Now, these constants could be calculated from our value of the free energy in the reaction $CO + S = COS$, and the equation given by Koref[1] for the dissociation of CS_2 as a function of the temperature, together with the free energy tables given by Lewis and Randall.[2] This calculation, which we shall not reproduce here, would lead to the conclusion that at the temperature of our experiments CO_2 and CS_2 would be present in larger amounts than COS. Koref used a heat of dissociation of CS_2 calculated from his own equilibrium measurements and this value would be largely affected by small errors in the degree of dissociation. That such errors were probable is evident from the fact that Koref made no allowance for the formation of CS, nor for such other substances as may be formed by heating CS_2.[3]

We may note, in passing, that the reaction $2COS = CO_2 + CS_2$ appears to be much more rapid than the reaction $CO + S = COS$ at the temperatures of our experiments.

Finally, although CS was not directly determined in any of our experiments, we may give an approximate estimate of the equilibrium constant in the reaction $CS_2 = CS + S_{\lambda\mu}$. Taking the amount of CS as equal to that of CO, we have $K_{575} = [CS]/[CS_2] = 0.004/0.08 = 0.05$.

Until more reliable calorimetric measurements are available we shall not attempt to reduce any of these results to standard temperature.

Summary.

When carbon monoxide and sulfur are heated together at 250° to 300° C., carbon oxysulfide, carbon dioxide, carbon disulfide and carbon monosulfide are formed by the reactions:

$$CO + S = COS;$$
$$2COS = CO_2 + CS_2;$$
$$CS_2 = CS + S.$$

The equilibrium in the first reaction was determined at 302° and less reliably at 260°. Approximate values were obtained for the equilibrium constants of the other two reactions.

BERKELEY, CAL.

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF CALIFORNIA.]

THE POTENTIAL OF THE RUBIDIUM ELECTRODE.

BY GILBERT N. LEWIS AND WILLIAM L. ARGO.

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The method used by Lewis and Kraus, and Lewis and Keyes for the determination of the electrode potential of sodium,[4] potassium[5] and

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[1] *Z. anorg. Chem.*, **66**, 73 (1910).

[2] THIS JOURNAL, **36**, 2468 (1914); and **37**, 458 (1915).

[3] See Arctowski, *Z. anorg. Chem.*, **8**, 314 (1895).

[4] THIS JOURNAL, **32**, 1460 (1910).

[5] *Ibid.*, **34**, 119 (1912).

lithium[1] seems at first sight inapplicable to the remaining two alkali metals, rubidium and cesium. That method consists in determining first the normal electrode potential of a dilute amalgam of the metal towards an aqueous solution of the ion of the metal, and second the difference in potential between the amalgam and the pure metal in a liquid amine solution of a salt of the metal in question. Potassium and sodium iodides were used in ethylamine and lithium iodide in propylamine. But rubidium iodide is so nearly insoluble in propyl and ethyl amines as to have no measurable electrical conductivity, while the metal rubidium is freely soluble in methylamine and ammonia. Rubidium amide was likewise found too little soluble in ethylamine and although there may be some rubidium salt of an oxygen acid which would dissolve more freely, such a salt would doubtless react with the metal.

Choice of Solvent: Preparation of Materials.

It seemed possible that by adding some inert solvent to ammonia a mixture might be obtained which would not dissolve rubidium but which would dissolve rubidium iodide sufficiently to permit measurements of electromotive force. Pentane was the first substance tried, but it was soon evident that neither this nor any similar substance would serve; for, although pentane and ammonia are miscible in all proportions, a small amount either of the iodide or of the metal sufficed to cause a separation into two liquid phases, and in the phase consisting chiefly of pentane neither iodide nor metal was dissolved to any measurable extent.[2]

Mixtures of ethylamine and ammonia were next investigated and found to offer an adequate, if not a completely satisfactory, solution of the problem. The solubility of both metal and iodide changes very markedly with small changes in the composition of the mixture. It was therefore necessary to prepare mixtures of accurately known composition. The anhydrous ethylamine was kept in a reservoir of the type described by Lewis and Kraus. The ammonia was kept in the form of a Divers solution (a saturated solution of ammonium nitrate in liquid ammonia), both the nitrate and the ammonia having been dried with great care. The two components of the mixed solvent were measured separately as vapors in bulbs of known volume at measured pressures, and were then condensed at a temperature of about —80° C. in the apparatus in which it was to be used.

