. Mercury vapor must be kept from contact with the solutions, at least during the preparative stages of an experiment. All manometers were either kept isolated from the solution during the preparative stages of the experiments, or had liquid air traps intervening. Once ammonia had been condensed onto the sodium and the ammonia vapor had established a diffusion barrier, we found little or no effect of the mercury, but if the sodium metal was exposed to mercury vapor without the ammonia "blanket," subsequent decomposition of the solutions almost invariably followed.

When prepared with the greatest care, solutions were obtained which showed decomposition rates as low as 0.1% per day and seldom as great as 0.1% per hour, even for potassium solutions at −33°. The mixed metal–salt solutions reported on in a subsequent paper showed somewhat greater tendency to decompose than the pure metal solutions, but even here the decomposition rate was rarely greater than 1% per hour and this only in the case of the most dilute solutions studied.

The stability of the light blue color of the very thin films of pure sodium or potassium afforded a convenient and sensitive test for the adequacy of the vacuum techniques. When sodium is distilled in glass the first metal which comes over generally forms a transparent blue-green film on the glass. This is a true absorption color. Whenever this blue-green color was unstable we obtained solutions of poor stability. Occasionally a transparent pink film was formed instead of the blue-green one; generally solutions prepared from such sodium were also unstable. Only when a blue-green film of sodium could be formed which did not decolorize appreciably on standing for half an hour at room temperature were the resulting ammonia solutions stable.

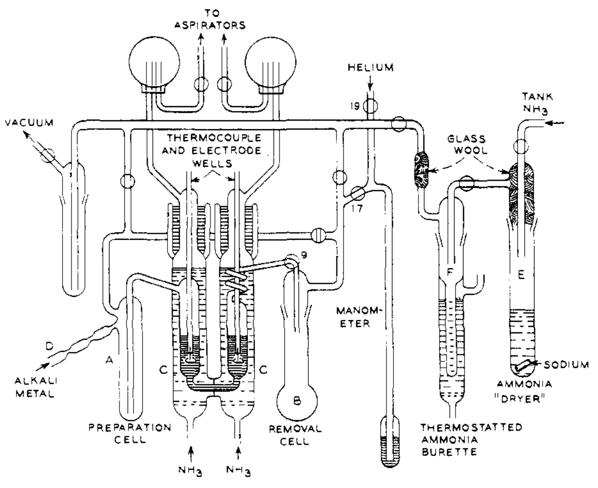

Fig. 1.—The thermocell and auxiliary handling equipment.

Further refinements in technique, such as the *complete* exclusion of mercury, the use of other container materials, and even greater care in vacuum manipulation might increase the stability of these solutions to the point where they could find practical application. For our purposes, however, and probably for most investigative needs, the decomposition rates obtained by the methods outlined above seem to be sufficiently small.

The Cell, Handling Equipment and Experimental Procedures.[6]—A diagram of the thermoelectric cell employed for our measurements at −33° is shown in Fig. 1.[7] The auxiliary handling equipment used for preparation, dilution, analysis, temperature control, etc., is also shown in Fig. 1. The alkali metal, freed of kerosene, was introduced at D. The metal was then distilled stepwise under high vacuum into A. Ammonia, which had previously been dried over sodium in E and then condensed into the ammonia buret F, was then condensed onto the metal in A. The buret was thermostated with boiling ammonia and appropriate corrections were made for the vapor left in the system.

Immediately after the preparation, the solution was syphoned into the cell, C, the preparation cell was rinsed several times with pure ammonia to transfer all of the sodium into C, and a stream of helium which had been passed through a charcoal trap was then bubbled through the solution *via* stopcocks 19, 17 and 9. This served to mix the solution, to control the position of the solution in the cell, and to prevent the formation of bubbles in the capillary tube during the course of a run. All of the preparative operations were carried out as rapidly as possible, and the conductivity of the solutions was measured immediately thereafter.

Electrical contact was made to the solution with copper leads dipping into mercury at the bottom of the thermocouple wells, the mercury making contact with the bright platinum electrodes which were attached to the cell with Kovar-glass seals.

In the work here reported for −33° thermal control was achieved by means of two independently controllable ammonia refluxing baths. Temperatures were measured with two copper–constantan thermocouples which had been calibrated at the dry ice, mercury, ammonia and Glauber's salt points. The reference junctions of these thermocouples were always kept at 0°, temperature differences being measured by bucking one of the couples against the other. In general, one leg of the cell was maintained at the boiling point of ammonia under atmospheric pressure while the other leg was successively cooled by reducing the pressure. Voltages were measured with a White double potentiometer.

