

No induction period was observed in the reaction. The energy of activation calculated from the termolecular velocity constants at 145 and 100° was 21,800 \pm 500 cal.

Summary

1. The rate of polymerization of purified styrene in thymol solution is strictly reproducible and follows a third order law.

2. No induction period exists.
3. The energy of activation is estimated to be 21,800 calories.
4. The average molecular weight of the polymer is approximately constant and in the neighborhood of 1000.
5. Interpretation of these experimental facts has been presented.

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[CONTRIBUTION FROM THE SANDERS LABORATORY OF CHEMISTRY, VASSAR COLLEGE]

The Sorption of Hydrogen by Metals. Temperature Variation Experiments

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Introduction

In 1927 the author pointed out¹ that in the sorption of hydrogen on massive copper it seemed possible that the process of solution was at play. This conclusion resulted from the observation of a low-pressure increase followed by a high-pressure decrease in the sorption of the gas when the copper had been poisoned with carbon monoxide. In another study² in which a thin coating of copper upon inert diatomite brick was employed a small amount of this poison did not cause the high-pressure decrease in hydrogen adsorption; this seemed to imply that here was a case of true adsorption without any secondary process. Further light was thrown upon the subject in a different attack by Benton and White³ who revealed that when massive copper sorbs hydrogen at -78.5° , the temperature is raised to 0° and again is brought to -78.5° , a series of sorptions result showing, first an initial adsorption at -78.5° , second, some rapid desorption at 0° followed by a slow secondary process of sorption (solution) at 0° , and finally readsorption when the temperature is returned to -78.5° . More recently the writer⁴ carried out experiments with a like temperature variation on a supported nickel sample; in this case the slow secondary action at 0° was quite small, and this is in accord with the fact that little or no diffusion or solution could be expected when practically all of the adsorbent is represented by surface.

To the present these experiments on supported

nickel constitute the only such study made with thin coatings of a metal. The present work was undertaken to obtain additional data with other metals, in both the massive condition and the supported state (each form of a given metal being prepared by identical procedure), the behavior of which, when compared among themselves, and with that of the previously mentioned supported nickel and with the massive copper of Benton and White, should point to rather definite conclusions regarding the secondary action.

Experimental

The apparatus, purification of hydrogen⁵ and of helium,⁴ used as a reference gas, have been described. The metals employed were cobalt and platinum. Massive cobalt was prepared by calcining cobalt nitrate at 350° and reducing in a silica tube at 650 to 700° . The metal was then partially reoxidized at 400° and reduced at 450 to 500° . This treatment was repeated in an effort to secure a final reduction at a lower temperature but it was necessary to reduce again at 450 to 500° before the reduction was practically completed.

The supported cobalt in the ratio of two moles of metal to 1000 g. of brick was prepared in a manner similar to the massive cobalt except that the nitrate was first dissolved and absorbed by the inert brick granules.

For the platinum examples the method of Willstätter⁶ was used. The powdery platinum black for the massive sorbent was pressed while wet so as to obtain a granular form instead of a fine

(1) Griffin, *THIS JOURNAL*, **49**, 2136 (1927).

(2) Griffin, *ibid.*, **57**, 1206 (1935).

(3) Benton and White, *ibid.*, **54**, 1379 (1932).

(4) Griffin, *ibid.*, **61**, 272 (1939).

(5) Pease, *ibid.*, **45**, 1196 (1923).

(6) Willstätter, *Ber.*, **45**, 123 (1921).

powder. (Sorption measurements on finely divided platinum black showed variable results, perhaps due to disturbance of the powder, and consequently the effective surface area, during evacuations of the containing bulb.) The supported platinum was prepared in the ratio of two moles of metal to 1000 g. of brick.

Results

On each of the four sorbents a run was first made to measure the sorption of hydrogen at 0° from a low pressure to atmospheric pressure. Then a run was made at -78.5°. After this three runs with "temperature variation" as previously described³ were carried out using progressively

