chromium oxide and on active copper was interpreted in terms of activated adsorption and ethylene decomposition.

The experimental observations lead to a concept of the surface-gas system in accord with our knowledge of various catalytic reactions on such surfaces. The conditions for exchange reactions between deuterium and ethylene or ethane are also defined by the adsorption measurements.

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[CONTRIBUTION FROM THE FRICK CHEMICAL LABORATORY, PRINCETON UNIVERSITY]

The Adsorption of Gases by Chromium Oxide Gel

BY JOHN HOWARD[1] AND HUGH S. TAYLOR

In a paper describing measurements of the heats of adsorption of hydrogen and carbon monoxide on zinc oxide, chromium oxide and mixtures of the two, Garner and Kingman[2] state, *inter alia*, that the adsorption of hydrogen on chromium oxide is too small to measure. Some data of Sherman reported in outline by Taylor[3] show, however, that chromium oxide, prepared by the methods of Lazier and Vaughen,[4] is an excellent catalyst for the reconversion of parahydrogen to the ortho form, suggesting, therefore, that appreciable activated adsorption of hydrogen must occur. Lazier and Vaughen show that chromium oxide, suitably prepared, is an excellent catalyst even for the hydrogenation of ethylene, in contrast to the behavior of other hydrogenating oxide catalysts. In view of these facts it seems desirable to investigate the adsorptive properties of chromium oxide of the type found "most convenient and reliable" by Lazier and Vaughen, special attention being paid, accordingly, to the preservation of the catalyst in the unglowed condition. There is already definite evidence in the literature[5,6,7,8] that adsorptive capacity for gases and in solution, and also the chemical and catalytic reactivity of chromium oxide, are very sensitive to this exothermic change from an amorphous to a crystalline state as revealed by Debye-Scherrer x-ray patterns.[4] The adsorption measurements of Schmidt[8] with a variety of gases indicate that he may have been using a glowed sample, with which Taylor and Sherman found negligible activity in the para hydrogen reconversion process. It was hoped also that such measurements might yield some reasons for the excellent behavior of chromium oxide as a catalyst for hydrogenation of ethylene in contrast to the behavior of, for example, manganese oxide-chromium oxide, the adsorption characteristics of which have been studied by Turkevich and Taylor.[9]

Experimental

Apparatus.—The adsorption measurements were carried out in the standard Princeton method.[10] The adsorbed gases could be recovered quantitatively with an automatic Sprengel pump[11] and could be analyzed in a Bone and Wheeler apparatus.[12]

Adsorbent.—The method of preparation of Lazier and Vaughen[4] was followed using 0.04 molar solutions of chromium nitrate to which was added, in the cold, with violent stirring, an equivalent quantity of 0.1 normal ammonium hydroxide. After washing by decantation, using a mechanical stirrer, for several days, until peptization began to occur, the precipitate was filtered and the voluminous gel so obtained was dried at temperatures gradually increasing to 200°. The drying was completed in a stream of purified hydrogen for twenty-four hours at 375°, *in situ*, in the tube used for the adsorption measurements. Five samples, from three different batches, prepared in an identical manner, were used: Cr_2O_3 I, 45 g. from batch 1; Cr_2O_3 II, 33 g., and Cr_2O_3 III, 38 g., both from batch 2; Cr_2O_3 IV, 5 g., and Cr_2O_3 V, 12 g. from batch 3.

Gases.—Helium was obtained by passing tank helium through a trap containing activated carbon and immersed in liquid air. The carbon had been evacuated overnight at 500°. Hydrogen prepared electrolytically was passed through a furnace containing platinized asbestos and then dried over calcium chloride and phosphorus pentoxide. Nitrogen from cylinders was passed over metallic copper shavings heated to 500° and dried over phosphorus pentoxide. Ethylene was obtained from cylinders, condensed in a liquid air trap and the middle fraction was used. Ethane from cylinders was dried over phosphorus pentoxide. A pronounced hysteresis in the adsorption of this gas at −78° indicates that the gas was not pure but a mixture of

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[1] Commonwealth Fellow, Princeton University, 1931–1933.

