[CONTRIBUTION FROM THE LABORATORY OF CATALYSIS, CHARKOW INSTITUTE OF CHEMICAL TECHNOLOGY]

Catalysis by Fusions

BY I. E. ADADUROW AND P. D. DIDENKO

The problem of the part played by solid surfaces in the catalytic process has been repeatedly the object of many discussions. Owing to the work of Schwab and Pietsch,[1] it has been more often repeated recently that not all places on the surface of the catalyzer possess an equal catalytic activity and that the latter is particularly inherent to places possessed of an elevated energy. Nevertheless, in a recent paper, Steacie and Elkin[2] attempted to demonstrate, on the example of the decomposition of methanol by solid and liquid zinc, that these places of elevated energy, active centers, etc., do not play any substantial part in the catalytic process. In their investigation these authors proceed from the conjecture that, if the activity of the catalyzer is essentially based on irregularities and disturbances of the crystalline surface (active places, edges and angles of crystals, etc.), it must fall abruptly if the catalyzer becomes fused. To verify this conjecture, Steacie and Elkin measured the dependence of the speed of decomposition of methyl alcohol vapors by zinc from the change of temperature between 360 and 440°, the size of the surface of the zinc remaining constant (for example, 0.5 sq. cm.). The time of increase of total pressure for a determined percentage rate was used by the authors as a standard of catalytic activity. An uninterrupted increase of activity with the rise of temperature was thus obtained, without interruption of this increase at the fusion point, *i. e.*, at 420°. The authors conclude from this that the surface of zinc is regularly active and that in general the activity of a solid substance cannot be attributed to a limited part of its surface.

We have repeatedly expressed[3] the idea that the nature of the catalytic action of a solid on the molecules of the catalyzed components of the reaction represents an influence of the field of the surface that deforms the molecules, which results in the obtaining of an active reacting condition by the molecules. But, for such a deformation to take place, two basic conditions are required. The first consists in a sufficient deforming power of the field to bring the molecule in an active condition. The second consists merely in the correspondence of the field of pertinent active places (edges, angles of disturbances, etc.) or centers (active points, points of the network) to the fields of the molecules that are being catalyzed, *i. e.*, in their possessing a necessary and definite texture and shape.[4]

From this point of view it is possible to agree with Steacie and Elkin only in the case if the form of the field that is necessary for the activation be maintained not only when approximating the fusing point, 420°, but also in the fused zinc; the power of the field yet retaining a value sufficient for the necessary deformation of the molecule that is being catalyzed.

Recently, in 1933, Randall and Rooksby[5] undertook an x-ray investigation of a whole series of liquid metals near their fusing points with the result that sodium, potassium, rubidium and cesium show in the Röntgenogram maxima at the points where intensive lines of these metals in solid condition are situated. Otherwise, near the fusing point fused metals can keep or obtain the reciprocal disposition of molecules which the metal possesses in the solid phase. It is clear that such a disposition of molecules can be fixed only by the field that is prevalent in the fusion. If not by the value of its tension, the field must in any case correspond in shape and texture to the shape and texture of the field of the crystalline network. Thus it is only necessary that its value be sufficient for the deformation of the molecule called forth by it to be able to produce in it the proper reacting power, and then the cata-

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(1) G. M. Schwab and E. Pietsch, *Z. physik. Chem.*, **1B**, 385 (1929); *Z. Elektrochem.*, **35**, 573 (1929); E. Pietsch, A. Kotowsky and G. Berend, *ibid.*, **35**, 582 (1929); *Z. physik. Chem.*, **5B**, 1 (1929); Smekal, *Z. Elektrochem.*, **35**, 567 (1929).

(2) Steacie and Elkin, *Proc. Roy. Soc.* (London), **A142**, 457 (1933).

(3) I. E. Adadurow, lectures on "Theory of Heterogeneous Catalysis" read in 1933–1934 at the Charkow University (stenotyped); I. E. Adadurow and W. A. Dzisco, *J. Phys. Chem. U. S. S. R.*, **3**, 489 (1932); I. E. Adadurow and P. J. Krainii, *ibid.*, **3**, 496 (1932); I. E. Adadurow, *ibid.*, **4**, 907 (1933); **5**, no. 7 (1934); and a series of other works by I. E. Adadurow and collaborators on vanadium and chrome catalyzers, published in *J. Applied Chem. U. S. S. R.*, 1930–1935.