Figure 2 shows the results of a typical run. In general, measurements were made at five or six temperatures in the range between −33 and −45°. Two or three minutes

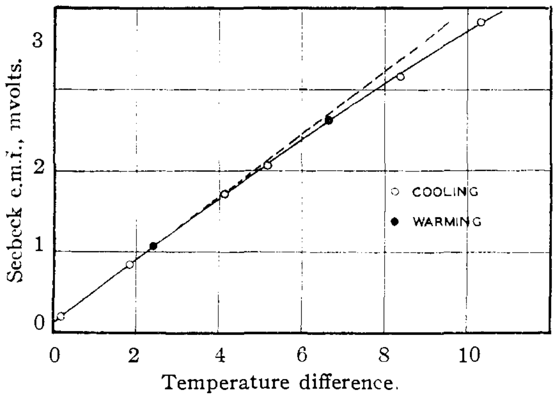

Fig. 2.—A typical run; note the absence of any hysteresis.

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[5] Occasionally a piece of the vacuum system would break and admit air containing carbon dioxide. When such a mishap occurred we were thereafter unable to prepare stable solutions without first taking down the exposed portions of the system, rinsing with water, and then reassembling. Presumably ammonium carbonate was formed under these conditions and could be outgassed only very slowly. Heating the exposed portions to decompose the ammonium carbonate only caused its accumulation in the stopcocks, from which it then could be dislodged only by washing.

[6] The detailed procedures employed in our work are described in the Ph.D. dissertation of Gerard Lepoutre, Yale Univrsity, 1953, and will only be summarized here.

[7] Our work at lower temperatures required only a slight modification of this cell, to be described in a subsequent paper.

usually sufficed to yield a thermal e.m.f. which subsequently showed less than 0.1% change in ten minutes. No evidence of any thermal diffusion effect has been observed. This is illustrated in Fig. 2 by the reproducibility of the data whether obtained on cooling or on subsequent warming after maintaining the maximum thermal difference for a period of about one hour. There may be a finite Soret effect in these solutions, but, if so, its attainment has been sufficiently retarded by the use of the capillary connection between the warm and cold sides of the thermocell as to render it inoperative.

The data from each run have been summarized by least squares fit of the Seebeck e.m.f. (E_s) to the function

$$E_s = A_0 + A_1\Delta T + A_2(\Delta T)^2 \tag{1}$$

Here A_1 represents the thermoelectric power of the solution at −33°, while $2A_2$ gives the Thomson coefficient, $d^2E_s/d(\Delta T)^2$. The A_0 term is at present not understood. It represents the voltage for zero temperature difference, which should, in principle, be zero. We call this the "parasitic e.m.f." but do not know its origin. Such a term might arise from a non-uniform concentration of the solution in the cell, but this seems highly unlikely since the solutions were thoroughly mixed prior to the thermal measurements. It might also arise because of slight differences in the nature of the platinum electrodes; if so, the differences are not permanent ones, for there seems to be no consistency to A_0, not even to the sign of the effect.

In most cases one preparation of metal was used to obtain data at four or five concentrations, the concentration of the solution being varied by one of the following methods: (1) addition or removal of measured amounts of ammonia, using buret F, the total metal content being kept constant; (2) removal of a portion of the solution through the capillary stopcock 9 into B with subsequent addition of ammonia to the solution remaining in C. The ammonia was added either from the solution in B or from the ammonia buret F. For the most part, method 1 was used with the concentrated solutions, method 2 for the dilute range. The method employed is implicit in the data reported in the tables below. If the quantity of sodium shown is the same as in the previous run (*e.g.*, 4b in Table I), method 1 was employed; if it is different, method 2 was used.

The concentration of the solutions was determined either by direct analysis after completion of a run or by measuring the conductance of the solutions and then comparing with Kraus' and our own conductance data.

In the direct analysis for sodium, the ammonia was distilled from the solution and the metal was then removed from the cell with absolute alcohol which was sucked into the cell through stopcock 9. The cell was then thoroughly rinsed with water and the alcohol and rinsings combined and evaporated to about one quarter their initial volume. (This removed alcohol and any residual ammonia which might still have been present.) The resulting solution was then titrated with standard acid to a methyl orange end-point. If method 2 was used for the dilution process, separate analyses were made on the residue in B and on the metal remaining in the cell. Proper care was taken to assure that the metal adhering to the tube walls and stopcock 9 was included in the portion removed.