[2] Garner and Kingman, *Trans. Faraday Soc.*, **27**, 322 (1931).

[3] Taylor, *Nature*, **128**, 636 (1931).

[4] Lazier and Vaughen, THIS JOURNAL, **54**, 3080 (1932).

[5] Wohler, *Kolloid Z.*, **38**, 97 (1926).

[6] Budnikoff and Krause, *ibid.*, **55**, 330 (1931).

[7] Nikitin, *Z. anorg. angew. Chem.*, **155**, 358 (1926).

[8] Schmidt, *Z. physik. Chem.*, **133**, 263 (1928).

[9] Turkevich and Taylor, THIS JOURNAL, **56**, 2254 (1934).

[10] *Cf.* (a) Taylor and Williamson, *ibid.*, **53**, 2168 (1931); (b) Taylor and Sickman, *ibid.*, **54**, 602 (1932).

[11] Dunoyer-Smith, "Vacuum Practice," G. Bell & Sons, London, England, 1926.

[12] Bone and Wheeler, *J. Soc. Chem. Ind.*, **28**, 10 (1908).

hydrocarbons. It contained no unsaturated hydrocarbons.

Temperature Control.—Vapor baths were used above 0°,[10] except at 375°, for which an electric furnace controlled by a platinum resistance thermometer in conjunction with an automatic regulator was used. Ice, solid carbon dioxide and liquid air were used for the low temperatures, the exact temperature of the liquid air being determined with an oxygen thermometer.

Procedure

As chromium oxide gel must be evacuated below 400° to avoid the glow effect, prolonged periods of pumping, of the order of twenty-four hours, were necessary to secure a clean and reproducible surface. The dead space of the apparatus was determined with helium. The use of nitrogen for such purposes with chromium oxide would have introduced a very considerable error. At or above 0°, it was assumed that there was no adsorption of helium and the volumes of the hot and cold portions of the dead space were calculated from these data with concordant results. Below 0° the adsorption of helium becomes appreciable.

All the helium, nitrogen and ethane experiments, the hydrogen results at 0° and below and the ethylene isotherm at −78.5° involved principally van der Waals adsorption. Adsorption was rapid and reversible (save in the case of ethane already cited) and all isotherms were followed in both directions with increasing and decreasing pressure, with concordant results.

The high temperature hydrogen adsorption equilibria at 338 and 375° were only slowly established and each isotherm required fourteen days of work. A known volume of gas was introduced and the pressure followed until constant for twenty-four hours. A small quantity of gas was removed, lowering the pressure by some 20 mm., to ascertain whether the pressure would build up toward the previous value.

The rate of adsorption of hydrogen between 110 and 218° was followed at constant volume.[10] The corresponding rate measurements with ethylene were made at constant pressure.[13]

Experimental Results

Helium.—The adsorption of helium was proportional to the pressure. At 760 mm. the adsorptions on Cr_2O_3 I were 0.272 cc. per gram at 82° K. and 0.029 at 194.5°K. These data give an isosteric heat of adsorption of 640 calories.

Nitrogen.—The adsorption varied linearly with pressure at 491 and 577°K. but at lower temperatures the curves were markedly concave to the pressure axis. On Cr_2O_3 I, the specific adsorptions were as shown in Table I. On Cr_2O_3I, some six months later, after the adsorbent had been used for several high temperature runs and contained an appreciable quantity of carbon, the adsorption at 273°K. and 760 mm. was 1.61 cc. per gram. Another sample of fresh adsorbent, Cr_2O_3 III, showed an adsorption of 1.758 cc. per gram. From the data at 383 and 491°K. on this latter sample a heat of adsorption of 6800 calories per gram is calculated for an adsorption of 0.1 cc. per gram.