(4) C. S. Taylor and D. B. Jones, "Variable Activity of Catalytic Surfaces," *Uspechi Chimii*, **2**, 701 (1934); Taylor, *Z. Elektrochem.*, **35**, 542 (1929).

(5) J. T. Randall and H. R. Rooksby, *Physik. Z.*, **33**, 473 (1932); W. I. Danilow, "Dispersion of x-Rays in Liquid Metals and Alloys," *Uspechi fisitch. nauk*, **14**, 449 (1934); *ibid.*, other literature on the same problem.

TABLE I

OXIDATION OF AMMONIA BY FUSED TIN

T, °C.	Velocity of air	Velocity of NH_3	Determined analytically % of NH_3	Determined analytically % of NO	% of contacting	Notes
300	300	30	10	...	..	A white vapor of nitrite appears
420	160	16	...	...	..	White nitrite vapor
460	143	55	...	...	..	Simultaneously with the vapor
540	143	28	...	...	..	a marked white grayish de-
610	179	55	...	...	..	posit appears on the discharge
640	197	55	...	...	..	tube growing as the temper-
650	210	58	7.6	2.3	32	ature increases
800	1300	70	4.4	1.8	40.9	Typical curve
800	1300	70	5.0	2.4	48.0	of the contact process
840	1300	70	5.0	4.0	80.0	
865	1300	70	4.6	1.7	36.9	See Fig. 2
900	1300	70	5.0	0.92	18.5	

lytic process by the fusion will result, in the same way that it had been secured by the solid body.

As a subject for investigation of catalysis by fusion we selected the catalytic oxidation of ammonia by fusions of metallic tin and silver, which melt at 231.8 and 960°, respectively. The oxidation was carried out in the apparatus schematically shown in Fig. 1. The apparatus consists of a test-tube (a), in whose neck a quartz tube (b), soldered at one end, for the thermocouple used in measuring the temperature of the fusion, is inserted through a stopper consisting of an acid-proof and thermally resistant plaster. Another quartz tube (c) is reserved for the introduction of the air–ammonia mixture that bubbles through the fused liquid metal or passes through the solid metal. To make it possible for the gas to pass through the solid metal (silver), it is first fused and then allowed to cool very slowly without interrupting the flow of the air–ammonia mixture, which thus works a series of thin channels through the hardening metal, through which the gas mixture passes afterward when the metal has completely solidified. Besides these two tubes, a quartz tube (d) for discharging the gases is also soldered into the stopper. The whole apparatus is put into an electric furnace and heated to the temperature required. In the lower part of the test-tube (c) is introduced the catalyzing metal. The analysis of the air–ammonia mixture and of the gases leaving the conversion apparatus was made by the usual method.

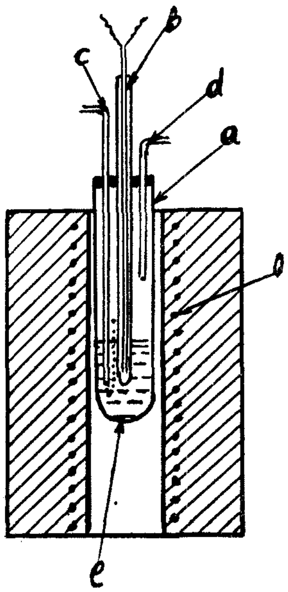

Fig. 1.

The experiments with tin gave the following results at about 300° and at a rate of 0.03 liter per minute of ammonia and 0.30 liter per minute of air: at a ratio of 10% ammonia to 90% air, a white vapor of the nitrite appears. With the increase of the velocity of the gas current to 0.05 liter/minute for ammonia and 0.50 liter/minute for the air, the development of ammonium nitrite increases. Only at about 650° the contacting action begins to be evident and the nitrite vapor disappears. But it is to be noted that simultaneously with the appearance of nitrite a grayish-white deposit forms on the tube discharging the converted gases, which upon investigation proved to be a mixture of tin oxide and tin dioxide ($SnO + SnO_2$). The results of the investigation are shown in Table I.

After opening the contact tube, it was found that nearly all the metal had been transformed to a grayish-white-green mixture of particles of metal that did not have time to oxidize with tin oxide and tin dioxide.

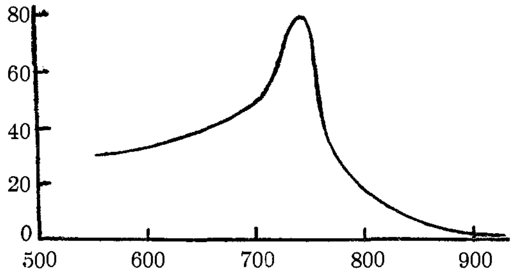

Fig. 2.