In order to test roughly the conductivity of a saturated solution of rubidium iodide as a function of the composition of the solvent, a glass tube about 5 mm. in diameter with two platinum electrodes (about 0.5 sq. mm. in area and 5 mm. apart) was used. A small crystal of rubid-

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[1] THIS JOURNAL, 35, 340 (1913).

[2] Sodium and not rubidium was the metal used in this experiment.

ium iodide was placed in this cell, which was then exhausted while being heated nearly to the softening point of the glass. After cooling, the solvent was allowed to enter. A potential of 110 volts was then applied across the two electrodes and the current roughly determined. Table I gives the results of four such experiments.

TABLE I.

Mol per cent. ammonia..........	7.9	9.0	11.0	13.4
Amperes (with 110 v.)...........	0.0002	0.0005	0.0007	0.0015

Similar experiments were made to determine the solubility of rubidium, which could be estimated roughly from the color. The solvent containing 7.9 mol per cent. of ammonia gave a very pale blue solution which may be estimated to be not over 0.001 *M* with respect to the metal. With increasing percentage of ammonia the blue color becomes more intense and at 13.4 mol per cent. of ammonia a second liquid phase of metallic appearance is formed. Except in one case, the solvent containing 7.9 mol per cent. of ammonia was used in the following experiments:

The rubidium amalgam was prepared by the electrolysis of an aqueous solution of Kahlbaum's rubidium carbonate with a mercury cathode. The amalgam thus formed was freed from traces of water and solid impurities, and collected in an exhausted reservoir. According to two analyses, 1 g. of the amalgam contained 2.696×10^{-5} and 2.701×10^{-5} equivalents of rubidium. The average taken is 2.698×10^{-5}.

The metallic rubidium obtained from Kahlbaum was used in all but one of the experiments. In that one, the rubidium was prepared by distilling a mixture of metallic calcium and rubidium iodide in an evacuated quartz vessel.

All measurements were made in an oil thermostat at 25° C.

Electromotive Force of the Rubidium—Rubidium Amalgam Cell.

The first cell used was similar to the one used by Lewis and Kraus in the case of sodium. A small amount of rubidium iodide, carefully dried, was introduced into the cell which was then exhausted. The rubidium was introduced in the molten state through a fine capillary. The amalgam from its reservoir was allowed to run into the other side of the H cell and the mixed solvent was introduced as previously described. The solvent was found to be too rich in ammonia, since it not only formed a deep blue solution of rubidium but also produced a concentrated layer, of metallic appearance, over the rubidium electrode. The electromotive force of this cell was about 0.9 volt, but inconstant. We attempted to reduce the concentration of ammonia in the following manner: A side tube which had been added to the cell for the original condensation of the solvents was now cooled until a certain amount of ammonia, which is far more volatile than the ethylamine, was condensed in it. This tube was then sealed off and the cell being placed in the thermostat showed only a pale blue color. The electromotive-force readings then obtained are given in Table II (Cell 1). The gradual fall in potential which was noticed in this and all other cases is undoubtedly to be attributed in part to a slow increase in the concentration of the amalgam, which is due to a transference of the metal from the rubidium electrode through the solution.

