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## Adsorption of Carbon Dioxide and Hydrogen on Bare and Oxygen-covered Silver Surfaces

BY LEONARD C. DRAKE AND ARTHUR F. BENTON

As part of a continuing study of the correlation between adsorption and catalytic activity of noble metals,<sup>1</sup> it was found by Benton and Drake<sup>2</sup> that silver surfaces may take up oxygen not only in the form of (1) low-temperature physical adsorption, but under suitable conditions also as (2) activated adsorption (or chemisorption) and (3) silver oxide. As a further step in the program we report herewith measurements of the adsorption of carbon dioxide and hydrogen by surfaces of free silver and by such surfaces carrying more or less chemisorbed oxygen or silver oxide. Hydrogen is only slightly adsorbed by any of these surfaces. Carbon dioxide shows only physical adsorption on bare silver; on oxygen-covered silver it may be adsorbed either physically or "chemically"; on oxide-covered surfaces it may be taken up not only in these two ways but also as carbonate. It has been possible definitely to distinguish these several processes and to measure their equilibria or rates.

### Method and Materials

The apparatus, previously described,<sup>2b</sup> determined adsorptions by comparison of the quantities of the desired gas and of helium, respectively, necessary to fill the bulb containing the adsorbent at the same temperature and pressure. Owing to the possibility of a slight adsorption of helium itself at  $-183^{\circ}$ , the free space at this temperature was obtained by calculation from the experimental values at each of the higher temperatures. The excellent agreement of the values thus calculated shows that helium was not measurably adsorbed down to  $-79^{\circ}$ .

The two silver samples Ag<sub>I</sub> (39.4 g.) and Ag<sub>II</sub> (45.86 g.) were the same as those previously studied with oxygen.<sup>2b</sup> Carbon dioxide was prepared by thermal decomposition of pure sodium bicarbonate followed by drying with "Dehydrite." Frequent tests showed that the gas was completely absorbed by sodium hydroxide solution. Electrolytic hydrogen was purified by repeated passage back and forth over heated platinized asbestos and "Dehydrite."

Between experiments with carbon dioxide or hydrogen the adsorbent was evacuated at  $300^{\circ}$ . After each experiment with oxygen the silver was gradually heated to  $300^{\circ}$  in a hydrogen atmosphere and then evacuated; the treatment with hydrogen was usually repeated once more.

(1) Benton and Elgin, (a) *THIS JOURNAL*, **48**, 3027 (1926); (b) *ibid.*, **49**, 2426 (1927); (c) *ibid.*, **51**, 7 (1929); Benton and Bell, *ibid.*, **56**, 59 (1934).

(2) Benton and Drake, (a) *ibid.*, **54**, 2186 (1932); (b) *ibid.*, **56**, 255 (1934).

All adsorbed volumes are given in cc. at  $0^{\circ}$ , 760 mm., taken up by the total weight of sample.

### Adsorption on Bare Silver

**Carbon Dioxide.**—Neither sample showed any measurable adsorption of this gas at  $175^{\circ}$ . Curves 2 and 4 of Fig. 1 give the results obtained with Ag<sub>I</sub> at  $-78.5^{\circ}$  and  $0^{\circ}$ , respectively, while the Curves 1 and 3 are for Ag<sub>II</sub> at the same two temperatures. Each curve was redetermined at least once, with results essentially identical with those shown. In all cases equilibrium was practically instantaneous as long as solid carbon dioxide had not been allowed to form. Moreover,

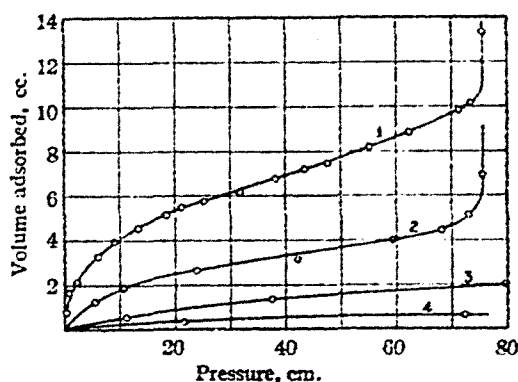


Fig. 1.—Adsorption of carbon dioxide: Ag<sub>I</sub>, Curve 2,  $-78.5^{\circ}$ ; Curve 4,  $0^{\circ}$ . Ag<sub>II</sub>, Curve 1,  $-78.5^{\circ}$ ; Curve 3,  $0^{\circ}$ .