Thus the catalyzing effect here is obtained not by metallic tin, but by tin oxide, which has been used already by Wortmann[6] as a contact mass for the oxidation of ammonia. The appearance of tin oxide here is also not unexpected, because tin that is resistant to the oxidizing action of atmospheric oxygen at an ordinary temperature goes over to oxides easily enough at temperatures above the fusing point.

Thus a metal should be selected which would not form compounds with oxygen at elevated temperatures approximating the melting point or

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[6] Oskar Kausch, "Catalyzers for the Production of Sulfuric and Nitric Acids and Synthetic Ammonia," NTWU, 1934, p. 140; also An., p. 79049.

above and at the same time would catalyze the reaction of oxidation of ammonia nitrogen compounds. Such a substance is silver, which, as has been said by D. I. Mendelejew, "is a metal that does not oxidize in the heat."[7] The silver is not oxidized by atmospheric oxygen at any temperature and its oxide, Ag_2O, decomposes when heated. According to Le Chatelier, the dissociation pressure of oxygen isolated by silver oxide at 300° is a trifle over 10 atm.; silver peroxide decomposes when being dried and heated to 150°, giving off oxygen.

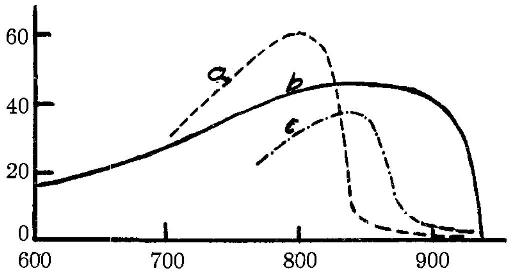

Fig. 3.

Because of the catalytic properties of silver W. Manchot and I. Haas[8] proposed to use it for the oxidation of ammonia, indicating that an active catalyst is obtained by reducing dry silver oxide at a temperature under 100°. The results of the experiments are shown in Table II.

TABLE II

T, °C.	% NH_3	% of conversion
Velocity 1700 cc./min. Curve A, Fig. 3.		
710	10.4	32.6
720	9.9	37.5
730	10.1	41.0
740	10.4	45.1
750	10.0	47.9
760	10.9	52.7
770	11.0	54.8
780	10.4	58.5
790	9.4	61.7
800	9.4	61.7
810	9.4	61.6
820	10.1	55.3
830	9.8	42.0
840	9.9	17.9
850	11	7.2
900	10.4	2.6
940	10.2	1.2
960	9.6	0.7
1000	6	1.9
Velocity, 2340 cc./min. Curve C, Fig. 3		
600	11.5	16.5
620	11.0	17.3
660	10.5	22.3
680	10.5	25.8
700	10.5	28.6
720	10.1	31.0
740	10.1	35.6
770	10.1	40.2
790	8.0	45.1
800	8.0	45.3
820	9.7	46.7
880	11.2	46.4
900	11.2	42.1
920	11.2	38.4
940	11.0	2.3
960	10.4	1.4
1000	5.0	2.0
Velocity, 3900 cc./min. Curve C, Fig. 3		
770	8	21.2
800	10.2	31.3
820	10.1	35.6
840	9.7	37.6
860	9.4	23.4
880	10.0	6.7
920	10.1	2.7
940	9.4	1.3
1000	9.4	1.9
Curve C		

These data form in certain temperature limits curves (a, b, c, Fig. 3) that are very like the conversion curves obtained by Andrusow[9] for the influence of velocity.

They differ, however, from the curves of Andrusow in that there is an abrupt fall in the rate of conversion in certain temperature intervals and that near the fusing point of silver the pyrometer always indicates an abrupt rise of temperature to 1000 or more degrees. This points to the fact that the reaction of oxidation of ammonia to nitric oxide is here substituted at the moment when the network dissociates owing to the transformation of the metal from the solid to liquid state by the reaction of dissociation of ammonia to elementary nitrogen and hydrogen, which oxidizes afterward to water. As can be seen from the equations, the latter reaction goes on with a much greater evolution of heat as compared with the first.

$$4NH_3 + 5O_2 = 4NO + 6H_2O + 215 \text{ cal.} \quad (1)$$
$$4NH_3 + 3O_2 = 2N_2 + 6H_2O + 315 \text{ cal.} \quad (2)$$

In the present case, therefore, an oxidation of ammonia by liquid fused metals cannot be brought about. In the case of tin the oxidation begins at the start of the oxidation of the fused metal and of the forming of a slow-fusing mixture of tin oxide and dioxide.

