lithium nitrate (Curve C). Moreover, the latter eutectic point does not agree with that found by Perman and Harrison[2a] for these curves.

While curves (A) and (B) agree with those found by the above-mentioned authors over the corresponding parts of their ranges, curve (C) for lithium nitrate does not agree at all. Although curve (C′) is drawn as a continuous curve, it might as well have been drawn as two straight sections with a sharp break occurring at about 135° between them.

Experiments with cooling curves of pure lithium nitrate by the authors do not reveal any evidence of two forms of lithium nitrate. However, other experimenters have obtained results (private communications) that lead them to suspect a second form of lithium nitrate.

The authors feel that perhaps the difference between their results and those of former determinations on this system may be explained as a result of the extreme care that was taken to dry the samples thoroughly without any possibility of decomposition, and to keep them dry during the various determinations.

All samples used in the cooling curve method were dried in boats, either heating to a low temperature in dry air or nitrogen or keeping in a high vacuum until no further loss of weight occurred. The boats were then slipped into weighing bottles and stoppered, while still in the stream of dry nitrogen. Moreover, the tube in which the melts were made was pre-swept with dry nitrogen and continually bathed in this medium during each entire determination.

TABLE I

EUTECTIC POINT (E) FOR CURVES (A) AND (C) (COOLING CURVE METHOD)

%, $LiNO_3$	Temp, °C.	
23.53	79.5	Av. = 79.5°
23.75	79.5	Eutectic composition =
24.97	79.5	25.3 ± 0.3%
24.84	79.5	
Av.	79.5	

TABLE II

EUTECTIC POINT (E′) FOR CURVES (B) AND (C) (COOLING CURVE METHOD)

%, $LiNO_3$	Cor. eut. Temp., °C.	
19.7	90.2	Av. = 90.4 ± 0.3°C.
24.6	90.8	Eutectic comp. = 26.6
25.2	90.9	(±0.3%) $LiNO_3$
25.6	90.6	
26.0	90.2	
26.5	90.4	
27.4	89.9	
27.6	90.6	
29.0	89.2	
31.4	91.5	

Considerable difficulty was experienced in obtaining reproducible results by all methods used for the data of curve (C) as well as that of the eutectic point at temperature 90.4 ± 0.3° as the figures in Tables I and II will indicate. As the same methods gave good results for curves (A) and (B) and had previously been carefully proven on the system ammonium nitrate–sodium nitrate by Holmes and Revinson,[3] the trouble could be attributed to some as yet unknown peculiar property of lithium nitrate. If two forms existed in an equilibrium that shifted very slowly, the observed results might be explained, or possibly, a double salt with ammonium nitrate might be slowly formed.

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[CONTRIBUTION FROM GULF RESEARCH & DEVELOPMENT COMPANY'S MULTIPLE FELLOWSHIP, MELLON INSTITUTE]

Chemisorption of Carbon Monoxide and the Heterogeneity of the Surface of Iron Catalysts

BY J. T. KUMMER AND P. H. EMMETT

Radioactive and non-radioactive samples of carbon monoxide have been added in succession as two separate fractions to a reduced iron synthetic ammonia catalyst at −195 or −78°. The chemisorbed carbon monoxide layer has then been removed by pumping and analyzed for $C^{14}O$. The results show that the second fraction of added carbon monoxide tends to desorb first. However, the results also show that a partial rapid exchange equivalent to a coverage of about 50% of the iron surface occurs between the two added fractions of chemisorbed carbon monoxide even if both fractions are added at −195°.

Many data have accumulated in the literature to indicate that metallic catalysts have heterogeneous surfaces. Some of the surface atoms appear capable of holding gas molecules much more tightly than do others. For example, measurements of the heats of adsorption of gases on metals usually show that the first few molecules picked up by the surface evolve considerably more heat per molecule than those picked up when the surface is partially covered with the chemisorbed gas.