Results and Discussion

Concentrated Solutions.—The results obtained in concentrated solutions are shown in Tables I and II and in Fig. 3. A number of qualitative results are immediately apparent. We observe first that the thermoelectric power of these solutions is of the order of magnitude characteristic of typical metals, 1–10 μvolts/degree. This of course is precisely what one would predict since the concentrated solutions show metallic properties in all other respects. We note also that the thermoelectric power increases monotonically as the concentration is decreased, indicating that conduction in these solutions is by means of electrons ("n" type conduction), a result previously always assumed but never conclusively demonstrated. Finally, we observe that the sodium and potassium solutions exhibit very similar behavior, again in accord with previous experience with these solutions.

TABLE I

THE THERMOELECTRIC POWER[a] OF SODIUM IN LIQUID AMMONIA–CONCENTRATED SOLUTIONS AT −33°

Run no.	Wt. NH_3, g.	Mmoles Na	Concn., moles Na/1000 g. NH_3	Thermoelectric power, μv./deg.	Thompson coefficient, μv./deg.²
F3-a	9.97	78.5	7.87	2.50	−0.00
F3-b	16.86	78.5	4.66	5.77	− .05
F4-a	10.12	108.4	10.70	-0.30_5	− .02
F5-a	9.90	103.7	10.47	-0.22_5	− .02
F5-b	13.40	103.7	7.72	2.68	− .04
F5-c	16.20	103.7	6.40	4.08	− .03
F5-d	8.65	39.65	4.58	5.67	− .04
F6-a	10.38	86.5	8.33	1.99_5	− .02
F6-b	8.89	83.5	9.40	1.11	− .02
F7-b	9.63	53.0	5.49	4.91	− .04
F7-c	13.74	53.0	3.85	6.78	− .05
F7-d	15.89	53.0	3.33_5	8.18	− .09
F7-e	18.69	52.7	2.81	9.95	− .13
F8-a	8.22	88.3	10.72	−0.43	− .04
F8-b	9.12	88.3	9.68	0.65	− .02
F9-a	8.91	19.20	2.15	16.6	− .11
F9-b	11.28	19.20	1.70_2	29.8	− .07
F9-c	14.53	19.20	1.32_1	57.0	− .04
F9-d	18.72	19.20	1.026	78.2	− .44

[a] The sign of the Seebeck voltage is taken as positive when the hot copper lead is positive, *i.e.*, when electrons tend to flow from hot to cold in the solution.

TABLE II

THE THERMOELECTRIC POWER OF POTASSIUM IN LIQUID AMMONIA–CONCENTRATED SOLUTIONS AT −33°

Run no.	Wt. NH_3, g.	Mmoles K	Concn., moles K/1000 g. NH_3	Thermoelectric power, μv./deg.	Thompson coefficient, μv./deg.²
K5-a	7.22	62.1	8.61	2.12	0.00
K5-b	6.30	62.1	9.87	1.48	+ .01
K5-c	8.16	62.1	7.62	2.75	− .01
K5-d	13.93	62.1	4.46	4.86	− .04
K6-a	6.48	35.6	5.49	3.99	− .02
K7-a	6.80	65.6	9.65	1.60	+ .01
K7-b	6.29	65.6	10.41	1.24	+ .02
K7-c	5.37	65.6	12.20	0.91	− .01
K7-d	7.08	65.6	9.29	1.82	+ .01
K7-e	7.20	65.6	9.12	1.89	+ .01
K7-f	7.97	65.6	8.23	2.40	+ .01
K7-g	8.85	65.6	7.41	2.86	+ .01
K7-h	10.17	65.6	6.46	3.40	− .01
K8-a	16.10	45.8	2.85	12.4	+ .02
K8-b	19.90	45.8	2.30	20.1	+ .03

A detailed quantitative theory of the thermoelectric power of these solutions is treated in a subsequent paper. It is shown there that the thermoelectric power in concentrated solutions, where the transference number of the positive ion is very small and the "solvation" of the electron is also small, may be well approximated by the theory of the thermoelectric power for pure metals. There are slight correction terms owing to the fact that since this is a two-component system, concentration gradients may be set up by the thermal diffusion process, but these are second-order corrections in concentrated solution.