the results at a given temperature were the same regardless of whether the experiment was conducted entirely at this temperature, or whether the gas was first introduced at higher or lower temperatures. These facts, together with the shape of the isotherms, furnish clear evidence that the adsorptions are of the physical type. By comparison of experimental points at one temperature with interpolated points at the other, the following heats of adsorption were calculated: for Ag<sub>I</sub>, 4.1 and 4.6 kcal. for adsorptions of 0.32 and 0.63, respectively; for Ag<sub>II</sub>, 5.9, 5.6 and 5.0 kcal. for adsorptions of 0.79, 1.68 and 2.12 cc. In our opinion the precision of the measurements does not justify the conclusion that the heat of adsorption is different for the two samples, or varies with the amount adsorbed. The aver-

age value,  $5.0 \pm 0.5$  kcal., is about 1.3 times the heat of vaporization of liquid carbon dioxide. For other cases of physical adsorption this ratio has commonly been found to lie between about 1.5 and 2.

With  $\text{Ag}_I$  at  $-78.5^\circ$ , after solid carbon dioxide had been allowed to form by raising the pressure above atmospheric, equilibrium at subsequent points at lower pressures was approached very slowly. As a result, in experiments where observations were continued for only ten to twenty minutes at each point, a marked hysteresis was observed, amounting to 0.5–1.0 cc. The same increases over the normal adsorption were found to persist when the sample was then heated to  $0^\circ$  and even to  $179^\circ$ . Here as elsewhere the apparatus was proved to be free from leaks and the carbon dioxide was completely adsorbed by caustic soda. Reaction of the gas with possible traces of alkali in the sample can hardly be the explanation since similar hysteresis was obtained in three successive experiments, and the values found on first ascending the three isotherms were practically identical. With  $\text{Ag}_{II}$  no slow rates were ever observed and adsorption and desorption values agreed closely. No adequate reason has been found for the effect on  $\text{Ag}_I$  produced by the formation of solid carbon dioxide.

Curves 1 and 2 of Fig. 1 strongly suggest that the adsorption is tending to approach a limiting value which is not reached because of the beginning of a second layer or of capillary condensation. When the familiar simple equation of Langmuir,  $V/V_{\text{sat.}} = ap/(1 + ap)$  was tested by plotting  $1/V$  versus  $1/p$ , nearly straight lines were obtained up to about 400 mm.; by extrapolation of these straight lines to  $1/p = 0$ , the limiting adsorption for a single layer,  $V_{\text{sat.}}$ , was found to be about 3.8 and 8.3 cc., respectively, for  $\text{Ag}_I$  and  $\text{Ag}_{II}$ . With oxygen on these same two samples,<sup>1b</sup> the corresponding limit of physical adsorption at  $-183^\circ$ , as well as the maximum activated adsorption at higher temperatures, amounted to about 3.5 and 9 cc. The fair agreement of the limiting values for carbon dioxide and oxygen definitely implies that these gases are adsorbed only on the surface, and that the limits correspond to unimolecular layers over the whole surface.

There is a notable difference in the behavior of carbon dioxide at  $-78.5^\circ$  and oxygen at  $-183^\circ$  at the higher pressures. Whereas in each case

the sorption must become indefinitely large at atmospheric pressure, at 650 mm. the adsorption of carbon dioxide is equivalent to about 1.1 unimolecular layers, while that of oxygen corresponds to about 4.0 such layers for  $\text{Ag}_I$  and about 2.8 for  $\text{Ag}_{II}$ . It seems probable that this difference between carbon dioxide and oxygen is to be accounted for by a considerable capillary condensation of liquid in the latter case but not in the former. On the same ground it could be concluded that the structure of  $\text{Ag}_I$  facilitated capillary condensation to a much greater extent than  $\text{Ag}_{II}$ . In this connection it may be noted that if the adsorptions of carbon dioxide by  $\text{Ag}_I$  at  $-78.5^\circ$  are multiplied by the factor 2.2, they fall almost exactly on the curve for  $\text{Ag}_{II}$  up to about 500 mm., but lie somewhat higher at higher pressures.

