and the results were compared with the values directly observed. The agreement is sufficiently good to indicate that these constants may now be considered as fairly well known, and affords striking support to Professor Ikeda's considerations concerning quasi-ideal solutions.

The present study was carried out under the kind guidance of Professor K. Ikeda, to whom my best thanks are due. Moreover, I express my thanks to Professor T. W. Richards for his valuable suggestions.

TOKYO, JAPAN.

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[CONTRIBUTION FROM THE CHEMICAL INSTITUTE OF THE SCIENCE COLLEGE, IMPERIAL UNIVERSITY OF TOKYO.]

# ON THE SYSTEM BENZENE-CARBONDISULFIDE.

BY JITSUSABURO SAMESHIMA.

Received April 9, 1918.

There are a great many cases in which solutions do not obey the criteria of ideal solutions, even when both components are considered to be normal substances and no chemical reaction takes place between them. When a solution is ideal no heat and volume changes occur on mixing. Furthermore, the vapor pressure of the solution should be equal to the sum of the partial vapor pressures of both components, which is calculated as the product of the molar fraction of the component in solution and the vapor pressure of that component in pure state. But in actual cases, most solutions deviate more or less from the above conditions. In order to discover whether there is any relation between the total energy change and free energy change occurring on mixing, I have carried out the vapor pressure measurement of binary mixtures.

## Materials.

**Benzene.**—Chemically pure material from Merck was dehydrated over calcium chloride and frozen twice. The substance thus obtained had the melting point 5.4–5.5°. By fractionation it gave the boiling point 80.05–80.08° under 760 mm. pressure. The specific gravity was 0.87345 at 25°.

**Carbondisulfide.**—Commercially pure material was allowed to stand over calcium oxide and then distilled. The distillate was well shaken with potassium permanganate powder, and decanted over metallic mercury and mercuric sulfate and again well shaken. Finally, it was fractionated over metallic mercury. The boiling point was 46.27–46.31° under 760 mm. pressure, and the specific gravity was 1.25585 at 25°.

## Vapor Pressures.

The method of vapor-pressure measurement was the same as described in the previous paper. The vapor pressures of the mixtures of benzene and carbondisulfide were as follows:

TABLE I.

Vapor Pressures of Benzene-Carbondisulfide Mixtures at 20°.

| Molar fraction of benzene in solution. | Total pressure. Mm. | Molar fraction of benzene in vapor. | Partial press. of benzene. Mm. | Partial press. of carbon-disulfide. Mm. | A. Calorie. |
|---|---|---|---|---|---|
| 0 | 297.4 | 0 | 0 | 297.4 | 0 |
| 0.1135 | 277.2 | 0.0484 | 13.4 | 263.8 | 30.16 |
| 0.2482 | 253.5 | 0.1002 | 25.4 | 228.1 | 53.22 |
| 0.3747 | 232.4 | 0.1461 | 34.0 | 198.4 | 64.47 |
| 0.4624 | 215.7 | 0.1848 | 39.9 | 175.8 | 66.66 |
| 0.6251 | 181.9 | 0.2763 | 50.3 | 131.6 | 60.76 |
| 0.8780 | 110.9 | 0.6161 | 68.2 | 42.5 | 27.88 |
| 1.0 | 75.2 | 1.0 | 75.2 | 0 | 0 |

TABLE II.

Vapor Pressures of Benzene-Carbondisulfide Mixture at 25°.