TABLE I

EFFECT OF CHANGING TEMPERATURE ON SORPTION OF HYDROGEN BY 5 G. OF MASSIVE PLATINUM

(1) Gas taken up at -78.5°	Press.	52.1	225.2	425.0
	Vol.	0.85	1.01	1.02
(2) Initial values after warming to 0°	Press.	83.7	335.4	616.5
	Vol.	0.67	0.68	0.68
(3) Total sorption at 0° at pressures given in (2)		0.77	0.90	0.97
(4) Differences of (2) and (3)		0.10	0.22	0.29
(5) Final values reached at 0°	Press.	79.0	324.2	600.0
	Vol.	0.75	0.87	0.96
(6) After cooling to -78.5°	Press.	48.3	216.7	413.3
	Vol.	0.94	1.21	1.30
(7) Direct values at -78.5° at pressures given in (6)		0.85	1.01	1.03
(8) Differences of (6) and (7)		0.09	0.20	0.27

TABLE II

EFFECT OF CHANGING TEMPERATURE ON SORPTION OF HYDROGEN BY SUPPORTED PLATINUM (3.9 G. PT ON 10 G. OF BRICK)

(1) Gas taken up at -78.5°	Press.	33.6	312.1	378.9
	Vol.	0.62	0.68	0.70
(2) Initial values after warming to 0°	Press.	48.8	436.7	531.0
	Vol.	0.55	0.57	0.55
(3) Total sorption at 0° at pressures given in (2)		0.58	0.61	0.61
(4) Differences of (2) and (3)		0.03	0.04	0.06
(5) Final values reached at 0°	Press.	46.9	435.4	529.0
	Vol.	0.61	0.61	0.61
(6) After cooling to -78.5°	Press.	33.1	311.1	378.1
	Vol.	0.64	0.72	0.74
(7) Direct values at -78.5° at pressures given in (6)		0.61	0.70	0.70
(8) Differences of (6) and (7)		0.03	0.02	0.04

TABLE III

EFFECT OF CHANGING TEMPERATURE ON SORPTION OF HYDROGEN BY 48 G. OF MASSIVE COBALT

(1) Gas taken up at -78.5°	Press.	14.8	215.1	489.3
	Vol.	0.51	1.35	1.55
(2) Initial values after warming to 0°	Press.	22.9	312.2	696.6
	Vol.	0.34	0.62	0.80
(3) Total sorption at 0° at pressure given in (2)		0.43	1.26	1.59
(4) Differences of (2) and (3)		0.09	0.64	0.86
(5) Final values reached at 0°	Press.	22.1	303.2	686.2
	Vol.	0.41	1.30	1.59
(6) After cooling to -78.5°	Press.	13.9	209.7	481.9
	Vol.	0.60	1.98	2.34
(7) Direct values at -78.5° at pressures given in (6)		0.49	1.35	1.54
(8) Differences of (6) and (7)		0.11	0.65	0.80

TABLE IV

EFFECT OF CHANGING TEMPERATURE ON SORPTION OF HYDROGEN BY SUPPORTED COBALT (5.9 G. OF COBALT ON 50 G. OF BRICK)

(1) Gas taken up at -78.5°	Press.	97.2	255.9	485.3
	Vol.	1.28	1.37	1.43
(2) Initial values after warming to 0°	Press.	139.8	362.4	684.8
	Vol.	1.04	1.14	1.16
(3) Total sorption at 0° at pressures given in (2)		1.05	1.17	1.23
(4) Differences of (2) and (3)		0.01	0.03	0.07
(5) Final values reached at 0°	Press.	139.6	362.1	683.8
	Vol.	1.05	1.16	1.23
(6) After cooling to -78.5°	Press.	96.8	255.3	484.8
	Vol.	1.27	1.43	1.48
(7) Direct values at -78.5° at pressures given in (6)		1.28	1.37	1.43
(8) Differences of (6) and (7)		-0.01	0.06	0.05

greater volumes of hydrogen. The results are condensed in the tables and figures. Table I lists the data obtained with massive platinum, Table II that for supported platinum, while Tables III and IV give the results for the cobalt samples. As has been explained before³ the values in Row (2) of the tables represent the adsorptions at 0° (provided no solution at -78.5° took place). The differences given in Row (4) are the volumes of hydrogen dissolved at 0° at pressures of Row (2) while the differences given in Row (8) are the volumes dissolved at 0° at pressures of Row (5). The sums of adsorption and solution are found in Rows (3) and (5).

The data of the several tables are shown graphically in the figures; it need be mentioned only that curve 3 in all the figures, giving the adsorption at 0°, is obtained by subtracting the amount of dissolved hydrogen at a given pressure from the total sorption at that pressure as found from curve 2. The open circles and triangles indicate points obtained in going from lower to higher pressures; full black circles and triangles, from higher to lower.

