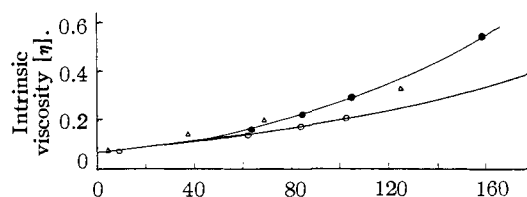


branching (about 1 PO₄-group/1000 is a branching point), was investigated as a function of chain length. In this work, the conditions which one of us employed in the first viscometric study²¹ (Paper V of this series) of a series of chain phosphates of varying length were repeated. The results are shown in Fig. 4. According to the new data, the branching becomes undetectably small when the number average chain length is reduced below ca. 50. Apparently, the formation of branches represents a gradual approach to the ultraphosphate region²² as Na₂O/P₂O₅ is reduced from values greater than one. The data of Fig. 4 give added support to Strauss' contention that the initially high viscosity is not due to the effect of impurities.

(21) J. R. Van Wazer, *THIS JOURNAL*, **72**, 906 (1950). The results of Fig. 4 should be substituted for those in Paper V.

(22) J. R. Van Wazer and E. J. Griffith, *ibid.*, **77**, 6140 (1955).



Number average chain length, \bar{n} , from end-group titration.

Fig. 4.—Variation of intrinsic viscosity of slightly branched and straight-chain phosphates from Na₂O/P₂O₅ glasses as a function of chain length. Zero-time extrapolated values for chains with some branching denoted by black circles; values after 12 hr. standing (with chain lengths corrected for ortho) by open circles; and the now obsolete data from Paper V¹⁷ by triangles.

Acknowledgment.—We wish to thank Dr. Editha Karl-Kroupa for her advice and assistance in the chromatographic part of this study.

DAYTON, OHIO

[CONTRIBUTION FROM THE FRANKLIN INSTITUTE LABORATORIES FOR RESEARCH AND DEVELOPMENT]

Heats of Adsorption of Oxygen on Nickel, Platinum and Silver¹

BY O. D. GONZALEZ AND G. PARRAVANO²

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The adsorption thermodynamics of oxygen was studied on powdered nickel, platinum and silver samples in the temperature range 150–300°, and surface coverages in the range 10⁻⁴ to 10⁻³. Data were obtained by means of decomposition equilibria of water vapor on the surfaces concerned. Values for the heat of oxygen adsorption on nickel were found to be similar to those related to the formation of bulk nickel oxide. On the other hand, large differences between surface and bulk heat values were found for platinum and silver. Similarly, the value of the adsorption equilibrium constant for oxygen was found to increase with increasing surface coverage on nickel, while the same quantity was found to decrease with increasing surface coverage on platinum and silver. These effects are interpreted in terms of current models of the adsorption process. For the same temperature range, no oxygen chemisorption could be detected on powdered gold.

A knowledge of the thermodynamic affinity of solid surfaces is important not only in respect to the formulation of a theory of catalytic action, but also in regard to the more fundamental problem of the physico-chemical properties of solid surfaces. Oxygen is known to combine by forming a bond, with practically all metal surfaces. Consequently, this bond should not be too dependent upon the detailed electronic structure of the metal, as is the case for hydrogen. Oxygen affinities, however, show considerable variations among metallic surfaces. In order to have more information on the important factors which control the interaction of a metal surface with oxygen, we have investigated the thermodynamics of oxygen chemisorption on three different metal surfaces. Furthermore, it is of interest to examine surface affinities in the light of the well known bulk affinities for oxygen. From such a comparison, a contribution can be made toward the goal of understanding surface behavior in terms of bulk properties. Finally, the catalytic activation of molecular oxygen, through chemisorption, is a necessary prerequisite to a large number of oxidation reactions, and the steady-state configuration of the catalytic surface is, under these

conditions, largely determined by its thermodynamic affinity for oxygen.