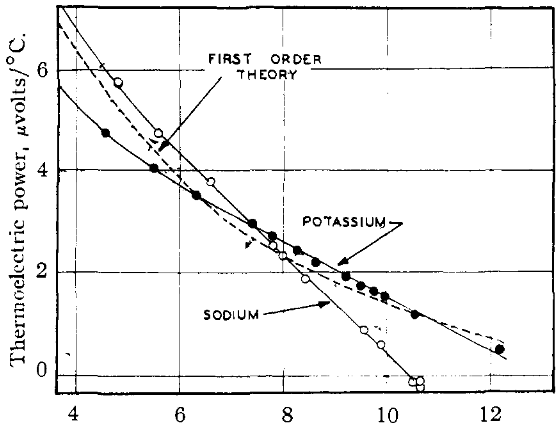

Fig. 3.—The thermoelectric power of concentrated metal-ammonia solutions at −33°.

Using an electron gas model and the Boltzmann collision equation one may derive an equation for the thermoelectric power of a thermocouple.[8]

$$\frac{\mathrm{d}E_{\mathrm{ab}}}{\mathrm{d}T} = \frac{\pi^2}{3} k^2T \left\{ \frac{1}{\mu_{0\mathrm{a}}} \left(1 + \frac{\mu_{0\mathrm{a}} l'_{0\mathrm{a}}}{l_{0\mathrm{a}}}\right) - \frac{1}{\mu_{0\mathrm{b}}} \left(1 + \frac{\mu_{0\mathrm{b}} l'_{0\mathrm{b}}}{\mu_{0\mathrm{b}}}\right) \right\} \tag{2}$$

If we make the approximation that $l' = 0$, that is, that the mean path of electrons is independent of their energy, this equation may be simplified to yield.

$$\frac{\mathrm{d}E}{\mathrm{d}T} = \frac{8m\pi^2}{3} \frac{k^2T}{h^2} \left(\frac{\pi V}{3N}\right)^{2/3} + \text{constant} \tag{3}$$

which gives us the concentration dependence of the thermoelectric power. This dependence is shown dotted in Fig. 3. We have assumed that the entire volume of the solution is available to the electrons[9] and have arbitrarily joined the theoretical curve to the sodium curve at 8 *m*. The agreement between the calculated and observed concentration dependence is remarkably good, considering all the approximations involved in the calculation.

This simple theory is, as one would expect, incapable of accounting for the detailed features of the thermoelectric power of the concentrated solutions. Explanation of the linear decrease in the thermoelectric power with concentration in the range from 4 to 11 *m* and the differences between sodium and potassium, for example, will surely require both a more accurate model and a more complete investigation of the irreversible effects.

Dilute Solutions.—The results obtained for sodium and potassium in dilute solution at −33° are shown in Fig. 4. We observe a monotonic increase in thermoelectric power with decreasing metal concentration. Below about 0.1 *M* the data for sodium are, within experimental error, essentially indistinguishable from the data for potassium. The variation is very closely logarithmic in the concentration, a behavior predicted both by the simple theory and by more detailed considerations. This behavior is in accord with the results of recent measurements on silicon and germanium[10] as well as with measurements on dilute aqueous solutions dating back to Richards' work[11] in the nineteenth century and continuing to the present day.[12,13]

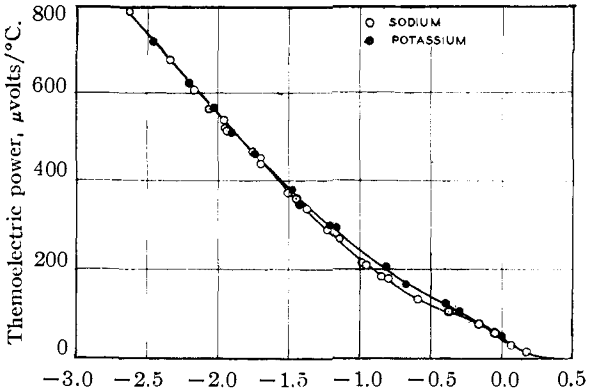

Fig. 4.—The thermoelectric power of dilute metal-ammonia solutions at −33°: ○, sodium; ●, potassium.