TABLE I

ADSORPTION OF NITROGEN ON Cr_2O_3 I

Temp., °K.	Adsorption in cc. at N. T. P. per gram and at $P_{mm.}$ =				
	50	200	400	600	760
273	0.431	0.890	1.207	1.466	1.640
383	...	0.107	0.189	0.258	0.315
491					.067
577					.027

Ethane.—The adsorption was linear at 491° and very nearly so at 428°K. The sample used was Cr_2O_3 IV. The adsorptions in cc. at N. T. P. per gram are shown in Table II.

TABLE II

SPECIFIC ADSORPTIONS OF ETHANE ON Cr_2O_3 IV

Temp., °K.	Adsorption in cc. at N. T. P. per gram and at $P_{mm.}$ =					
	25	50	200	400	600	760
194.5	4.6	6.5	12.5	18.2	23.4	27.6
273	0.8	1.12	2.44	3.58	4.56	5.02
329	.1	0.22	0.70	1.10	1.46	1.78
353	.07	.13	.40	0.70	0.88	1.14
383	..	.06	.20	.34	.50	0.62
428				.21		.36
491						.04

Even at 491°K. there was no evidence of any activated adsorption and at 574°K. it is certainly not greater than 0.08 cc. per gram in three hours. From the isosteres, a heat of adsorption of 10,860 calories was calculated for a specific adsorption of 0.06 cc. per gram in the temperature limits 329–353°K. In the same temperature limits, the heat of adsorption for 1 cc. per gram was 6600 calories.

Hydrogen.—With this gas there was a slow drift, due to activated adsorption, at 273°K. amounting to 4 cc. during the six hours occupied by the experiment. By plotting pressure change against time it was possible to introduce at each point an approximate correction for this small drift giving values for van der Waals adsorption consistent with the data for adsorption and desorption. The data for this temperature in Table III do not, on this account, possess the same accuracy as those for the two lower temperatures.

TABLE III

SPECIFIC ADSORPTIONS OF HYDROGEN ON Cr_2O_3 III

Temp., °K.	Adsorption in cc. at N. T. P. per gram and at $P_{mm.}$ =					
	7	25	200	400	600	760
85	2.32	3.74	9.63	12.57	14.92	16.21
194.5	..	0.08	0.30	0.46	0.60	0.69
273	..	..	.04	.08	.13	.14

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[13] Taylor and Strother, THIS JOURNAL, 56, 586 (1934).

From the data at 83 and 194.5°K. a heat of adsorption of 1800 calories for 1 cc. adsorbed per gram can be calculated.

In the temperature range 373–491°K. measurements of the velocity of activated adsorption may conveniently be made. The following Table IV reproduces the data given by Cr_2O_3 I, expressed as cc. adsorbed at the given times by the 45-g. sample.

TABLE IV

VELOCITY OF ADSORPTION OF HYDROGEN ON Cr_2O_3 I

Time in min.	Cc. at N. T. P. adsorbed at temp. °K. =			
	373	405	428	457
2	...	2.4	2.9	5.5
6	2.9	3.0	5.3	9.5
20	3.4	4.6	8.2	17.6
30	3.7	5.4	9.6	21.2
60	4.4	7.2	12.6	26.4
90	4.9	8.65	14.7	27.85
200	6.4	14.0	...	..
400	8.4	...	...	..
1320	13.45	...	...	..

The velocity of adsorption varied somewhat with the different samples studied. The data of Table V show the specific adsorption in cc. per gram after 1 hour for three different samples.

TABLE V

SPECIFIC ACTIVATED ADSORPTION OF HYDROGEN AFTER 60 MINUTES

Adsorbent	Cc. at N. T. P. adsorbed after 1 hour at temp. °K. =			
	373	405	428	457
Cr_2O_3 I	0.1	0.16	0.28	0.6
III	...	0.15	0.26	0.47
IV	...	..	..	0.87

Since the velocity measurements were in this case observed at constant volume and varying pressures they can only give an approximate measure of the activation energy. By correcting all the velocities to one atmosphere pressure, assuming that the velocity is directly proportional to the pressure, the activation energy of adsorption between 405 and 457°K. varies from 14 to 21 kilocalories for the adsorption of from 0.07 to 0.33 cc per gram with increasing energies for increased coverage, on both Cr_2O_3 I and Cr_2O_3 III. With the sample Cr_2O_3 IV an activation energy of 25–27 kilocalories was found, from the velocities at 457–491°K., for specific absorptions of 0.4–1 cc. per gram.