Although this rapid falling off in the heat of chemisorption with fraction of the surface covered is usually taken as an indication of the heterogeneity of the surface, it might also be accounted for, as pointed out by a number of workers, by the influence of one adsorbed molecule on the adsorption of others. Thus it has been argued that even on a uniform surface one would expect that the exothermicity of adsorption would decrease as the surface became more and more covered with adsorbate molecules purely as a result of the tendency of adsorbed molecules to repel partially those that are being adsorbed in adjoining positions.

Several years ago, Roginskii and Todes[1] pointed out that these two explanations for the observed behavior of gases being adsorbed on solids could be

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(1) S. Z. Roginskii and O. Todes, *Acta Physicochim. (U. R. S. S.)*, **21**, 519 (1946).

TABLE I

	Addition of first fraction			Addition of second fraction			Gas phase analysis		
Run No.	Temp., °C.	Volume, cc.	Activity, c./min./cc.	Temp., cc.	Volume, cc.	Activity, c./min./cc.	Time, hr.	Gas activity, c./min./cc.	% of way to complete equilibrium
1	−78.5	27.5[a]	0	−78.5	60.6	3050	0.25	2440	59
							1.5	2580	44
							3.0	2470	56
							20.0	2360	68
2a	−78.5	16.68	11900	−78.5	35.6	0	0.3	2700	71
							1.3	2990	79
							8	2960	78
2b	−78.5	27.5[a]	0	−78.5	9.34	11500	0.1	5000	76
							3	3840	89
							23	3300	95
3	−195	11.7 in presence of He	11500	−195	154.3	0	0.3	380	47
							1.25	380	47
							3.25	386	47
6	−78.5	27.5[a]	3100	−195	119.6	0	0.25	25	4.5
							4.0	28	5.0

[a] These samples were pumped at −78.5°. Past experience showed that about 27.5 cc. of chemisorbed CO remained on the sample after such evacuation as a monolayer.

differentiated one from the other by covering one fraction of the surface by one form of an adsorbate and another part by an isotopic form. They suggested that if the surface is heterogeneous, the portion of adsorbate added first should desorb last, and that, on the other hand, if the ease of desorption is determined merely by molecular interaction among the adsorbate molecules on a homogeneous surface, the ratio of the two isotopic adsorbates would, throughout the desorption, be equal to the ratio in which the isotopic forms were added. We have now completed a number of experiments of this kind on a promoted iron catalyst, using $C^{14}O$ and $C^{12}O$ as adsorbates.

Experimental

In all the experiments to be described in this paper, a 30-g. sample of promoted iron catalyst was used. The promoters were 2.26% Al_2O_3, 0.21% ZrO_2 and 0.62% SiO_2. The 30-g. sample of catalyst had a nitrogen monolayer of 114 cc. and a free iron surface capable of chemisorbing 27.5 cc. of carbon monoxide in experiments 1 to 8; in runs 9 to 11 after intervening sintering the nitrogen monolayer was 108 cc. and the free iron surface was equivalent to between 19 and 21 cc. of chemisorbed carbon monoxide. This chemisorption of carbon monoxide has been shown by Emmett and Brunauer[2] to be a measure of the number of atoms of free iron on the surface of the catalyst. Before each experiment, the catalyst sample was freshly reduced several hours at 500°, and evacuated overnight at this same temperature. In experiments 1 to 8 inclusive, the activity of evolved radioactive carbon monoxide was determined by converting the gas to carbon dioxide, precipitating it and counting it as barium carbonate. In experiments 9 to 11 inclusive, the carbon monoxide activity was measured by the Geiger counter modified[3] by the addition of an external gas chamber through which the gas to be counted could be circulated.