In all the following experiments the solvent contained 7.9 mol per cent. of ammonia. Experiments with Cell 1 showed the desirability of producing a fresh surface of rubidium during the electromotive-force measurements. An arrangement similar in principle to a sodium press was therefore added to the cell. It is shown in Fig. 1. A heavy-walled glass tube (T) was drawn out to a capillary, also heavy-walled, and sealed into the top of one arm of the cell at (N). Over this tube was fitted a brass collar (C), threaded at the upper end to admit the screw (S). The rubidium was introduced and forced quickly down to the bottom of the tube to the position (R). A leather plug (L) and a brass rod (P) were then inserted. By turning the screw (S) any desired pressure within the limits of strength of the glass cylinder could be exerted evenly on the rubidium. Being quite soft at 25°, it flowed gradually through the capillary and emerged at the opening in the form of a bright "worm," free from oxide coating. For electrical connection a thin platinum wire was inserted through the chamber and a short distance into the capillary before the rubidium was introduced.

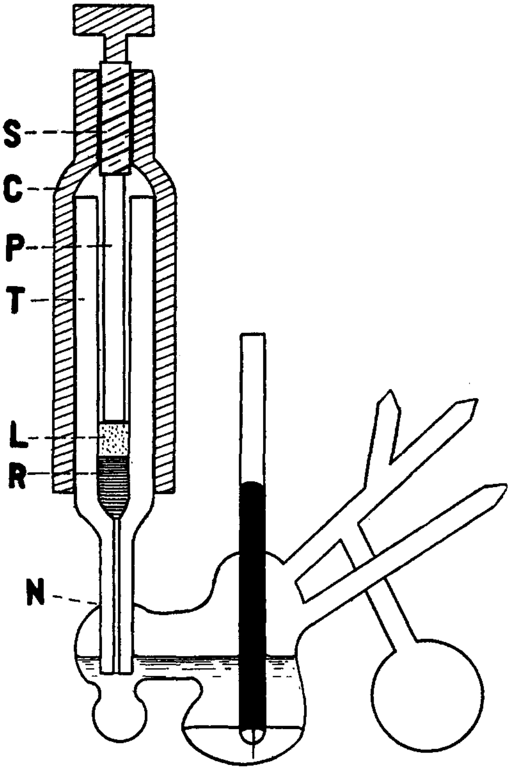

Fig. 1.

Cells 2 and 3 gave results which do not contribute much to our knowledge of the electromotive force in question, since in Cell 3 we know that during the manipulation a certain amount of metallic rubidium was carried into the amalgam,[1] and there was a strong suspicion that this was also the case with Cell 2. The effect of concentrating the amalgam is obviously to diminish the observed e. m. f. These cells, however, furnished valuable experience in manipulation and also offered an opportunity to determine the result of stirring the electrolyte, and of renewing the rubidium surface. It is for this reason that these cells are included in Table II. The cells were stirred before nearly every reading and the rubidium surface was renewed after readings 1 and 4 with Cell 2 and after reading 6 with Cell 3. The results show that little, if any, effect is produced by either of these changes.

After the experience gained with these cells, a new cell, No. 4, was filled and manipulated with great caution, and gave results so satisfactory that its electromotive force, which agrees with that obtained in Cell 1, may be confidently taken as the true electromotive force between rubidium and the rubidium amalgam. It is to be noted that Kahlbaum's rubidium was used in Cell 1 and our own preparation in Cell 4. Allowing for a possible slight diminution in electromotive force while the cell was being placed in the thermostat, we may take *1.0745 volts* as the final value. The last figure is probably not significant.

TABLE II.

Cell 1.		Cell 2.		Cell 3.		Cell 4.	
Time. (Min.)	E. (Volts.)	Time. (Min.)	E. (Volts.)	Time. (Min.)	E. (Volts.)	Time. (Min.)	E. (Volts.)
0	1.0742	0	(1.0695)	0	(1.0629)	0	1.0742
35	1.0735	2	(1.0697)	8	(1.0631)	5	1.0742
45	1.0736	25	(1.0695)	13	(1.0628)	8	1.0745
60	1.0733	35	(1.0696)	14	(1.0629)	10	1.0741
82	1.0732	100	(1.0697)	30	(1.0629)	12	1.0740
92	1.0731	175	(1.0694)	60	(1.0629)	14	1.0738
125	1.0724	190	(1.0700)	817	(1.0620)	25	1.0734
225	1.0720	203	(1.0693)	960	(1.0621)	30	1.0738
241	1.0719					31	1.0737
729	1.0685					33	1.0738
						35	1.0736

There may be some question as to the influence of the solubility of rubidium upon this electromotive force, but it is to be observed that the blue color did not extend completely from one electrode to the other, since the solution immediately above the amalgam was always colorless. We believe that the small amount of metal in solution produced no appreciable effect upon the initial electromotive force, especially as the concentration of rubidium was not the same in Cells 1 and 4, which gave the same e. m. f.