| Molar fraction of benzene in solution. | Total pressure. Mm. | Molar fraction of benzene in vapor. | Partial press. of benzene. Mm. | Partial press. of carbon-disulfide. Mm. | A. Calorie. |
|---|---|---|---|---|---|
| 0 | 361.1 | 0 | 3.5 | 361.1 | 0 |
| 0.0211 | 356.2 | 0.0097 | 7.1 | 352.7 | 0 |
| 0.0468 | 351.2 | 0.0202 | 16.0 | 344.1 | 0 |
| 0.1153 | 337.4 | 0.0474 | 24.0 | 321.4 | 29.11 |
| 0.1824 | 323.1 | 0.0744 | 24.2 | 299.1 | 41.55 |
| 0.1886 | 322.1 | 0.0752 | 35.1 | 297.9 | 41.62 |
| 0.3002 | 298.7 | 0.1175 | 48.2 | 263.6 | 54.54 |
| 0.4388 | 266.9 | 0.1808 | 53.7 | 218.7 | 63.27 |
| 0.4986 | 251.1 | 0.2137 | 59.8 | 197.4 | 62.95 |
| 0.5738 | 233.6 | 0.2561 | 63.5 | 173.8 | 62.44 |
| 0.6302 | 220.1 | 0.2886 | 75.3 | 156.6 | 57.19 |
| 0.7663 | 177.8 | 0.4233 | 83.8 | 102.5 | 42.67 |
| 0.8714 | 144.0 | 0.5818 | 89.5 | 60.2 | 26.59 |
| 0.9419 | 117.4 | 0.7627 | 94.9 | 27.9 | 11.21 |
| 1.0 | 94.9 | 1.0 | .. | 0 | 0 |

TABLE III.

Vapor Pressures of Benzene-Carbondisulfide Mixture at 30°.

| Molar fraction of benzene in solution. | Total pressure. Mm. | Molar fraction of benzene in vapor. | Partial press. of benzene. Mm. | Partial press. of carbon-disulfide. Mm. | A. Calorie. |
|---|---|---|---|---|---|
| 0 | 434.6 | 0 | 0 | 434.6 | 0 |
| 0.0800 | 413.1 | 0.0355 | 14.7 | 398.4 | 20.78 |
| 0.2286 | 378.9 | 0.0945 | 35.8 | 343.1 | 48.16 |
| 0.3723 | 340.8 | 0.1564 | 53.3 | 287.5 | 60.28 |
| 0.6516 | 259.1 | 0.3151 | 81.6 | 177.5 | 52.32 |
| 0.8845 | 169.5 | 0.6333 | 107.3 | 62.2 | 23.78 |
| 1.0 | 119.3 | 1.0 | 119.3 | 0 | 0 |

These relations are shown in Figs. 1, 2 and 3.

## Theoretical Discussion.

We denote:

$X$ = molecular chemical potential.

$X_0$ = molecular thermodynamic potential in the isolated state.

$p$ = partial pressure.
$p'$ = calculated partial pressure when the solution is looked upon as an ideal solution.
$x$ = molar fraction of the first component.
$P$ = vapor pressure of the component in the isolated state.

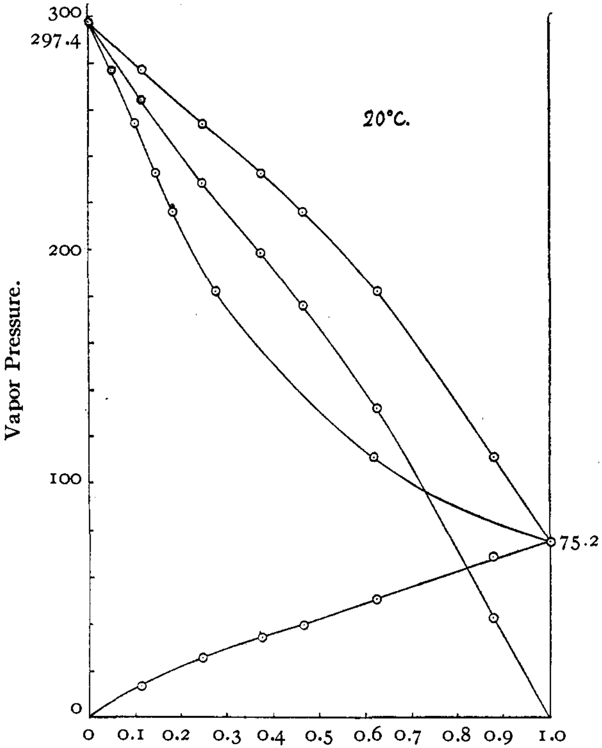

Fig. 1.