Detailed consideration of the problem made it evident that because of the extremely rapid rate of chemisorption of carbon monoxide even at −195° it would not be easy to add a chemisorbed layer in two different fractions and still give each fraction a chance to seek out any active points that might be present. If only a fraction of a monolayer is added, there is no assurance that the carbon monoxide has distributed itself uniformly rather than deposited itself on the first part of the catalyst coming in contact with the gas. Even adding the carbon monoxide in helium to slow down adsorption would not necessarily give the carbon monoxide molecules a chance to be adsorbed on any active points that might exist, for there is evidence that only a very small energy of activation is involved in the adsorption of the carbon monoxide and that accordingly the gas might well deposit where it strikes the catalyst. Such random distribution might give the appearance of a homogeneous surface even though active points exist. Accordingly, in an endeavor to put the first fraction of added carbon monoxide on only the most active points, in most experiments the gas was put on the surface at −78° and then pumped at either −78, −30 or at 0° for many hours. During this pumping, the evolved gas was collected by a gas collecting diffusion pump[4] so that a figure could be obtained for the amount of tightly bound carbon monoxide held by the surface at the end of this pumping period. The second fraction of carbon monoxide was then added at −78 or −195°. If a gas phase remained after the addition of the second portion of the adsorbate, its activity was obtained as a function of time; the sample was then degassed by the collecting diffusion pump at successively higher temperatures and each sample of evolved gas analyzed for radioactivity.

Results

Table I shows the results of adding two portions of carbon monoxide of different C^{14} content successively to the sample and observing the gas phase as a function of time. It is evident that there is an immediate partial exchange between the two portions put on the catalyst. However, some of the carbon monoxide chemisorbed on the surface will not participate in the rapid exchange, but seems to exchange very slowly if at all. In this connection it will be noted that at −195° the exchange of physically adsorbed and gas phase carbon monoxide is much more rapid with a chemisorbed layer put on at −195° (run 3) than with one put on the surface at −78 (run 6). This is attributed to the fact that the heat of chemisorption of carbon monoxide at −78°[5] is about twice as large as at −195°.

After run 6 had proceeded for four hours, the catalyst sample was warmed up and evacuated at −78, 0 and 120°. The gas so removed showed C^{14} contents that increased with an increase in the temperature of degassing. Thus, the activity of the gas evolved on pumping to −78° (117 cc.) was 135 counts per minute per cc.; that of the gas evolved (7.8 cc.) on evacuating the sample as the temperature was raised from −78 to 0° was 1960 counts/min./cc.; and that evolved between 0 and 120° (13.4 cc.) had an activity of 2250 counts per minute per cc.

The tendency for the second added fraction to be desorbed first is shown even more clearly by the data in Tables II, III and IV for runs 9, 10 and 11. Experiment 9 in which the

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[2] P. H. Emmett and S. Brunauer, THIS JOURNAL, **59**, 310 (1937).

[3] J. T. Kummer, *Nucleonics*, **3**, 27 (1948).

[4] I. E. Puddington, *Ind. Eng Chem., Anal. Ed.*, **16**, 592 (1944).

[5] Beebe and Stevens (THIS JOURNAL, **62**, 2137 (1940)) have shown that the heat of chemisorption of carbon monoxide on iron at −195° is ~17 kcal. for the first small amount of carbon monoxide taken up. At −78 and at 0°, the corresponding value is 35 kcal.

TABLE II

EXPERIMENT 9

Iron catalyst #423 was exposed to $C^{14}O$ at −78° and then pumped at −30°, until 14.05 cc. of $C^{14}O$ was left chemisorbed (activity 4840 c./min./cc.). Then at −195°, 22.2 cc. of normal CO was added. The CO was then removed by pumping with an automatic Sprengel pump and analyzed for $C^{14}O$.

