rich in carbonate gave solids which analyzed at 99.89 and 99.91% of K_2SO_4, respectively, after correction for the small amount of adhering solution; from this we conclude that the direction of the tie lines was influenced by a small systematic error in the analytical work and that solid solution does not occur in the system at 25° to a measurable extent.

Summary

The solubility of potassium carbonate and potassium sulfate in the ternary system with water at 25° has been measured. Solid solution has not been found to occur.

NEW YORK CITY

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

A GENERAL METHOD OF MEASURING THE PARTIAL PRESSURE OF MERCURY AT ROOM TEMPERATURES

BY L. L. HIRST AND A. R. OLSON

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Two methods of determining the activities of amalgam constituents have been used. In the first of these methods the calculation is based on measurements of the electromotive forces of concentration cells. This method has been used successfully in investigating a number of amalgams. In some cases, however, a serious difficulty is encountered. Thus with cesium and barium amalgams, no liquid is known which dissolves enough of the salt to make the liquid sufficiently conducting, and which at the same time is unreactive enough so that no side reactions occur with the metal. In the second method, vapor pressures of amalgams have been measured at high temperatures. The data so obtained must be extrapolated to 25° in order to be used in connection with other data. Because of these difficulties, we have devised a general method of obtaining the partial pressures of mercury over any amalgam at room temperatures.

When light from a mercury arc under properly controlled conditions falls on mercury vapor, the resonance line 2536 Å. is absorbed according to the equation $I = I_0e^{-\alpha pd}$, in which I is the intensity of the transmitted light, I_0 is the intensity of the incident light and α, p and d are the absorption coefficient, the pressure of mercury and the thickness of the absorbing gas layer. If α were a constant, we could determine p directly by measuring the quantity I/I_0. However, it has been shown by Hughes and Thomas[1] that α is not a constant even when a mercury resonance lamp is substituted for the mercury arc. α is also affected by the pressure of foreign gas even though these gases themselves have a negligible absorption for this line. Fortunately it was possible to determine p without evaluating α.

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[1] Hughes and Thomas, *Phys. Rev.*, **30**, 466 (1927).

In the work of Olson and Meyers[2] it was shown that if mercury resonance radiation falls on a mixture of hydrogen, ethylene and mercury vapor, a reaction occurs which results in a pressure decrease. It was further shown that this reaction was sensitive only to the resonance line (somewhat broadened due to the presence of gases). This reaction, therefore, can be used to measure the amount of mercury resonance light falling on it in a given time.

The experimental arrangement of our apparatus is shown in Fig. 1. Light from the mercury arc X was passed through the absorption cells A,A′ and then into the reaction chambers R,R′. The shield S was used to limit the region of the arc from which light could come. The arc was water cooled and subjected to a magnetic field in the usual way. The absorption chambers were connected to side tubes TT′ in which mercury or amalgam could be placed and kept at any desired temperature, and also to the vacuum line so that they could be evacuated or specific gases at known pressures admitted. The reaction chambers were connected to the vacuum line through the stopcocks H and E. They were also connected to the two sides of the differential pressure gage which we have already described.[3] During these experiments the above apparatus with the exception of the arc and the side tube T′ was kept in a water thermostat at a temperature of 26.0 ± 0.02°.

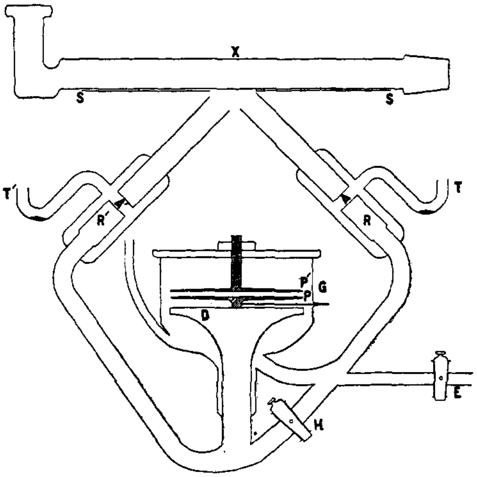

Fig. 1.

The reaction chambers were filled with a mixture of 93 mole % of hydrogen and 7 mole % of ethylene and saturated with mercury vapor. Stopcocks H and E were then closed. Pure mercury was placed in the side tubes TT′ together with 10 cm. of hydrogen. The temperature of the mercury in T′ varied from liquid air temperatures to the thermostat temperature. Light from the arc was then permitted to pass through the absorption cell A, and the time required to produce a given pressure change in R was noted. The light was next passed through A′ for a long enough time to produce the same pressure change in R′. This was repeated a number of times and the average rate for each side was calculated. The average rate was necessary in order to minimize the error due to fluctuations in the arc. The change of composition of the reacting mixture was small, for the gage was sensitive to small pressure changes. Even if it had been large, it would have introduced no error for the change was the same in both R and R′. The temperature of T′ was then changed, and the above process repeated. The rate of reaction in R decreased with time due to a gradual blackening of the lamp walls, and so the average rates in R′ were corrected by the factors necessary to make the rates in R constant. The following table will serve to show how the experimental data were treated.