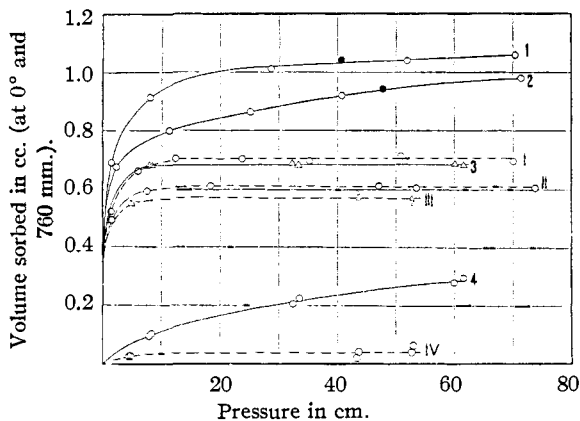


Fig. 1.—Sorption of hydrogen on platinum. Solid curves indicate massive platinum; broken curves indicate supported platinum, two moles of platinum per 1000 g. of brick: curves 1 and I, total sorption at -78.5° ; 2 and II, total sorption at 0° ; 3 and III, adsorption at 0° ; 4 and IV, solution at 0° .

The isotherms for the supported metals either attain a saturation limit or more nearly reach a limitative value than those for the massive metals. This is accounted for if there is only little solution taking place when the metal exists largely in a surface condition. With both platinum and cobalt curve 4 shows very small volumes of hydrogen involved for the supported sorbents as contrasted with the considerable quantities for the massive metals. It is seen in curves 3 and 4 of Fig. 2 that between a pressure of about 250 and 700 mm. the adsorption proper is even less

	Solution	Sorption	% Solution
Massive platinum	0.26	0.94	28
Supported platinum	0.04	0.61	7
Massive cobalt	0.74	1.45	51
Supported cobalt	0.05	1.20	4
Massive copper of Benton and White ³	2.9	9.6	30
Supported nickel ⁴	0.09	2.23	4

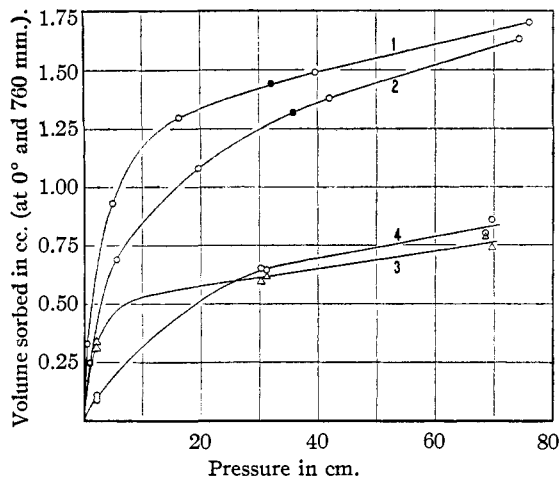


Fig. 2.—Sorption of hydrogen on massive cobalt: curve 1, total sorption at -78.5° ; 2, total sorption at 0° ; 3, adsorption at 0° ; 4, solution at 0° .

than solution. This is the first such case encountered. In order to draw a comparison of the cases so far studied, Table V is included. From this it is clear that for the supported metals the secondary action accounts for around 5% of the total sorption at 0° , whereas with the massive metals it may amount to some 25 to 50%. It seems feasible to conclude, therefore, that this action provisionally regarded as solution is certainly subjacent to the surface and fundamentally differs from true adsorption, a conclusion previously reached² after the study of the poisoning effect of carbon monoxide on the sorption of hydrogen by copper.

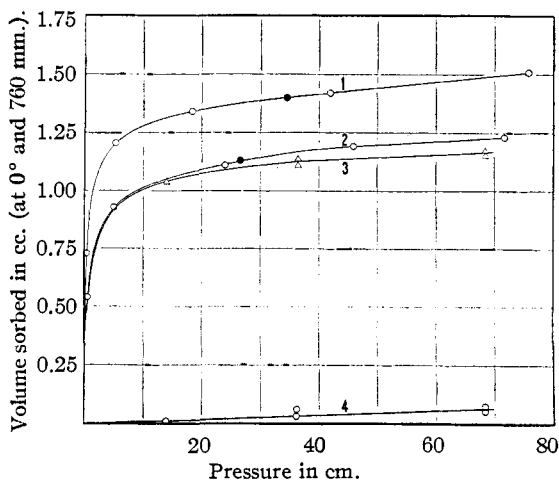


Fig. 3.—Sorption of hydrogen on supported cobalt, two moles of cobalt per 1000 g. of brick: curve I, total sorption at -78.5° ; 2, total sorption at 0° ; 3, adsorption at 0° ; 4, solution at 0° .