Evacuation temp., °C.	Increment of CO removed, cc.	Activity	CO left on the surface, cc.	Cumulative counts/min. removed
−195	2.34	70	33.91	164
−172	1.27	116	32.64	311
−150	4.65	264	27.99	1571
−130	5.02	539	22.97	4271
−110	2.19	932	20.78	6311
− 78.5	5.02	1860	15.76	15651
− 30	2.12	2960	13.64	21931
0	3.58	3600	10.06	34831
+ 50	3.12	4060	6.94	47491
+110	2.55	4200	4.39	58191
As CH_4	2.51	3500	1.88	66991
As CH_4	1.98	3240	−0.1^a	73401^a
As CH_4	1.68	3190	−1.78^a	78761^a
As CH_4	2.1	(3200)	−3.88^a	85461^a
As CH_4	0.74	(3200)	−4.62^a	87831^a

^{a} The sample was supposed to contain only 36.25 cc. of $C^{14}O$ having a total count of 68,200 counts per minute. Actually 40.87 cc. with a total count of 87,831 was removed.

TABLE III

EXPERIMENT 10

The reduced 30 g. iron sample was allowed to adsorb 26.1 cc. of $C^{14}O$ of an activity of 1512 c./min./cc. of which 12.7 cc. was evacuated at 0°. At −78.5°, 6.85 cc. of normal CO was added, and the sample evacuated at −78.5, −30, 0, 60 and 110°. The results of this evacuation are given.

Evacuation temp., °C.	Evacuation time, hr.	Evacuation increment, cc.	Activity c./min./cc.	Left on, cc.	Cumulative c./min. removed	Average activity left on
−78.5	3.75	3.37	500	16.88	1685	1100
−30	3	2.77	820	14.11	3955	1150
0	3.7	1.70	958	12.41	5585	1180
60	19	7.51	1170	4.90	14390	1195
110–300	12	1.46	1280	3.44	16260	
310	As CH_4	4.25	1122	−0.81	21030	

TABLE IV

EXPERIMENT 11

Sample originally contained 11.05 cc. of normal CO left from evacuation at 0°, and 8.10 additional cc. of radioactive CO added at −78.5°, and of an activity of 3615 c./min./cc.

Evacuation temp., °C.	Evacuation time, hr.	Removed, cc.	Activity c./min./cc.	Left on, cc.	Cumulative c./min. removed	Activity of gas left on
−78	15	4.50	2220	14.65	10000	1318
−30	5.5	2.47	1748	12.18	14310	1230
0	24	2.64	1370	9.54	17930	1192
+58	20	4.65	1260	4.89	23780	1130
+58–300		1.13	..	3.76		
>300°—as CH_4		0.88	1070	2.88		

second added fraction was non-radioactive is especially illuminating in that it reveals a gradual increase in radioactive count from 70 to 4200 counts per minute per cc. as the sample is increased slowly in temperature from −195 to 110°. Unfortunately, in run 9 the total evolved count was some 30% higher and the total evolved carbon monoxide (or methane) was about 13% higher than expected. Possibly an error was made in the amount of radioactive carbon monoxide put on the sample at the start of the run. If one assumes that initially 18.2 cc. rather than 14.05 cc. of radioactive carbon monoxide was left on the sample after the −30° evacuation, the total volume and activity of the gas recovered in the experiment are approximately accounted for. Regardless of this discrepancy in the volume and total count of the evolved gas, there is no question but that the second portion of added carbon monoxide was evolved more rapidly than the first addition.

Experiments 10 and 11 are approximate duplicates except that the order of putting on the radioactive $C^{14}O$ was reversed in the two runs. In experiment 10 the first fraction added was radioactive; in experiment 11 it was non-radioactive. The activity of the first fraction added was altered in this way in order to eliminate any possible isotope effect that might result in a preferential adsorption of $C^{14}O$ compared to $C^{12}O$. These runs like runs 9 and 6 clearly indicate that the second portion of added carbon monoxide tends to come off preferentially. Furthermore, they are more conclusive than runs 6 and 9 because in runs 10 and 11 the second portion of carbon monoxide was added at the same temperature (−78°) as the first portion rather than at a much lower temperature (−195°) than that at which the first portion was added. However, runs 10 and 11, like runs 1, 2a, 2b and 3 show also a very rapid initial exchange of part of the carbon monoxide of the second fraction with part of the first fraction.