On Cr_2O_3 III adsorption isotherms were determined at 611 and 648°K. by the method already mentioned. The equilibrium data thus obtained are given in Table VI.

TABLE VI

ISOTHERMS OF ACTIVATED ADSORPTION OF HYDROGEN ON Cr_2O_3 III

Temp., °K.	Adsorption in cc. at N. T. P. per gram and at $P_{mm.}$ =						
	15	18	60	208	350	500	740
611	1.27	..	2.11	2.56			
648	..	1.12	1.56	2.02	2.27	2.41	2.62

From these data a heat of activated adsorption, for 2 to 2.5 cc. per gram, of approximately 27 kilocalories may be calculated. This is in marked contrast to the low temperature heat of adsorption of 1800 calories.

The sample Cr_2O_3 II, from the same batch as Cr_2O_3 I, was ignited at 723°K. and during this time undoubtedly suffered the glow phenomenon. The capacity for activated adsorption was all but completely destroyed by this treatment. Only 0.06 cc. per gram was adsorbed in one hour at 491°K. whereas with Cr_2O_3 I ten times this volume was adsorbed in the same time at the lower temperature of 457°K.

Ethylene.—At 194.5°K. this gas showed a rapid and reversible adsorption. Owing to the low pressures at which large amounts of the gas are adsorbed it is difficult indeed to recover the gas at the same temperature. The adsorption data for ethylene at this temperature on Cr_2O_3 IV are shown in Table VII.

TABLE VII

ADSORPTION ISOTHERM OF ETHYLENE AT 194.5°K. ON Cr_2O_3 IV

P_{mm}	1	2	5	20	100
Cc. ads. per g. at N. T. P.	4.4	8.1	10.8	13.2	16.2
P_{mm}	..	200	400	600	700
Cc. ads. per g. at N. T. P.	..	18.3	21.1	24.0	26.3

It will be noted that at 20 mm. pressure the adsorption is half of that at 700 mm. On the same catalyst two runs were made at temperatures of 353 and 383°K. In each case the change in adsorption with time was followed with the results shown in Table VIII.

TABLE VIII

VELOCITY OF ADSORPTION IN CC. AT N. T. P. PER GRAM ON Cr_2O_3 IV

$P_{C_2H_4}$ = 1 atmosphere

Time in min.	2	5	10	15	30	60
Ads. per g. at 353°	1.5	1.8	2.25	3.04	4.6	7.16
Ads. per g. at 383°	4.0	5.8	7.8	9.74	13.8	20.0
Time in min.	..	90	120	160	180	200
Ads. per g. at 353°	..	9.2	10.9	12.8	13.8	14.4
Ads. per g. at 383°	..	24.5	28.1	..	..	..

Evidence to be presented indicates that, at these temperatures, little decomposition of ethylene occurs. The data given yield for the activation energy of adsorption a value $E = \sim 14.7$ kilocalories.