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[1] Owing to the extremely poor conductivity of the solution it was necessary to design the cell so that very little space intervened between the two electrodes.

The Normal Electrode Potential of the Rubidium Amalgam.

The potential of the rubidium amalgam in a 0.1 *M* aqueous solution of rubidium hydroxide was measured against the normal calomel electrode in the same type of apparatus as was used for the other alkali metals. The cell consisted of the chain, Rb amalgam, RbOH (0.1 *M*), RbCl (0.1 *M*), N. E. The rubidium hydroxide was prepared by treating some of the amalgam with pure water; the rubidium chloride, by mixing a solution of rubidium iodide with an ammoniacal solution of silver chloride, filtering, evaporating to dryness, and heating to drive off ammonium salts.

A device which has been developed in this laboratory, and which will be described in another place, allowed repeated renewals of the liquid junction between RbCl and RbOH. The amalgam surface, which also could be renewed at will, reacted far more rapidly than in the case of the amalgams of the other alkali metals. This may be an intrinsic property of rubidium amalgam, or it may be due to the greater difficulty of preparing pure salts owing to the small amount of the expensive material used.[1] After forming a new amalgam surface in the electrode chamber, the electromotive force would fall, slowly at first, and then more rapidly. During the first minute the change would amount to 0.1 to 0.2 millivolt. Two series of measurements were made several weeks apart and with different normal electrodes. These two series are given in Table III. Before each measurement both the amalgam surface and the liquid junction were changed. The measurements do not show as high a degree of constancy as might have been hoped for, but owing to the constantly changing conditions the variations are at a maximum, and we may therefore be sure that the average result, *2.1805 volts*, cannot be seriously in error.

Table III.

Series 1. E.	Series 2. E.		Series 1. E.	Series 2. E.
2.1810	2.1794		2.1802	2.1806
2.1800	2.1808		2.1805	2.1812
2.1796	2.1815		2.1804	2.1811
2.1802	2.1808		2.1805	2.1808
2.1806	2.1800		2.1805	2.1802
		Average,	2.1804	2.1806

Since the mobility of Rb^+ is almost exactly the same as that of K^+, the liquid potential RbOH (0.1 *M*), RbCl (0.1 *M*) may be taken the same as that of the corresponding junction with potassium salts, namely,

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[1] The extraordinary effect of small impurities in accelerating the reaction between an amalgam and an aqueous solution has been shown by Walker and Patterson, *Trans. Am. Electrochem. Soc.*, 3, 185 (1903); and by Lewis and Jackson, *Z. phys. Chem.*, 56, 198 (1906).

—0.0165 volt[1] at 25° C. Likewise, since it is the custom to neglect the potential KCl (0.1 *M*), KCl (1.0 *M*), we may neglect the equal potential RbCl (0.1 *M*), KCl (1.0 *M*). Thus, for the above cell without liquid potentials we would have Rb amalgam, RbOH (0.1 *M*) || N. E.; E = *2.1970.*

In order to calculate the potential of the rubidium amalgam against Rb^+ at (hypothetical) molal concentration, we shall assume the "corrected" degree of dissociation of RbOH (0.1 *M*), in the absence of any direct measurements, to be the same as that of KCl (0.1 *M*), namely 0.76.[2] We have, therefore, Rb amalgam, RbOH (0.1 *M*) || Rb^+ (1 *M*), Rb amalgam, E = —0.05915 log 0.076 = 0.0662 volt. Subtracting this from the above value we have Rb amalgam, Rb^+ (1 *M*) || N. E.; E = *2.1308 volts.*

Electrode Potential of Rubidium and of Lithium, Sodium and Potassium.