Suffix 1 represents the value relating to first component and 2 the second component. If the solution satisfies the criteria of the ideal solution, then the molecular chemical potential of the first component in that solution is expressed by the following equation:

$$X_{\text{ideal}} = X_o + R\,T\,ln\,(p_1'/P_1)$$

In the actual case, however, the solution does not obey the conditions of ideal solution, and the equation of molecular chemical potential passes into the following form:

$$X_{\text{actual}} = X_o + RT\,ln\,(p_1/P_1)$$

Therefore, the difference of free energy between ideal and actual case is given by the equation

$$x(X_{\text{ideal}} - X_{\text{actual}}) = xRT\ (ln\ (p_1'/P_1) - ln\ (p_1/P_1)) \\ = xRT\ ln\ (p_1'/p_1).$$

Similarly, in the second component it becomes

$$(1 - x)\ RT\ ln\ (p_2'/p_2).$$

Thus, the deviation of the solution from ideal one is

$$xRT\ ln\ (p_1'/p_1) + (1 - x)\ RT\ ln\ (p_2'/p_2) = A.$$

Evidently, the relations exist:

$$xP_1 = p_1' \quad \text{and} \quad (1 - x)P_2 = p_2'$$

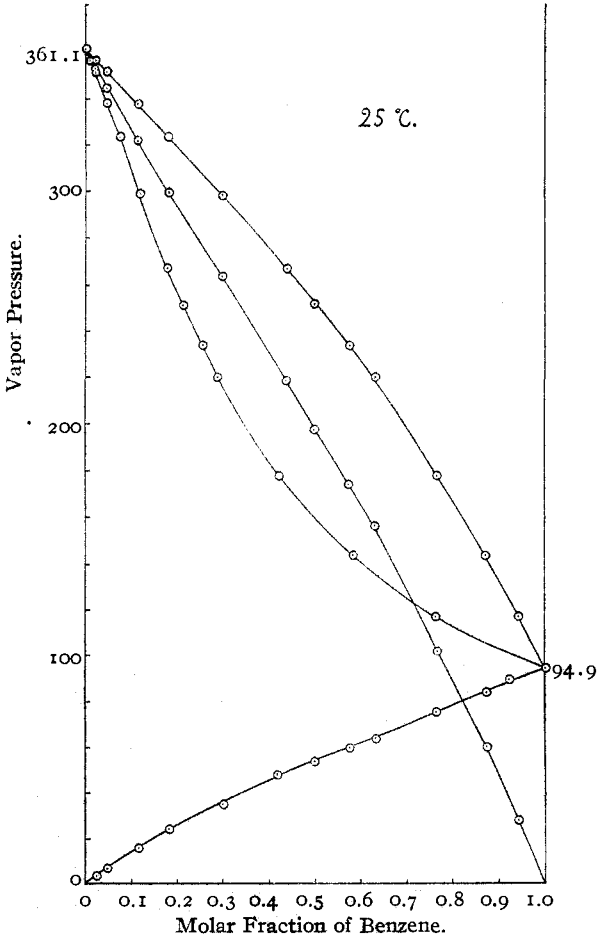

Fig. 2.