At 491°K. a rapid adsorption process was accompanied by decomposition with release of ethane and methane from the surface, the maximum adsorption occurring about fifteen minutes after the first admission. A sample of adsorbent which had been loaded with 55.3 cc. of ethylene at 273° and then raised in temperature suddenly to 491°K. showed first desorption presumably of gas held by van der Waals forces, then adsorption to a maximum at twenty minutes followed by the same process of desorption due to saturated products. Analyses of the gases removed in each case at this temperature were:

	C_2H_4	H_2	C_2H_6	CH_4	CO_2
(a)	6.0	4.4	76	13.2	0
(b)	0	4.3	70	20	0

A surface saturated at 194.5°K. and 1.5 mm. pressure and holding 240 cc. of adsorbed gas gave, on raising the temperature to 273°K., first an evolution and then a readsorption of gas. This suggests that activated adsorption is occurring even at this temperature. On raising the temperature to 405°K. the same process of evolution and readsorption occurred, there being 223 cc. adsorbed at 16 mm. pressure after four hours. In view of this low pressure, the absence of desorption and the ethane adsorption measurements, it would appear that ethane formation at 405°K. is negligible, and hence the rate measurements for ethylene already given (Table VIII) represent actually activated adsorption of ethylene at 353 and 383°K.

The large amounts of gas which were adsorbed in this temperature range could only be recovered by exhaustion at 648°K. and the recovered gas consisted predominantly of hydrogen, as the following analyses show. The carbon dioxide content appeared to increase with the time the gas is left on the surface.

	C_2H_4	H_2	C_2H_6	CH_4	CO_2
(a)	5.0	81	1.8	4.2	5.8
(b)	0	64.5	2.3	13.2	20.0

A few experiments were made to see if this complex decomposition of ethylene occurred in the presence of hydrogen. For example, 85.7 cc. of hydrogen was adsorbed at 491°K. and the dead space gas removed; 50.2 cc. of ethylene was then added. The adsorption passed through a maximum and then decreased. The gases removed gave the following analyses:

	C_2H_4	H_2	C_2H_6	CH_4	CO_2
Dead space at 491°K.	19	6	51	18	0
Prolonged evacn. at 491°K. . .	9.6	64	27	. . .	. . .
Prolonged evacn. at 648°K. . .	0	92	2.8	1.3	3.8

It will be evident that ethylene behaves on chromium oxide surfaces in a manner qualitatively similar to ethylene on manganese oxide–chromium oxide as investigated in detail by Turkevich and Taylor.[9]

Discussion

The van der Waals adsorption of the chromium oxide gel here studied is very high. On a volume basis it is almost as good as charcoal, considerably better than silver gel but not so efficient as chabazite. Weight for weight it is from one-fifth to one-tenth as adsorptive as charcoal, varying with the extent of adsorption on the sample. Per unit volume of adsorbent it is from one-half to one-third as efficient.

In the range above 0°, chromium oxide gel is strikingly superior to charcoal as an adsorbent for hydrogen. This is to be attributed to the activated adsorption of the gas, the activation energy of which is about 19 kilocalories and the binding energy approximately 27 kilocalories.

The data obtained for chromium oxide now permit a more complete exposition than hitherto of the influence of promoter action on the energy of activated adsorption. In the following Table IX are collected measurements of van der Waals adsorption of hydrogen at 194.5°K. and one atmosphere as an index of the extent of surface per gram in the case of zinc, manganese and chromium oxides and their mixtures. A casual inspection shows that the promoter action is not due to increase in available surface. The predominant effect is on the activation energy of adsorption.

TABLE IX

ACTIVATION ENERGY AND VAN DER WAALS ADSORPTION ON OXIDES AND THEIR MIXTURES

Adsorbent	Van der Waals ads. of H_2 at 194.5°K. in cc. per gram	Activation energy in kg. cal. for hydrogen adsorption at 0.2 cc. per gram	Reference
ZnO	0.2	11	10b
Cr_2O_3	.7	19	. . .
$ZnO–Cr_2O_3$	.6	1	13
MnO	$<$ .1	20	10a
$MnO–Cr_2O_3$	.5	6	10a