Discussion

On the basis of calculations made from the data in Tables I to IV, one can summarize the results of the present paper succinctly by saying that about 50% of the surface holds chemisorbed carbon monoxide in such a way that it can rapidly exchange with any physically adsorbed or gaseous carbon monoxide present and can also rapidly form a homogeneous chemisorbed phase if added in two successive portions. The other 50% of the surface holds its chemisorbed carbon monoxide in such a fashion that it cannot exchange rapidly at either −78 or −195° with physically adsorbed or gaseous carbon monoxide and is distinguishable from other portions of added chemisorbed gas. If one were to follow the original suggestion, one would probably conclude, therefore, that one half the surface behaves as though it were heterogeneous and the other half behaves as though it were homogeneous. However, a more detailed consideration of the matter leads to the conclusion that such clear cut deductions as to the nature of the catalyst surface are not warranted on the basis of the data here reported.

The difficulty in interpreting the results arises from the fact that under certain conditions a heterogeneous surface could, in these isotope exchange experiments, appear to be homogeneous, and a surface that is entirely homogeneous with no active points could appear to be heterogeneous. For example, if by some process the molecules of a completed layer of chemisorbed carbon monoxide are able to trade places with each other very rapidly over the entire surface, one would arrive at the conclusion that the surface is homogeneous even though it might actually be very heterogeneous and contain many active points of varying adsorptive strength. On the other hand, a heterogeneous appearance could be simulated by a homogeneous surface if the chemisorbed carbon monoxide molecules occupy fixed positions and if the projected molecular area is larger than the area *per site* on the catalyst. For such a gas solid system, there will be left, after the adsorption even of molecules of very high heat of adsorption, discontinuities in the adsorbed layer at those spots where adsorption sites occur but where adsorption of a molecule or atom cannot occur due to steric hindrance. This would cause a homogeneous surface to behave as though it were partly heterogeneous. Accordingly, it seems possible to conclude that half of the surface is homogeneous and half is heterogeneous only if one assumes that on a heterogeneous surface the chemisorbed molecules occupy fixed positions and do not exchange rapidly with the gas phase, with physically adsorbed carbon monoxide or with other molecules of chemisorbed carbon monoxide; and that on a homogeneous surface the chemisorbed carbon monoxide molecules are not sterically hindered from becoming equivalent to each other.

The question next arises as to how one can account for the observed very rapid displacement of part of the first fraction of chemisorbed carbon monoxide when one adds the second fraction. Three explanations occurring to the authors appear to warrant brief comment.

(1) A possible explanation of the rapid initial mixing of the first and second additions of carbon monoxide as shown in Tables I to IV seemed to be that molecules of the first fraction might be desorbed by the rather high heat of adsorption of the second fraction. To test this hypothesis, oxygen, which has a heat of adsorption of 122 kcal. per mole, was added at −78° to a catalyst surface covered with about 27 cc. of chemisorbed carbon monoxide having an activity of 13500 counts per minute per cc. The oxygen adsorption is almost instantaneous. In spite of the fact that the oxygen penetrated the carbon monoxide layer and oxidized the equivalent of approximately 10 layers of iron atoms, no appreciable quantities of carbon monoxide were displaced to the gas phase.[6] When 272 cc. of oxygen was allowed to react with the catalyst at −78°, only 0.12 cc. of gas of an activity of 1900 counts per minute per cc. was left in the gas phase. This is equivalent to the displacement of only 0.02 cc. of the original 27.5 cc. of chemisorbed carbon monoxide. On degassing the sample at room temperature after the run, 4.7 cc. of gas was evolved containing about 14% carbon dioxide and 86% carbon monoxide, both having an activity of 13500 counts per minute per cc. It thus appears that the evolution of a high heat of adsorption of carbon monoxide by the second fraction of added carbon monoxide cannot account for the rapid initial evolution of part of the first fraction of carbon monoxide chemisorbed.