An apparent anomaly arises, however, when we consider the quantitative aspects of the logarithmic increase of the thermoelectric power with dilution, for the thermoelectric power rises just about twice as fast as all previous experimental work indicates it should. No such anomaly has been observed in measurements with thermocells of the type studied by Tyrell and Hollis.[13]

$$\underset{T_1}{\mathrm{Ag}\ |}\ \mathrm{AgNO_3}\ \underset{T_2}{|\ \mathrm{Ag}} \tag{5}$$

or with cells reversible to the anion such as

$$\underset{T_1}{\mathrm{Hg, Hg_2Cl_2}\ |}\ \mathrm{MCl}\ \underset{T_2}{|\ \mathrm{Hg, Hg_2Cl_2}} \tag{6}$$

which were studied by Richards.[11] The slopes of the thermoelectric power *vs.* $\log_{10} C$ curves approximate the theoretical value of 198 μv./degree quite well and the discrepancies are all in the opposite sense of our results. Tyrell and Hollis, for example, obtained slopes of 189, 188 and 180 μv./degree, using silver–silver nitrate electrodes and solutions of silver nitrate mixed with other metal nitrates. In no case is a slope greater than the theoretical value observed.

The anomaly is at present of uncertain origin. If one uses the equations for the thermoelectric power given by DeGroot[14] one would expect a logarithmic dependence of thermoelectric power with slope 198 μv./degrees in the dilute range of concentration corresponding to the concentration dependence of the entropy of electrons. In this region the entropy of electrons should rise approximately logarithmically with dilution and the heats of transfer should be essentially concentration independent. Furthermore, activity or association effects should operate on the entropy in the direction to make the discrepancy between theory and experiment even

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[8] J. E. Mayer and M. G. Mayer, "Statistical Mechanics," John Wiley and Sons, Inc., New York, N. Y., 1940, p. 414.

[9] It can be shown that this involves a relatively small error if the "excluded" volume can be approximated as a sphere of radius equal to or less than the N–H bond length.

(10) T. H. Geballe, personal communication.

(11) T. W. Richards, *Z. physik. Chem.*, **24**, 39 (1897).

(12) J. C. Goodrich, *et al.*, THIS JOURNAL, **72**, 4411 (1950).

(13) H. J. V. Tyrell and G. I. Hollis, *Trans. Faraday Soc.*, **48**, 893 (1952).

(14) DeGrott, "Thermodynamics of Irreversible Processes," North Holland Publishing Co., Amsterdam, 1951, p. 151.

larger. Effects of a pronounced ion–electron interaction of some sort seem to be indicated by our experiments with mixed metal–salt solutions which will be reported shortly. Present theoretical calculations indicate that perhaps the use of equation 4 is not justified. No alternative is yet at hand however so detailed consideration of the data in the dilute range of concentration will be postponed until a more adequate theory is available.

MURRAY HILL, N. J.

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF FLORIDA STATE UNIVERSITY AND THE SCHOOL OF APPLIED CHEMISTRY OF THE NEW SOUTH WALES UNIVERSITY OF TECHNOLOGY]

The Spectra and Structure of Dicobaltoctacarbonyl[1]

BY JOE W. CABLE,[2] RONALD S. NYHOLM AND RAYMOND K. SHELINE

RECEIVED FEBRUARY 12, 1954

The infrared spectrum from 2.5–15 μ and the visible and ultraviolet spectra from 2100–7000 Å. were obtained for dicobaltoctacarbonyl. The presence of a carbonyl frequency at 1858 cm.$^{-1}$ in the infrared spectrum and the peak at 2800 Å. in the ultraviolet spectrum indicate the presence of bridged carbonyls in the molecule. Four feasible structures with bridging carbonyl groups were proposed and critically examined. It was concluded that the most probable structure was that of two trigonal bipyramids joined at an edge.

Introduction

In recent years there has been a great amount of work done concerning the structures of the metal carbonyls. This class of compounds is particularly interesting to the structural chemist because of the wide variety of structure types which these compounds may assume. It was found[3] that in the case of $Fe_2(CO)_9$ the infrared spectrum revealed the presence of a bridged, ketone-type carbonyl, thus confirming the bridged structure previously proposed. A similar approach was taken in this study of dicobaltoctacarbonyl.