It is of interest also to call attention to the fact that the energies of activation on the various catalysts discussed in the preceding Table IX by no means provide a measure of the rate of adsorption for a given extent of surface covered. Table IX indicates that the available surfaces as judged by van der Waals adsorption at 194.5°K. are all of similar magnitude. The rates at which activated adsorptions occur, at 405°K., in cc. per gram per minute are, respectively: ZnO, 2.8×10^{-2}; Cr_2O_3, 1.1×10^{-3}; $ZnO{\cdot}Cr_2O_3$, 5×10^{-1}; $MnO{\cdot}Cr_2O_3$, 2.7×10^{-2}. Manganous oxide is not included in the comparison owing to its very much smaller adsorption capacity even at low temperatures, indicating a much smaller specific surface. The actual ratio of adsorption rates for ZnO and Cr_2O_3 is about 25. On the assumption that the velocity of adsorption was determined by collision, with the surface, of molecules with the ascertained activation energies, the relative rates of adsorption should be $\exp\,(19{,}000-11{,}000)/810 = e^{9.9} = 2 \times 10^4$. The mixed oxides, $ZnO{\cdot}Cr_2O_3$ and $MnO{\cdot}Cr_2O_3$ show even more pronounced divergencies, when compared with the single oxides, between observed ratios of adsorption rates and ratios calculated from the activation energies observed. These results force one to the conclusion that the kinetic theory interpretation of activated adsorption as the number of molecules striking the surface per unit time which have an activation energy, E, equal to that observed experimentally is not in harmony with the experimental data on a series of oxide surfaces. Two other lines of experimental evidence leading to the same conclusion have already been given,[14,15] the one based on the observed velocity of adsorption of hydrogen on zinc oxide, the other on an entirely independent observation of the identity of the velocities of adsorption of hydrogen and deuterium on a given catalytic surface.

Examination of the experimental data in Table IX shows that if the velocity of adsorption, k, be expressed by means of an equation $k = Ae^{-E/RT}$, then, as the activation energy increases, the value of A must increase also, tending to balance out the difference in E in the several cases. If A be calculated in each case from the experimental values of k and E, it is found that there is a straight line relationship between log A and E, that, therefore, an equation of the form

$$\log A = aE + b$$

expresses the relationship between the two magnitudes. The straight line plot so obtained passes through the origin. Hence, in this particular case, $b = 0$. A similar relation between the activation energies of heterogeneous reactions and the specific activity, A, of the catalyst has been found by Schwab,[16] by Balandin[17] and latterly by Eckell.[18] As the latter justly remarks, the interpretation of this relation between A and E is very much a matter for discussion with as yet no general agreement. None of the explanations suggested by these authors for the cases of chemical reaction meets the simpler case of adsorption here involved. A further observation may be made which is fundamental to the method of deducing the activation energies. The quantity, A, has been shown to vary with the activation energy, E, on different surfaces. If this relation holds for different catalysts it probably also holds for areas of different activation energies on the same catalyst so that the relation between k and E should really be of the form

$$k = e^{aE}\, e^{-E/RT} = e^{-E(1/RT - a)}$$

The method of calculation of the activation energy does not reveal that the quantity A can vary on different areas of the same surface; any variation in A with coverage appears in the value of E calculated from the equation $d \ln k/dT = E/RT$,[2] the assumption being made that E is constant for a given extent of adsorption, and that the same surface is covered at the different temperatures on adsorption of the same amount of gas. This latter assumption is particularly worthy of scrutiny especially in view of the recent data of Gould, Bleakney and Taylor,[19] who found that, on chromium oxide gel, even at liquid air temperatures, interaction of the two species of hydrogen and deuterium occurred, pointing to activated adsorption, and that, in addition, desorption from the surface was also freely occurring. This points to activated adsorption with lower energies of activation and lower heats of adsorption than are discussed in this present study. The method of deducing heats of adsorption from isosteres at different temperatures is also open to objection similar to that obtaining with respect to activation energies.

Analysis of the experimental data presented in the preceding section of this paper indicates that

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(14) Taylor, *Trans. Faraday Soc.*, **28**, 137 (1932).

(15) Pace and Taylor, *J. Chem. Phys.*, **2**, 578 (1934).

(16) Schwab, *Z. physik. Chem.*, **5B**, 406 (1929).