(2) Another mechanism that might account for this initial rapid exchange is suggested by a consideration of the structure of iron enneacarbonyl, $Fe_2(CO)_9$, as described by Pauling.[8] In $Fe_2(CO)_9$ each of the two iron atoms (2.46 A. apart) is bound separately to three carbon monoxide molecules and each is also bound to three carbon monoxide molecules shared between the two irons. Now, the closest approach of iron atoms in body centered alpha iron is 2.48 Å. It, therefore, does not seem unreasonable that on certain faces (such as the 110 face, for example) of the iron crystals it would be possible to have two carbon monoxide molecules held at least momentarily between two adjacent iron atoms. If the binding energy of the second molecule added to such a pair of iron atoms already containing one carbon monoxide molecule is small and if the two bound carbon monoxide molecules then become equivalent, a limited rapid exchange of the type observed would be expected. Unfortunately, no way of testing the part played by this particular mechanism seems to be available.

(3) The third possible mechanism for the rapid equilibration of the carbon monoxide on the 50% of the surface that appears to be homogeneous is the usual one in which it is assumed that as the per cent. coverage of a surface increases, the heat of adsorption decreases due to repulsive forces among the adsorbed molecules. If the coverage is sufficient to drop the heat of adsorption to a few kilocalories per mole of carbon monoxide, then the observed rapid exchange could be accounted for. Either this mechanism or the one mentioned under item (2) could satisfactorily account for the rapid desorption of part of the carbon monoxide from the catalyst surface when the second fraction of the gas is added. It should be emphasized, however, that such a rapid exchange by either (2) or (3) is limited to the carbon monoxide on about one-half of the surface.

In conclusion it should be pointed out that the experiments discussed in the present paper are all in substantial agreement with previous observations reported for the chemisorption of carbon monoxide on iron catalysts.[2,5] Specifically, it has been reported in previous papers that the layer of carbon monoxide chemisorbed on iron at −195° is not removed by pumping the catalyst for one hour at −78°; only the physically adsorbed carbon monoxide is removed by such pumping. In runs 9, 10 and 11 it will be noted that after extensive pumping at −78°, 15.8 cc., 16,9 and 14.7 cc. of carbon monoxide, respectively, appear to be left on the surface even though the chemisorbed layer for the sample used in runs 9, 10 and 11 was, as stated above, between 19 and 21 cc. This has been confirmed by some work that is as yet unpublished in which we have found that long-continued pumping at −78° can slowly remove carbon monoxide chemisorbed at −195° (perhaps 25% of a layer in 24 hours of pumping). However, the one-hour pumping at −78° specified in the initial paper[2] as one that was to be used in ascertaining the amount of chemisorbed carbon monoxide on an iron catalyst will actually remove only a negligible quantity (less than 5%) of the chemisorbed carbon monoxide.

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[6] It is somewhat suprising that the oxygen can penetrate through a layer of chemisorbed carbon monoxide and oxidize the underlying iron atoms in view of the observation by Brunauer and Emmett[7] that the chemisorption of carbon monoxide is markedly inhibited by first treating the catalyst with oxygen at −78 or −183°. Presumably the present experiments constitute evidence that sufficient holes exist in a layer of chemisorbed gas to permit the penetration of a reactant to underlying layers, and that if the carbon monoxide becomes chemisorbed before the oxygen is added, no displacement of the carbon monoxide by oxygen occurs.

[7] S. Brunauer and P. H. Emmett, THIS JOURNAL, **62**, 1732 (1950).

[8] L. Pauling, "Nature of the Chemical Bond," Cornell University Press, Ithaca, N. Y., 1944, p. 254.