**Hydrogen.**—Neither sample measurably adsorbed hydrogen at 0 or  $100^\circ$ . At  $-183^\circ$  a very small reversible adsorption occurred: for  $\text{Ag}_I$  0.03 cc. at 84 mm. and 0.16 cc. at 341 mm.; for  $\text{Ag}_{II}$  0.08 cc. at 74 mm. At  $300^\circ$ , however, both samples showed adsorption which is undoubtedly of the activated type. Thus when  $\text{Ag}_I$  was heated for thirty minutes in hydrogen at  $300^\circ$  and then cooled to  $0^\circ$  the adsorption amounted to 0.22 cc. at 99 mm. Evacuation at  $0^\circ$  left nearly the same amount (0.17 cc.) still adsorbed. On subsequent evacuation at  $300^\circ$ , 0.16 cc. was recovered. In three similar experiments with  $\text{Ag}_{II}$ , after twenty to sixty minutes in hydrogen at  $300^\circ$ , the adsorption at  $0^\circ$  amounted to 0.4–0.6 cc., scarcely any of which was removed by pumping at  $0^\circ$ , but which was completely recovered at  $300^\circ$ . The adsorption measured directly at  $300^\circ$  amounted to 0.28 cc. at 475 mm. The smaller value obtained in this way indicates that for some distance below  $300^\circ$  the activated adsorption increased with falling temperature. Thus in spite of the very small adsorptions a complete isobar for hydrogen on silver would show the same qualitative trend as those for the numerous other systems previously studied. It should be noted that earlier workers<sup>3</sup> were unable to detect any solubility of hydrogen in silver at temperatures below  $400^\circ$ .

#### Silver Surfaces Occupied by Adsorbed Oxygen

The following experiments were made with silver surfaces, initially bare, which had been

(3) Sieverts and Hagenacker, *Z. physik. Chem.*, **68**, 115 (1910); Steacie and Johnson, *Proc. Roy. Soc. (London)*, **A117**, 662 (1928).

allowed to adsorb various amounts of oxygen, usually at 179–197°, followed by evacuation of the free space. Conditions were always chosen so as to preclude the possibility of any oxide formation. Since physical adsorption and solubility of oxygen have been found to be negligible in the range of temperature employed, the oxygen was present on the surface as chemo- or activated adsorption.

**Carbon Dioxide.**—While carbon dioxide was adsorbed on bare silver only slightly at 0° and not at all at higher temperatures, it was taken up strongly but slowly by oxygen-covered surfaces in the range 0–197°. A summary of the measurements is given in Table I, where Column 2 is the amount of oxygen on the surface (for complete saturation 3.5 and 9.0 cc. of oxygen are required for Ag<sub>I</sub> and Ag<sub>II</sub>, respectively), and Columns 4–7 give the amount of carbon dioxide adsorbed at the times indicated, and at the temperatures shown in Column 3 and the pressures in Column 8. All measurements with a given amount of oxygen on the surface were made successively without intermediate removal of the adsorbed carbon dioxide.

TABLE I  
ADSORPTION OF CARBON DIOXIDE BY OXYGEN-COVERED SILVER

| Sample           | O <sub>2</sub> on, cc. | Temp., °C. | CO <sub>2</sub> adsorbed in <i>x</i> hrs., cc. |      |      |      | Average pressure, mm. |
|------------------|------------------------|------------|--|------|------|------|-----------------------|
|                  |                        |            | <i>x</i> = 0.1                                 | 0.5  | 2    | 10   |                       |
| Ag <sub>I</sub>  | 2.14                   | 197        | 0.87   | 0.95 | 1.02 | 1.10 | 32                    |
|                  |                        |            | 1.16   | 1.23 | 1.30 | 1.45 | 613                   |
| Ag <sub>II</sub> | 2.88                   | 197        | 0.67   | 0.73 | 0.76 | 0.81 | 144                   |
|                  |                        |            | .95  | ..   | ..   | 1.07 | 495                   |
|                  |                        |            | 1.58   | ..   | ..   | 1.63 | 740                   |
| Ag <sub>II</sub> | 6.8                    | 0          | 2.07   | 2.28 | 2.43 | ..   | 313                   |
|                  |                        | 139        | 0.59   | 0.80 | 1.03 | 1.38 | 489                   |
| Ag <sub>II</sub> | 6.4                    | 0          | 2.38   | 2.52 | 2.65 | ..   | 307                   |
|                  |                        | 139        | 1.26   | 1.32 | 1.43 | 1.61 | 477                   |