Experimental

(a) **Preparation of Sample.**—The $Co_2(CO)_8$ used in taking these spectra was received from Dr. Irving Wender of the Synthetic Liquid Fuels Division of the Bureau of Mines. Since the compound is unstable and oxidized by air, the samples were purified by vacuum sublimation immediately before use. The vacuum system was the usual high vacuum pump used in conjunction with a mercury diffusion pump. The sublimation was carried out at room temperature. It was found that the sample in this finely divided condition was oxidized very readily, and the solutions had to be made very quickly.

The *n*-hexane used as a solvent was obtained from Phillips Petroleum Company and was purified by the following procedure: 300 ml. of *n*-hexane was washed with 100 ml. of pyrosulfuric acid, then with six successive 100-ml. portions of water. The *n*-hexane was then dried over magnesium perchlorate, and distilled through a column of activated silica gel.

(b) **Infrared Spectrum.**—The absorption spectrum was taken on a Perkin-Elmer model-21 spectrophotometer using NaCl optics. The sample was run at room temperature in *n*-hexane solution with a cell thickness of 0.5 mm. The spectrophotometer was calibrated by obtaining the spectrum of water vapor in the air and checking the peaks recorded against standard values. These corrections have been applied to the reported values where necessary. The absorption curve is given in Fig. 1. This spectrum has been previously reported[4] and used as an analytical tool in a study of cobalt hydrocarbonyl. The values reported agree very well with those obtained in this study.

(c) **Visible and Ultraviolet Spectra.**—The visible and ultraviolet spectra were taken from 2100 to 7000 Å. on the Beckman DU spectrometer. Solutions of concentration 1.6 $\times 10^{-5}$, 1.6 $\times 10^{-4}$, 2.86 $\times 10^{-5}$ and 2.86 $\times 10^{-4}$ *M* in *n*-hexane were used.

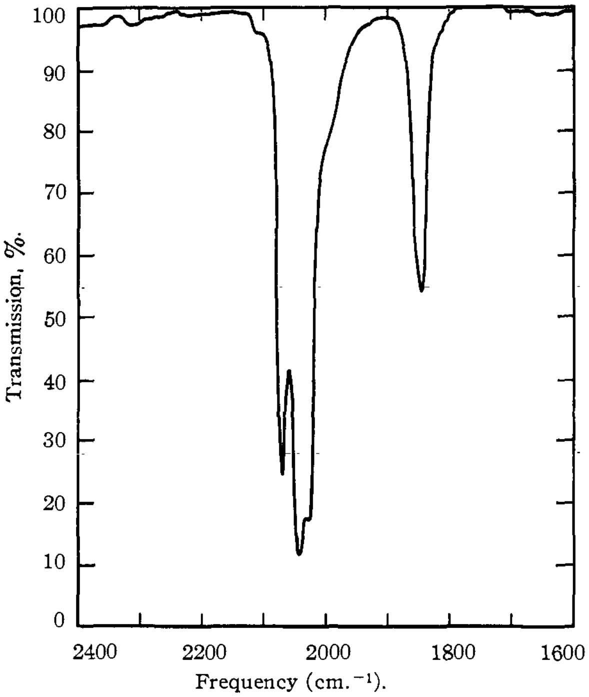

Fig. 1.—The infrared spectrum of $Co_2(CO)_8$. Those portions omitted showed negligible absorption in the rocksalt region.

Discussion

The infrared spectrum exhibits three strong carbon monoxide type carbonyl bands at 2070, 2043 and 2025 cm.$^{-1}$. In addition there is a strong band at 1858 cm.$^{-1}$ which indicates the presence of a ketone type carbonyl. The ultraviolet spectrum exhibits a curve sloping downward smoothly from an intense peak at a shorter wave length. There are two slight peaks; one at 2800 Å. with a molar extinction coefficient of 372 ± 64, and the other at 3520 Å. with a molar extinction coefficient of 315 ± 100. The peak at 2800 Å. is attributed to a forbidden $n \rightarrow \pi^*$ transition found in all saturated alde-

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[1] This investigation was partially supported by a research grant from the Office of Air Research under Contract No. AF 33(616)-368.

[2] From portions of a thesis submitted by J. W. C. to the Graduate School of the Florida State University in partial fulfillment of the requirements for the degree of Doctor of Philosophy.

[3] R. K. Sheline and K. S. Pitzer, THIS JOURNAL, **72**, 1107 (1950).

[4] H. W. Sternberg, *et al.*, *ibid.*, **75**, 2717 (1953).