By making tests with such a metal as silver, for which the forming of slow-fusing oxides is excluded owing to the natural properties of this metal, we see that at temperatures below the melting point the reaction of oxidation of ammonia goes on with a greater or lower percentage of conversion, but near the fusing point the rate of oxidation falls abruptly, what is most clearly seen from Curve C, Fig. 3, for the velocity 2340. At the fusing point the reaction changes its character, being substituted by the reaction of decomposition of ammonia to elementary nitrogen with an abrupt change in the rise of the temperature of the reaction.

This fact, independently or not of our admitting a catalytic inhomogeneity of the surface, is con-

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(7) D. I. Mendelejew, "Principles of Chemistry," Vol. II, 1932, p. 228.

(8) M. Manchot and I. Haas, German Patent 30,065.

(9) Z. Andrusow, *Z. angew. Chem.*, **39**, 321 (1926); **40**, 166 (1926); **59**, 458 (1927); **60**, 536 (1927).

nected with an abrupt change of the field of the elements of the network under the influence of temperature at the fusing point, when the energy of the structure has fallen to naught and when further on the attractive power between the elements of the network is substituted by a repulsing power. It is quite clear that at this moment the potential of the outer field ceases to be adequate not only to the intramolecular field of the molecule that is being catalyzed, but it changes not only by size, but also by form and therefore it is difficult to admit that the catalytic process that takes place when a solid catalyzer is being used takes place also if it is substituted by a liquid fusion.

Therefore the work of Steacie and Elkin appears to us as not irreproachable. The dissociation of methyl alcohol takes place according to Bone and Davies[10] by the equation $CH_3OH = CH_4 + O$, and it is quite certain that the cause of the uninterrupted growth of activity in the limits of 360 to 440°, with no exception for the fusing point of zinc at 420°, does not lie in the equal activity of the surface of zinc; similarly to the case of the attempt with the catalytic oxidation of ammonia by fused tin, where the catalysis takes place not on the surface of the fused metal, but on the oxide, in the case of zinc the catalysis takes place not on the fused metal, but on the surface of the solid zinc oxide that forms in proportion to the atomic oxygen that separates the moment the dissociation of methyl alcohol takes place.

The higher the temperature, the more zinc oxide is being formed, and it is plain why the work of Steacie and Elkin demonstrates here an uninterrupted growth of activity with the increase of temperature. A check test made of the dissociation of methyl alcohol by zinc chips demonstrated quite clearly that at 360–400° the zinc chips are transformed first from the surface and then nearly completely (depending on the quantity of the vapor passed), to zinc oxide when methyl alcohol vapors are passed through them. Furthermore with the growth of the quantity of zinc oxide that is being formed the speed of the reaction of the dissociation of methyl alcohol increases. The fact that finely ground zinc or zinc dust acts as a reducing agent even on water, which is easily decomposed at low temperatures (100°) with simultaneous formation of zinc oxide being known, it was easy to foresee this result.

What concerns the catalytic action of the zinc oxide that is being formed on the decomposition of methyl alcohol, it has been investigated by Adkins and Perkins,[11] who indicated that zinc oxide, under 350°, possesses a nearly imperceptible catalytic faculty for the decomposition of methyl alcohol. If the temperature is being raised, an increasing amount of gaseous products is being formed such as methane, hydrogen, ethane, carbon monoxide and carbon dioxide, which are being obtained also when the decomposition over aluminum oxide (Al_2O_3) is carried out.

Messrs. Deutsh and Prozorowsky, scientific laborers of the laboratory, took part in the experimental part of the work.