The two experiments at 197° show that carbon dioxide is taken up by the adsorbed oxygen as an activated adsorption, 0.6–0.8 cc. being adsorbed rapidly, and the further quantities with increasing slowness. The final value reached in the first experiment was 1.52 cc. after a total time of fifty-six hours. On then cooling to 0° an additional 1.40 cc. was immediately taken up at 337 mm., obviously as physical adsorption on the surface complex and to a minor extent on the unoccupied silver surface. In the second experiment the final value of 1.74 cc. was increased 2.70 cc. (at 391 mm.) by cooling to 0°. The occurrence of physical adsorption at 0° is also indicated by

the fact that in the last two experiments in Table I nearly 2 cc. were adsorbed instantaneously at this low temperature, and further by the immediate decrease in adsorption on heating to 139°, which amounted to 1.91 and 1.52 cc. in the two cases. In the third experiment the final value after nineteen hours at 139° was 1.55 cc.; on cooling to 0°, there was an immediate increase of 1.96 cc. (at 284 mm.) which remained unchanged for four hours. In the fourth experiment the final value of 1.68 cc. after eighteen hours at 139° similarly underwent an increase of 1.82 cc. (at 287 mm.) to 3.50 cc. on cooling to 0°. Subsequent temperature changes gave the following immediate equilibria: 139°, 1.65 cc. at 472 mm.; –78.5°, 7.43 cc. at 153 mm. Since it is practically certain that the physical adsorption would be negligible at 139°, all the above results agree in showing that at 0° and about 300 mm. the total sorption by Ag<sub>II</sub> consists of about 1.9 cc. of instantaneous physical adsorption plus a smaller amount of slow, activated adsorption. At the higher temperatures activated adsorption alone occurs.

The results in Table I show that the rate of activated adsorption of carbon dioxide is much greater with larger quantities of oxygen present, and that under roughly comparable conditions the rate was much greater with Ag<sub>I</sub> than with Ag<sub>II</sub>. Comparison of the final rates at 0° with the initial rates at 139° gives values of about 5 and 4 kcal. for the activation energy. While obvious difficulties make these values mere approximations, there can be no doubt that the activation energy is unusually small.

A possible interpretation of these chemisorptions might be that oxygen is taken up as oxide ions on the surface of the silver and that these are converted by carbon dioxide into surface carbonate ions. On this view the adsorption of carbon dioxide should be twice that of the underlying oxygen (measured as molecules). Instead the maximum observed, at 197°, was only 0.7 as much as the oxygen. Even though equilibrium was not reached it is doubtful that indefinitely long exposure to carbon dioxide would have raised this ratio above unity.

**Hydrogen.**—When the silver samples carrying adsorbed oxygen were treated with hydrogen at 0° there was at first a rapid apparent adsorption, which soon became very slow. In each of

five experiments, with times of observation up to thirty hours, the apparent sorption gradually approached the volume of oxygen already present. Even at  $-78.5^\circ$   $\text{Ag}_{\text{II}}$  with 6.5 cc. of adsorbed oxygen showed a slow, apparent sorption of hydrogen of 0.68 cc. after fourteen hours. These observations could be explained as (1) activated adsorption of hydrogen on top of adsorbed oxygen, analogous to the action of carbon dioxide, or as (2) interaction to form water which would be practically completely condensed at these temperatures, or (3) both processes occurring together. At  $100^\circ$  and above reaction to form water undoubtedly took place. However, definite evidence that some of the hydrogen was adsorbed as such at  $0^\circ$  was found in the fact that even after many hours of treatment by hydrogen at  $0^\circ$ , evacuation through a "Dehydrite" drying tube removed in two experiments 0.4 and 0.3 cc. more hydrogen than had been present in the "free space." Obviously these values set only a lower limit to the possible activated adsorption of hydrogen, since this process might well be largely irreversible at  $0^\circ$ .

#### Oxide-Covered Silver Surfaces

The experiments in this section deal exclusively with  $\text{Ag}_\text{I}$ , since the other sample never formed measurable quantities of oxide. Any desired extent of oxide formation on  $\text{Ag}_\text{I}$  could be produced and measured by treating it with oxygen at  $179^\circ$  at pressures above the equilibrium pressure of 525 mm. The oxide thus formed decomposed in vacuum only very slowly at  $159^\circ$ , and not at all at  $139^\circ$ .