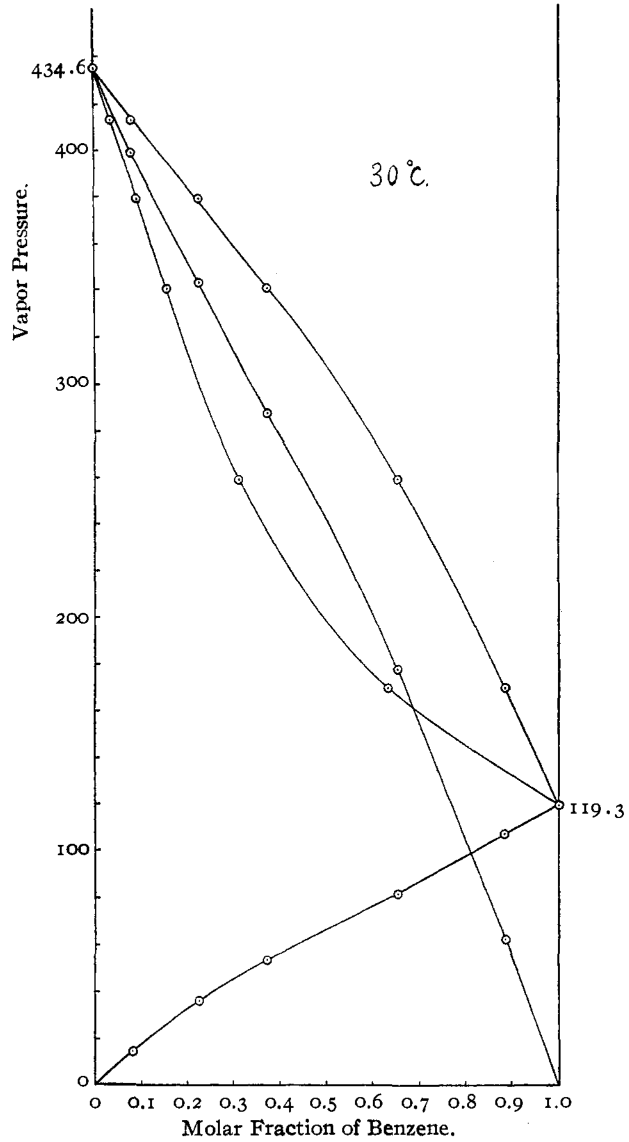

Fig. 3.

If the quantities $p_1$ and $p_2$ corresponding to every value of $x$ are obtained, we can calculate $A$ by the above equations. The results thus calculated have just been shown in Tables I, II and III. Values of $A$ and $q$ at 25° are compared in Table IV.

TABLE IV.

Change of Free Energy and Heat of Mixing at 25°.

| Molar fraction of benzene. $x$. | $A_{\text{calorie}}$. | Heat of mixing $q$. Calorie. | $q/A$. |
|---|---|---|---|
| 0.0975 | 25.4 | 54.2 | 2.13 |
| 0.1616 | 37.8 | 81.1 | 2.15 |
| 0.2741 | 52.7 | 111.2 | 2.11 |
| 0.3771 | 61.0 | 129.2 | 2.12 |
| 0.4776 | 64.0 | 134.9 | 2.11 |
| 0.7980 | 38.1 | 80.8 | 2.12 |

The values of $A$ in second column have been obtained by interpolation on the $x$ — $A$ curve which is constructed by means of the data given in Table II. The third column is the value of $q$, the heat of mixing for one mol of solution at 25° obtained by H. Hirobe.[1] It is to be observed that the ratio $q/A$ is constant for all values of $x$ as shown in the fourth column. It appears, then, that there is a comparatively simple relation between heat of mixing and loss of free energy. Regretfully, however, I was not able to continue this study longer, and could not decide the general relation between them.

I express my heartfelt thanks to Professor K. Ikeda for his kind guidance during this investigation.

TOKYO, JAPAN.

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF PRINCETON UNIVERSITY.]

# A STUDY OF THE OCCLUSION OF HYDROGEN AND OXYGEN BY METAL ELECTRODES.

BY EARLE A. HARDING AND DONALD P. SMITH.

Received June 26, 1918.

The purpose of the present study was to confirm and extend observations recently reported[2] upon the changes of electrical resistance which result from the cathodic occlusion of hydrogen by small palladium wires. The most important observation of the previous investigation was a continued increase in the electrical resistance of palladium-hydrogen after electrolysis had been interrupted, and a relation between the current strength and the steady value of resistance attained during electrolysis. In the present experiments the observations upon the changes produced in the electrical resistance of palladium wires and ribbons have been supplemented by measurements of the accompanying changes of length, by studies upon the corresponding effects of oxygen occlusion, and by some similar experiments upon wires of platinum, tantalum, and iron.

## Experiments with Palladium.

The experiments upon palladium, which constitute the greater part of those to be described, involved simultaneous measurements of electrical

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[1] The paper has not yet been published.

[2] THIS JOURNAL, 38, 2577 (1916).