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[2] Olson and Meyers, This Journal, **48**, 389 (1926).

[3] Olson and Hirst, *ibid.*, **51**, 2378 (1929).

TABLE I

TREATMENT OF EXPERIMENTAL DATA

R at 26°, rate div./min.	10	9	9.7	9.6	9.8	9.0	9.0	8.6	9.4
R' at 0°, rate div./min.	26.0	24.0	26.5	26.0	25.5	24.5	25.5	26.5	26.0

R at 26°, rate div./min.	8.9	9.0	8.6	8.2	9.2	9.8	Av.	9.2
R' at 0°, rate div./min.	25.0	24.5	25.0	25.0	25.5	..	Av.	25.4

Standard rate for R = 12.3. Therefore corrected rate for R' = (12.3/9.2) × 25.4 = 34.0.

Table II lists all of the corrected average rates.

TABLE II

CORRECTED AVERAGE RATES

Temp., °C.	88	273.1	277.9	282.8	287.0	291.1	299.1
Av. rate div./min.	43.0	34.0	31.3	27.0	21.6	16.9	12.3
Press. Hg, cm. × 10^5	0	1.98	3.20	4.92	7.36	10.72	20.1

The vapor pressures of mercury in the last line of Table II were calculated by the equation of Randall and Langford[4] for the free energy of mercury. In Fig. 2 we have plotted the average rate against the mercury pressure in the absorption cell A′.

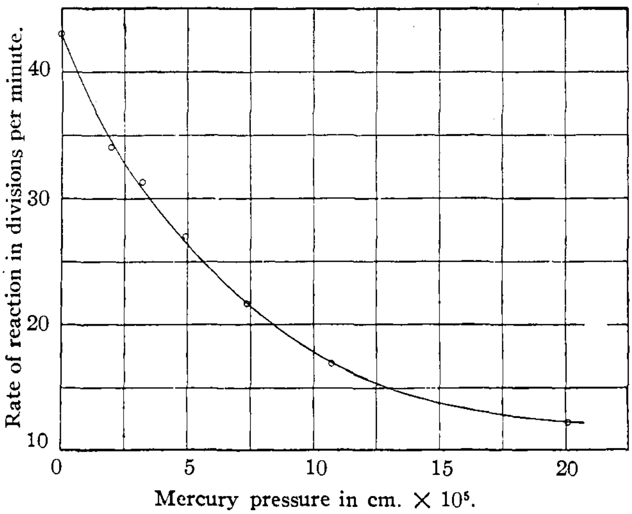

Fig. 2.

Thallium amalgams were then substituted for pure mercury in T′, and kept at the temperature of the thermostat. The rate of change of pressure with time was determined as before. The amalgams were analyzed by the method of Richards and Daniels.[5] The pressure of mercury corresponding to each rate was then obtained from the curve in Fig. 2. From

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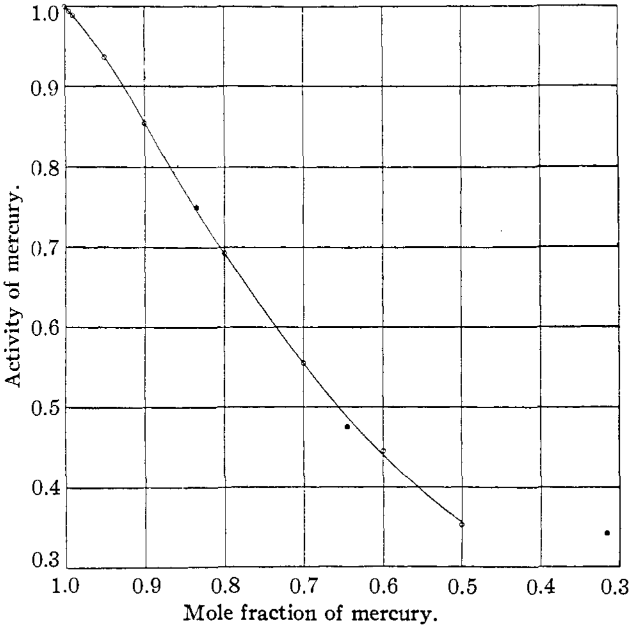
[4] Randall and Langford, unpublished work.

[5] Richards and Daniels, THIS JOURNAL, **41**, 1731 (1919).

these pressures and the pressure of pure mercury at 26°, the activities of the mercury in the amalgams were calculated. Table III summarizes these measurements and calculations. The activity of mercury is plotted in Fig. 3, together with the activity calculated from the electromotive force measurements of Richards and Daniels.[6] It is to be noted that the most concentrated amalgam is a solid.



○, Richards and Daniels; ●, Hirst and Olson.

Fig. 3.