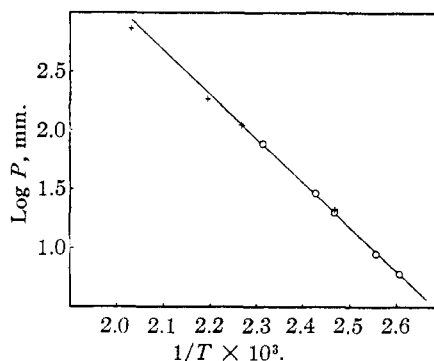
**Carbonate Equilibrium.**—The dissociation pressures of the oxide prepared in the manner described above were previously found<sup>2a</sup> to be rather less than the values obtained by extrapolation of the results of other workers at higher temperatures. To test whether this apparent discrepancy could be due to some exceptional state of our oxide, we have determined the equilibrium between this oxide, carbon dioxide, and carbonate. The results are given in Table II. All pressures were checked by repeated approach from both sides, within the accuracy of the wood-scale manometer, which we estimate at not less than 0.5 mm. There were approximately 161 cc. of oxygen on the sample, or 7.8%, in the form of silver oxide, and carbonate equivalent to 3–26 cc. of carbon dioxide. In another set of experi-

ments with oxide equivalent to only 17 cc. of oxygen, and varying carbonation from 10–40%, equilibrium pressures identical with those in Table II were obtained at  $132$  and  $139^\circ$ . Repeated formation and decomposition of carbonate did not alter the equilibrium pressures.

TABLE II

| DISSOCIATION PRESSURES OF SILVER CARBONATE |                 |                 |                   |
|--|-----------------|-----------------|-------------------|
| $t, ^\circ\text{C.}$                       | $P, \text{mm.}$ | $\text{Log } P$ | $1/T \times 10^3$ |
| 111  | 6               | 0.778           | 2.607             |
| 118  | 9               | .954            | 2.557             |
| 132  | 20              | 1.301           | 2.469             |
| 139  | 29              | 1.462           | 2.427             |
| 159  | 77              | 1.887           | 2.315             |

In Fig. 2, which is a plot of  $\log P$  against  $1/T$ , the circles represent the data of Table II. The points evidently fall on a satisfactory straight line whose slope gives for the heat of reaction

Fig. 2.—Dissociation pressure of  $\text{Ag}_2\text{CO}_3$ .

( $\Delta H$ ) 17,340 cal. per mole. When combined with the best available data (I. C. T.) for the heats of formation of  $\text{Ag}_2\text{O}$  (6950 cal.) and of carbon dioxide (94,400 cal.), the heat of formation of silver carbonate becomes 118,700 cal. Berthelot's calorimetric determinations give 120,900 and 117,100, respectively, for crystalline and precipitated silver carbonate. The crosses in Fig. 2 represent the data of Colson.<sup>4</sup> Where they overlap the two sets of measurements are in good agreement, although Colson's values lead to a slightly smaller heat of reaction, 16,450 cal. The evidence seems to justify the conclusion that our silver oxide was "normal" thermodynamically.

**Rate of Formation of Carbonate.**—Except where otherwise noted below, there was oxide equivalent to 19 cc. of oxygen on the silver.

(4) Colson, *Compt. rend.*, **132**, 467 (1901). Centnerszwer and Krustinson, *Z. physik. Chem.*, **124**, 225 (1926), found values in fair agreement with Colson.

The effect of pressure on the rate of formation of carbonate is shown in Table III. Since the rate decreases markedly with increasing formation of carbonate under otherwise comparable conditions, comparisons must be confined to experiments with approximately equal amounts present. Column 2 gives these amounts as the average of the initial and final values; the measured intervals varied from 0.5–1.5 cc. Column 3 gives the average pressure over these intervals and Column 5 the cc. of carbon dioxide taken up per minute. Because of the small values of the dissociation pressures  $P$ , the rate of the reverse reaction is almost negligible except at low working pressures. On the assumption that the net rate equals  $k_1p - k_2 = k_1(p - P)$ , a constant should be obtained when the observed rates are divided by  $p - P$ . The values of  $k_1$  thus obtained will be seen from the table to be fairly constant in each case, the variations being no greater than in a pair of experiments under identical conditions. It may be noted that the rate of formation of carbonate from our oxide showed none of the peculiarities reported by Spencer and Topley.<sup>5</sup>