Summary

Measurements have been made of the sorption of hydrogen on platinum and on cobalt in both the massive and the supported states under conditions in which the temperature was varied from -78.5 to 0° and back to -78.5° . The results, pointing to a distinction between adsorption and

a second factor, apparently solution, indicate that the sorptive process is largely confined to straight adsorption only when the sorbent is spread almost wholly as surface. With massive metals the secondary action assumes a role some five or ten times as great as with supported sorbents.

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[CONTRIBUTION FROM THE CHEMICAL LABORATORIES OF THE UNIVERSITY OF MICHIGAN]

The Molecular Weight of Potassium Bromide and the Atomic Weights of Silver, Bromine and Potassium

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Although oxygen is the standard for atomic weights, the values for most of the elements have been determined, not by direct comparison, but indirectly by the use of secondary standards. In the experimental studies typified by the work of Stas, Richards, Baxter and Hönigschmid the importance of the atomic weight of silver is well recognized. There are, however, relatively few sets of data in the literature which permit the atomic weight of silver to be calculated without reference to a third element. An important recent piece of work in this field is that of Hönigschmid,² in which the ratios $\text{Ba}(\text{ClO}_4)_2:\text{BaCl}_2$ and $\text{BaCl}_2:2\text{Ag}$ were determined, leading to a calculated ratio of $\text{Ag}:4\text{O}$.

The present research was suggested in connection with the drying of potassium bromate for use as an analytical reagent. The direct thermal decomposition of potassium bromate as a basis for a new determination of the atomic weights of silver, bromine and potassium seemed feasible because of its slow decomposition at moderately elevated temperatures. Potassium bromate was particularly suitable for such determinations for the following reasons: (1) it crystallizes without water of hydration; (2) it has a very favorable temperature coefficient of solubility and is easily freed from bromide and chloride by recrystallization with centrifugal drainage; (3) it decomposes directly into potassium bromide and oxygen on heating; (4) the decomposition can be carried out at a low enough temperature so that no fusion

occurs with its resultant loss of spray as bubbles of oxygen break at the surface. Its main defect is that it cannot be dried completely without some decomposition. Therefore, it is necessary to make a moisture determination, and the true weight of potassium bromate is obtained by subtracting the moisture correction from the weight of the original sample.

Preparation and Purification of Materials

All the materials for this work were carefully purified before use. The chemicals used as the starting point were reagent quality and met A. C. S. specifications. Water, nitric acid, hydrochloric acid and ammonium hydroxide were purified by well-known distillation methods. Potassium permanganate was purified by recrystallization; pure hydrogen by electrolysis.³ The phosphorus pentoxide was sublimed in a current of oxygen. The sulfuric acid was fumed twice with a few crystals of potassium permanganate to remove halides and to destroy traces of organic matter. The potassium hydroxide used, although a commercial preparation, was shown by direct tests with hydrogen sulfide and silver nitrate to contain a negligible amount of heavy metals and less than 0.01% of chloride. The latter was adequately removed from the potassium bromate by recrystallization.

The preparation of pure silver, pure bromine and pure potassium bromide followed well-known methods in atomic weight work. In the case of silver, after preliminary recrystallization of silver nitrate, reduction to metallic silver by ammonium formate and fusion of the silver, the large buttons were subjected to electrolytic purification, and the crystals then fused in hydrogen on a lime support. After etching with dilute nitric acid and washing, the buttons were dried in hydrogen at 400° and stored in small petri dishes over fused potassium hydroxide. The bromine was dissolved in hot potassium hydroxide solution, followed by evaporation to crystallize out a mixture of potassium bromide and bromate. The crystals were converted to potassium bromide by heating at 500° , and the

(1) This paper contains material from a dissertation presented to the Graduate School of the University of Michigan in partial fulfillment of the requirements for the degree of Doctor of Philosophy, June, 1938.

(2) Hönigschmid and Sachtleben, *Z. anorg. allgem. Chem.*, **178**, 1-32 (1929).

(3) J. P. Cooke and T. W. Richards, *Am. Chem. J.*, **10**, 102 (1888).