By combining the normal electrode potential of the rubidium amalgam with the difference in potential between rubidium and the amalgam we find Rb, Rb^+ (1 *M*) || N. E.; E = 2.1308 + 1.0745 = 3.2053 volts. We shall take, therefore, as the normal electrode potential of rubidium at 25° against the normal calomel electrode, *3.205 volts.*

There seems to be little hope at present of determining the potential of cesium by the same method, for in the solvents which we have investigated the metal is more soluble and the iodide less soluble than in the case of rubidium. We may therefore summarize at this point the results obtained for the four alkali metals.

In Table IV the second column gives the normal electrode potential measured against the normal calomel electrode. The values previously given for sodium and potassium were based upon the old international volt and upon the assumption that the degree of dissociation of NaOH (0.2 *M*) is 0.828 and that of KOH (0.2 *M*) is 0.830. We have recalculated these values in terms of the new international volt and on the assumption that the "corrected" degree of dissociation is the same as that of KCl (0.2 *M*), namely, 0.71. This assumption may not be entirely correct, but it gives the best estimate which is possible at present. The new value of the corrected degree of dissociation also changes the lithium potential by 0.0007 volt. The third column gives the normal electrode potentials of these elements against the normal hydrogen electrode taken as zero. This column is obtained by subtracting 0.2776 from the figures of the preceding column.[3] The potentials of the

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[1] See Lewis and Randall, THIS JOURNAL, 36, 1969 (1914).

[2] The corrected degrees of dissociation here employed differ slightly from those obtained by Lewis, THIS JOURNAL, 36, 1969 (1914). The revision of these values will be discussed in another paper.

[3] Lewis and Randall, *Loc. cit.*

alkali metals follow a curious order, namely, lithium, rubidium, potassium, sodium. It is interesting, however, to observe that this is the order of the heats of formation of the several ions in aqueous solution. In order to illustrate this fact the heat of formation of the chlorides of the four metals in aqueous solution are given in the last column.

TABLE IV.

	Potential against N. E.	Potential against hydrogen.	Heat of formation of chlorides.
Li	3.305	3.027	102000
Rb	3.205	2.928	101000
K	3.203	2.925	101000
Na	2.993	2.715	96000

The heat of formation of aqueous cesium chloride is given as 105,000 calories, and if this figure is correct we might predict the potential of cesium to be higher than that of any of the other alkali metals.

We wish to express our indebtedness to the Bache Fund of the National Academy for financial aid in this series of investigations.

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[CONTRIBUTION FROM CHEMICAL LABORATORY, BRYN MAWR COLLEGE.]

A STUDY OF ALCOHOLIC SOLUTIONS OF CADMIUM IODIDE.

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I. Conductance.

The data for the conductance of cadmium iodide in alcoholic solutions was found to be very meager. Zelinsky and Krapiwin,[1] and Jones and Carroll,[2] measured the conductance of various solutions of cadmium iodide with methyl alcohol as the solvent, but there is great disagreement between the two sets of values, and when plotted neither set gives a smooth curve. Jones and Carroll[2] also measured the conductance of cadmium iodide with ethyl alcohol as the solvent. As far as recorded, only one series of measurements was made in each case. It therefore seemed advisable to redetermine the conductance of cadmium iodide in methyl and ethyl alcoholic solutions.

In the work, the results of which are here given, extreme care was taken to avoid, as far as possible, all known sources of error. The purest cadmium iodide obtainable was powdered and allowed to stand in a desiccator over phosphorous pentoxide for several days. The alcohols were dehydrated over pure lime for several weeks and then distilled, using a fractionating column and collecting in a dry receiver protected from the gases and moisture of the atmosphere by means of a soda-lime tube. The boiling point of the ethyl alcohol was 77.3° at 743.1 mm. and the boiling point

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[1] *Z. physik. Chem.*, **21**, 35–52 (1896).

[2] *Bull. Carnegie Inst.*, **80**, 41–73 (1907).