TABLE III

| EFFECT OF PRESSURE ON RATE OF FORMATION |                                |                   |               |                   |          |
|---|--------------------------------|-------------------|---------------|-------------------|----------|
| Temp.,<br>°C.                           | Average cc.<br>CO <sub>2</sub> | Average<br>press. | $p_{av.} - P$ | Rate,<br>cc./min. | $103k_1$ |
| 100                                     | 2.5                            | 187               | 184           | 0.22              | 1.18     |
|   | 2.7                            | 539               | 536           | .58               | 1.08     |
| 139                                     | 6.2                            | 129               | 100           | .38               | 3.8      |
|   | 6.0                            | 513               | 484           | 1.58              | 3.3      |
| 139                                     | 8.8                            | 45                | 16            | 0.033             | 2.1      |
|   | 9.1                            | 406               | 377           | .60               | 1.6      |

The decrease in rate as carbonation proceeds, when corrected for changing pressure, is brought out by Table IV, which represents a complete experiment at 139°. Evidently the first carbon dioxide is taken up very rapidly, after which the rate decreases steadily and, as shown by other experiments, gradually approaches zero as carbonation nears completion. With 19 cc. of oxygen as oxide, 33.4 cc. of carbon dioxide was finally taken up; with 16.9 cc. of oxygen 29.65 cc. of dioxide reacted. The rates had then become very small but not zero ( $k_1 \times 10^3 = 0.002$ ).

The effect of temperature is shown in Table V. The average energy of activation  $E_1$  is 13 kcal. This value may be contrasted with the 4–5 kcal. found for the activated adsorption of carbon dioxide on surfaces carrying *adsorbed* oxygen in-

stead of oxide. With an  $E_1$  of 13 kcal. and about 6 cc. of carbon dioxide, of the possible 38 cc. present as carbonate, the rate of formation at unit pressure may be expressed by the equation,  $k_1 = 3.0 \times 10^4 e^{-13,000/RT}$ . If every collision between gaseous carbon dioxide and the oxide surface, in which the activation energy is exceeded, resulted in carbonate formation, the factor  $3.0 \times 10^4$  would be the rate of collision at 100–139° and 1 mm. pressure. On this basis a simple calculation shows that a surface of 50 sq. cm. of oxide would be required. This value is rather remarkable in view of the fact that the oxygen adsorptions previously measured on AgI led to a figure of  $7.8 \times 10^4$  sq. cm. for the area of the bare silver surface.

TABLE IV

| RATE AS A FUNCTION OF AMOUNT OF CARBONATE |                                  |                        |                                   |
|---|----------------------------------|------------------------|-----------------------------------|
| Total time,<br>min.                       | CO <sub>2</sub> taken<br>up, cc. | $p_{av.} - P$ ,<br>mm. | $k_1 \times 10^3$<br>cc./min./mm. |
| 1   | 3.24                             | 248                    | 13                                |
| 2   | 4.18                             | 180                    | 5.2                               |
| 3   | 4.80                             | 155                    | 4.0                               |
| 5   | 5.84                             | 129                    | 4.0                               |
| 7   | 6.59                             | 100                    | 3.8                               |
| 10  | 7.50                             | 74                     | 4.1                               |
| 17  | 8.59                             | 42                     | 3.7                               |
| 32  | 9.09                             | 16                     | 2.1                               |
| 67  | 9.28                             | 5                      | 1.1                               |

TABLE V

| RATE OF REACTION AND TEMPERATURE |                              |                        |                                   |                |
|----------------------------------|------------------------------|------------------------|-----------------------------------|----------------|
| Temp.,<br>°C.                    | Reaction<br>interval,<br>cc. | $p_{av.} - P$ ,<br>mm. | $k_1 \times 10^3$<br>cc./min./mm. | $E_1$<br>kcal. |
| 100                              | 3.55–4.65                    | 137                    | 0.80                              |                |
| 139                              | 3.24–4.80                    | 170                    | 4.6                               | 13.7           |
| 100                              | 5.51–6.50                    | 81                     | 0.82                              |                |
| 139                              | 5.84–6.59                    | 100                    | 3.8                               | 11.5           |
| 139                              | 5.22–6.79                    | 484                    | 3.3                               |                |
| 56.5                             | 8.20–8.63                    | 85                     | 0.046                             |                |
| 139                              | 7.50–8.59                    | 42                     | 3.7                               | 13.5           |
| 139                              | 6.79–8.51                    | 432                    | 2.0                               |                |

A few measurements of the rate of formation of carbonate were made with 161 cc. of oxygen present as oxide. At 139° with an average carbonate content equivalent to about 2.5 cc. of carbon dioxide, a specific rate ( $k_1$ ) of  $5.5 \times 10^{-3}$  was found, and  $3.9 \times 10^{-3}$  with about 3 cc. of carbonate. It will be noted that these rates are practically identical with those obtained above, where only 19 cc. of oxygen was present.