Conclusions

1. The work of Steacie and Elkin is subject to no objections as to its principal points, if it will be taken into consideration that x-ray investigations demonstrate that the orientation of the elements of the network is retained by some metals near the fusing point and in fused condition, which indicates that the shape of the field is being retained in any case. And if its potential is sufficient for the needed deformation of the catalyzed molecule, there is no impossibility of catalysis by fusions near the fusing point.
2. But in the special case of decomposition by Steacie and Elkin of methyl alcohol in the temperature range of 360 to 440° attention is attracted by the too great interval of temperature and the growing activity with the increase of temperature inherent to the solid as to the fused catalyzer, which does not take place in usual catalytic processes and calls forth a doubt as to the correctness of the explanation of the causes given by the authors.
3. The oxidation of ammonia by fused tin as carried out by us demonstrates the same increasing activity of the liquid catalyst at high temperatures (up to 840°), where nothing similar to an orientation of the crystalline network can last. The growth of the catalytic activity with time as with the increase of temperature clearly indicates the necessity of searching for other causes of its growth.
4. In the course of the investigation it has been quite clearly demonstrated that the oxidation of ammonia begins only from the moment of the formation of tin oxide and dioxide, which

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(10) W. A. Bone and H. Davies, *J. Chem. Soc.*, **105**, 1691 (1914).

(11) H. Adkins and P. D. Perkins, *J. Phys. Chem.*, **32**, 221 (1929).

has been recommended as a catalyzer for the oxidation of ammonia by Wortmann.

5. The example of silver taken as a catalyzer which does not form oxides and does not change its metallic individuality with rise of temperature demonstrated that near the fusing point the catalytic activity falls abruptly simultaneously with a change of the type of the reaction itself at the fusing point.

6. From this it becomes likely that in the process of decomposition of methyl alcohol by zinc the nature of the increasing activity may be explained by the formation of zinc oxide similarly to what had been demonstrated by us in the case of oxidation of ammonia by fused tin, where the increasing activity is related to the formation of tin oxide.

7. The formation of tin oxide in the process of decomposition of methyl alcohol is very probable, as Bone and Davies have demonstrated that its thermal decomposition takes place according to the equation $CH_3OH \longrightarrow CH_4 + O$, and the reaction takes place according to the equation $2CH_3OH \longrightarrow CH_3OCH_3 + H_2O$.

The formation of zinc oxide in proportion to water vapor is also quite evident, as in the case of $CH_3OCH_3 \longrightarrow C_2H_6 + O$; the formation of zinc oxide is inevitable.

8. The attempted decomposition of methyl alcohol vapor by zinc chips at 360–400° undertaken by us showed experimentally that zinc chips either are partially covered by zinc oxide on their surface or go over to it completely, depending on the quantity of methyl alcohol that has been passed and the time this has taken.

9. From the aforesaid, it is to be acknowledged that the conclusion of Steacie and Elkin that the surface of zinc is equally active and that in general the catalytic activity of a solid matter cannot be ascribed to a limited part of its surface, is baseless and results from an insufficient cleanness of the experiment.

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NOTES

Thermocouples from 2 to 90° Absolute

BY J. ELSTON AHLBERG AND WALTER O. LUNDBERG

In the establishment of temperature scales, several methods are being employed. Due to the necessity of setting up an accurate temperature scale between 20 and 70°K. it was thought desirable to test mathematical equations relating the electromotive force of thermocouples to temperature. The general trend of the data given by Giauque and associates[1,2] for a copper–constantan thermocouple (ice reference junction) between 13 and 90° K. made it apparent that the following simple equation might accurately represent the results

$$E = A + BT^2 + CT^3 + DT^4$$

E is the thermocouple voltage in microvolts, T is the absolute temperature, A, B, C and D are constants. The third law of thermodynamics requires that the term associated with the first power of temperature be equal to zero. Terms associated with powers of temperature higher than the fourth are assumed negligible.

Using the values by Giauque and associates[1,2] at 15, 20, 70 and 90°K. we find $A = 6681.26$, $B = -1.6547 \times 10^{-1}$, $C = 5.5460 \times 10^{-4}$ and $D = -9.878 \times 10^{-7}$. The agreement between the data of Giauque and associates and the above equation is as follows: from 13 to 23°K. better than 0.008°; from 24 to 35°K. better than 0.05°; and from 40 to 90°K. better than 0.03°. The agreements are well within the limits of accuracy claimed by them. The agreements additionally indicate the validity of the temperature scale at the University of California and of the data used in its establishment.[3] Moreover, the average deviation of the temperature coefficients of voltage from the calculated values is but 0.3%.

At the Johns Hopkins University we have experimentally compared a copper–constantan ther-

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[1] Giauque, Buffington and Schulze, THIS JOURNAL, **49**, 2343 (1927).

[2] Giauque, Johnston and Kelley, *ibid.*, **49**, 2367 (1927).

[3] Onnes, Keesom and Associates, *Comm. Phys. Lab. Univ. Leiden*; Simon and Lange, *Z. Physik*, **15**, 312 (1923).