TABLE III

VAPOR PRESSURE AND ACTIVITIES OF THALLIUM AMALGAMS AT 26°

N_1	1.000	0.835	0.644	0.316
Av. rate	12.3	13.6	18.3	22.5
Press. Hg, cm. × 10^5	20.1	15.15	9.6	6.9
Activity	1.000	0.755	0.477	0.344

It was mentioned above that hydrogen was admitted to the absorption cells. This was necessary in order to make the breadth of the absorption line of mercury about equal to that of the mercury in the reaction chambers. The pressure of hydrogen necessary to do this was determined by measuring the reaction rates for a given pressure of mercury and variable pressures of hydrogen in the absorption cell. Figure 4 shows the depen-

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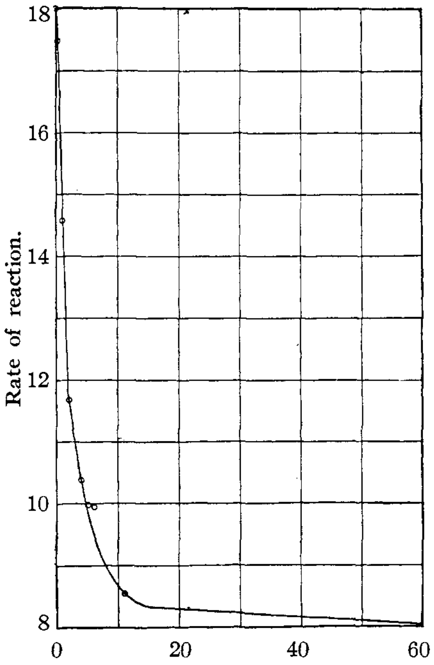
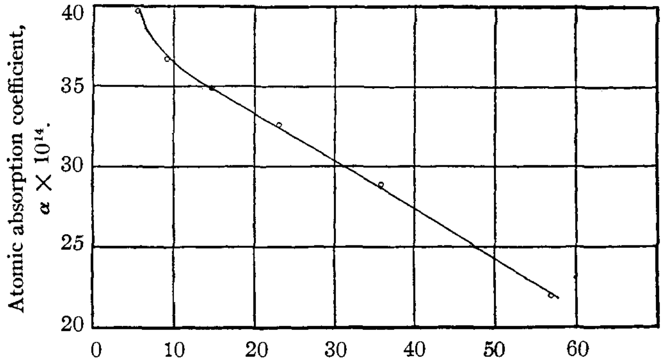
[6] Lewis and Randall, "Thermodynamics and the Free Energy of Chemical Substances," McGraw-Hill Book Co., Inc., New York, 1923, p. 270.

dence of the rate on the hydrogen pressure. A slow rate corresponds to a large absorption in the cell. This is the condition for high sensitivity with respect to mercury pressure in the absorption cell. The curve is practically horizontal at 10-cm. pressure; a further increase of hydrogen pressure would slow up the establishment of equilibrium and a decrease would make the method less sensitive to changes in mercury pressure.



Pressure of hydrogen, cm.

Fig. 4.



Number of mercury atoms per cc. $\times 10^{-12}$.

Fig. 5.

From the known pressures and rates as plotted in Fig. 2, it is possible to calculate an average atomic absorption coefficient form ercury at various pressures when subjected to a pressure of 10 cm. of hydrogen. This calculation has been made and the results are plotted in Fig. 5. The absorption coefficient shows the same type of variation that was noted by Hughes and Thomas[1] for pure mercury under its own vapor pressure.

Conclusion

The vapor pressures of mercury over thallium amalgams at 26° have been determined. From these the activities have been calculated and shown to agree reasonably well with those calculated from the electromotive force measurements of Richards and Daniels. The broadening of the absorption line of mercury by hydrogen for its own resonance light has been studied, and the change in the atomic absorption coefficient of mercury in the presence of hydrogen for its resonance line has been determined.

BERKELEY, CALIFORNIA

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF BROWN UNIVERSITY]

STUDIES RELATING TO METHYL TIN DERIVATIVES. I. INTRODUCTION. II. ACTION OF ZINC ON TRIMETHYL TIN BROMIDE. III. TRIMETHYL TIN PHENOLATE. IV. DECAMETHYLSTANNOBUTANE

BY CHARLES A. KRAUS AND ARTHUR M. NEAL

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I. Introduction

The heavier elements of the fourth group are, in many respects, analogous to carbon. Various hydrides of these elements have been prepared and their properties have been found to correspond fairly closely with those of corresponding carbon compounds. The stability of the hydrides decreases with increasing atomic number, so that their study is not generally practicable. We have but few radicals of these elements corresponding to methyl, ethyl, phenyl, etc.

However, if the hydrogen atoms attached to an element, such as tin, are substituted by alkyl or aryl groups, radicals are obtained whose properties correspond closely to those of similar carbon radicals. Thus the group $(C_6H_5)_3Sn$, or triphenylstannyl, bears a close physical and chemical resemblance to triphenylmethyl, $(C_6H_5)_3C$. In the case of most carbon compounds, the tendency of two unsaturated carbon atoms to combine with each other is so great that stable coupling occurs and the group becomes inactive. On the other hand, in the case of the corresponding tin compounds, the coupling is relatively weak and the groups exhibit marked reactivity.