(17) Balandin, *ibid.*, **19B**, 451 (1932).

(18) Eckell, *Z. Elektrochem.*, **39**, 859 (1933).

(19) Gould, Bleakney and Taylor, *J. Chem. Phys.*, **2**, 362 (1934).

the data on velocity of adsorption on chromium oxide gel are representable within the limits of experimental accuracy by means of an equation of the form $dx/dt = cx^b$ where c and b are constants characteristic of the surface and gas in question, independent, over wide intervals, of the volume of gas, x, adsorbed. An inquiry is in progress in this Laboratory, at present, to ascertain whether this result can be generalized for various surface-gas systems and to ascertain the theoretical significance, if any, of such an equation for velocity of adsorption.

Since the data of Gould, Bleakney and Taylor[19] with respect to hydrogen adsorption on chromium oxide gel point to activation of hydrogen at temperatures as low as liquid air, it follows that the high temperature of hydrogenation of ethylene required on such surfaces must be determined either by the rate of activated adsorption of ethylene or the rearrangements of the adsorbed species on the surface to form ethane or by ethane desorption. Our experiments indicate that desorption of ethane is rapid compared to the other two. The activation energy of the rearrangement processes should be small since they involve interaction of adsorbed atoms or radicals. This reasoning would, therefore, point to the activated adsorption of ethylene as the rate controlling process. Lazier and Vaughen[4] have shown that the hydrogenation reaction is much more rapid on chromium oxide gel than on any chromite studied. From our studies and those of Turkevich and Taylor[9] on manganese chromite we conclude that this difference is largely to be ascribed to the activation of the ethylene. We have shown that activated adsorption of this gas is occurring on chromium oxide already at 273°K. whereas, on manganese chromite, activated adsorption does not set in below 373°K. At 457°K. we compute, from the velocity of adsorption at 353°K. and from the observed activation energy of 14,700 calories, a velocity of adsorption of 3.85×10^2 cc./g./min. on chromium oxide whereas Turkevich and Taylor adsorbed only 12 cc. on 96 g. in three hours at the same temperature; chromium oxide, therefore, adsorbs ethylene 10^5 times as fast as manganese chromite under the same conditions. This difference in speed corresponds to a difference in activation energy of 13 kilocalories if one neglects the variation that may occur in the value of A in the expression connecting the rate with the activation energy. Any change in A operating to compensate the influence of the activation energy term would increase this difference in the activation energy of adsorption of ethylene on the two surfaces. The large differences found by Lazier and Vaughen between chromium oxide gel and the chromites become understandable on this assumption that it is the rate of activated adsorption of ethylene which is the rate determining step.

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Summary

1. Isotherms have been obtained for van der Waals adsorption of nitrogen and ethane over a considerable temperature range, for hydrogen and helium at 85 and 194.5°K. and for ethylene at 194.5°K. on chromium oxide gel.

2. The heats of van der Waals adsorption have been calculated from isosteres for helium, nitrogen, ethane and hydrogen.

3. The rates of activated adsorption of hydrogen from 373 to 457°K. and of ethylene at 353 and 388°K. on chromium oxide gel have been measured and activation energies calculated.

4. From high temperature isotherms, the heat of activated adsorption of hydrogen on chromium oxide gel has been computed.

5. Decomposition of ethylene which accompanies activated adsorption at high temperatures has been studied analytically.

6. Comparisons have been made of the activation energies of adsorption of hydrogen on zinc, manganese and chromium oxides and their mixtures in reference to the problem of promoter action.

7. It has been shown that, on surfaces similar in area as deduced from van der Waals adsorption, there is a variable proportionality factor between velocity of activated adsorption and the activation energy term in the kinetic expression for velocity of adsorption. A similar variation in heterogeneous reaction velocity expressions has been noted and the problem discussed.

8. It has been concluded that the rate of activated adsorption is the rate determining step in the hydrogenation of ethylene and that variations in this rate account for differences in the observed activities of various oxides.

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