A number of attempts were made to measure rates of decomposition of carbonate in vacuum but the equilibrium pressures are so low that satisfactory accuracy was not attained. In a very

(5) Spencer and Topley, *J. Chem. Soc.*, 2633 (1929); *Trans. Faraday Soc.*, **27**, 94 (1931).

general way it may be stated that the results were consistent with values calculated from  $k_1$  and the equilibrium constant.

#### Adsorption of Carbon Dioxide and Hydrogen.—

When oxide-covered silver surfaces were treated with carbon dioxide at pressures less than the dissociation pressure of the carbonate, a slow activated adsorption occurred. Thus with oxide equivalent to 19 cc. of oxygen, equilibrium was very closely approached when 1.8 cc. of carbon dioxide had been adsorbed at 132° and a pressure of 9 mm. With 161 cc. of oxygen present, 1.26 cc. of carbon dioxide was adsorbed at 139° and 11 mm., but equilibrium had not quite been reached.

When hydrogen was admitted to oxide-covered silver at -78.5° and 390 mm., 0.1 cc. disappeared from the free space in nine hours and 0.3 cc. in twenty-two hours. In a similar experiment at 0° with 8.8 cc. of oxygen present, 3.0 cc. of hydrogen were taken up in four hours and 7.3 cc. in thirty hours. Although the disappearance of hydrogen seemed to be approaching the quantity of oxygen present, instead of twice this value as would be expected if water were formed, evacuation at 0° removed the calculated amount of gas in the free space and no more. Consequently if there is any adsorption of hydrogen at 0° it must be practically irreversible.

#### Summary

The adsorption of carbon dioxide and hydrogen has been studied on the same two silver samples

previously used in measuring the rates and equilibrium of oxygen adsorption and oxide formation. On bare silver carbon dioxide showed only an instantaneous physical adsorption, with a heat of 5 kcal. Complete covering of the surfaces apparently required very nearly the same volume of carbon dioxide as of oxygen. The physical adsorption of hydrogen was very small even at -183°, but above 200° an activated adsorption occurred which could readily be removed by evacuation at 300°.

On silver surfaces occupied by adsorbed oxygen there was from 0-200° a slow activated adsorption of carbon dioxide, with physical adsorption also occurring at 0°. The energy of activation of the former process was about 4-5 kcal. Evidence of a small activated adsorption of hydrogen at 0° was obtained.

Silver surfaces occupied by silver oxide reacted with carbon dioxide to form carbonate as low as 56°. The equilibrium pressures agreed well with accepted values—a fact which indicates that the oxide was the same as "ordinary" silver oxide thermodynamically. The calculated heat of formation was 17.3 kcal. The rate of formation was proportional to the pressure, was apparently uninfluenced by the amount of oxide present, but decreased markedly as carbonation proceeded. The energy of activation was 13 kcal. Below the equilibrium pressure of the carbonate an activated adsorption of carbon dioxide occurred.

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[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF BROWN UNIVERSITY]

## Properties of Electrolytic Solutions. X. The Freezing Point of Solutions of an Electrolyte in a Non-Polar Solvent

BY CHARLES A. KRAUS AND RAYMOND A. VINGEE<sup>1</sup>

### I. Introduction

Solutions of electrolytes in non-polar solvents have been under investigation in this Laboratory for several years. The electrical conductance of such solutions has been studied and reported in preceding papers of the present series.<sup>2</sup> At the same time, the thermodynamic and the dielectric properties of the same solutions have been studied. In the present paper, results of an investiga-

tion of the thermodynamic behavior of solutions of tetraisoamylammonium nitrate in dioxane are reported.

If the results of a study of the thermodynamic properties of electrolytic solutions are to be interpreted, it is necessary that the measurements be carried out at very low concentrations and with a relatively high degree of precision. The freezing point of aqueous solutions of electrolytes has been measured successfully down to concentrations as low as  $10^{-3} N$ . Although the freezing

(1) Du Pont Fellow in Chemistry at Brown University.

(2) Kraus and Fuoss, *THIS JOURNAL*, **55**, 21 (1933); Fuoss and Kraus, *ibid.*, **55**, 2387 (1933).