In the present work, thermodynamic quantities for chemisorption have been derived by means of the adsorption equilibrium function. This is given by

$$K = \frac{\text{Activity of occupied sites}}{\text{Activity of vacant sites} \times \text{activity of adsorbate mols.}}$$

It has been shown that K varies in a characteristic manner with conditions at the surface during adsorption.³ If the activity coefficients for vacant and unoccupied sites are assumed equal, the above equation becomes

$$K = \frac{\theta}{(1 - \theta) \times C}$$

where θ is the fraction of surface covered and C is the activity of free molecules. The quantity K is independent of θ only for the case of localized, non-interacting adsorbed molecules. Since $RT \ln K = -\Delta F^\circ$, the equilibrium constant can be related to the free energy change, resulting from the transfer of one mole of free adsorbate molecules, at their standard state, to the adsorbed layer at the standard state. K is thus representative of the nature of the adsorption bond. The quantity ΔF° , and consequently K increases with increasing

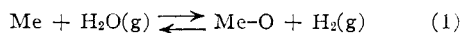
(1) Presented at the Delaware Valley Regional Meeting of the A.C.S., Philadelphia, Pa., February, 1956.

(2) Department of Chemical Engineering, University of Notre Dame, Notre Dame, Indiana.

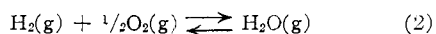
(3) D. Graham, *J. Phys. Chem.*, **57**, 665 (1953).

θ when mutual, attractive interactions, between adsorbed molecules predominate, and decreases with increasing θ for a non-uniform surface, because sites with higher activity are occupied first.³ Since K is also related to the enthalpy change, ΔH , occurring as a result of the adsorption reaction, the method of employing K to characterize adsorption is essentially equivalent to the usual procedure of using ΔH to distinguish among adsorption processes, except that in the former method the experimental isotherms are used directly without the further calculations of the heat of adsorption. There is also the possibility of deducing values of ΔS without the use of an assumed model.

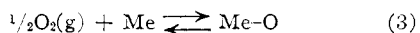
We have studied the equilibrium



where Me is a metal surface, preconditioned by a standard procedure. We have chosen to investigate four metals with widely different bulk affinities for oxygen: nickel, platinum, silver and gold. If K_1 is the equilibrium constant of reaction (1) and K_2 that of the well known gas phase reaction



it can be shown easily that $K_1 \times K_2 = K_3$, where K_3 is the equilibrium constant of the reaction



Reaction (3) represents the oxygen chemisorption process. Thus, by measurements of K_1 , combined with values of K_2 , values of K_3 can be computed and, therefore, thermodynamic functions for reaction (3) derived for different metal surfaces. Essentially a similar method was used previously for studying chemisorption of oxygen and nitrogen on iron.⁴⁻⁶

Experimental

Materials.—Nickel powder was prepared *in situ* by careful reduction at 300° of nickel oxide, obtained by decomposing nickel nitrate (C.P. J. T. Baker) in air at 500°. A stream of hydrogen (100 cc./min.) was used for the reduction. This was assumed to be complete when the increase in weight of a magnesium perchlorate tube, located in series with the nickel sample, was less than 1 mg./hr. The BET surface area, determined on a separate sample prepared under similar conditions, was found to be 1.8 m.²/g. After reduction, the nickel sample was evacuated at 1×10^{-6} mm. for 12 hours at 300°.

Platinum, silver and gold powders were obtained by precipitation from a metal salt-formaldehyde solution by addition of potassium hydroxide. For platinum, a chloroplatinic acid (C.P. J. T. Baker) solution was used; for silver, a silver nitrate (reagent pure, Merck) solution was used; and for gold, a gold chloride (C.P. Merck) solution was employed. The precipitated metals were washed for 36 hours in a Soxhlet extractor and oven dried at 110°. Weighed amounts of metallic powders were charged into the equilibrium apparatus and subjected to a reduction treatment with hydrogen, and a subsequent evacuation, under conditions similar to those used for nickel. The BET surface area of platinum black was found to be 1.99 m.²/g. Silver powder was assumed to have a surface area of 2 m.²/g.

Hydrogen from a commercial tank was purified by passage through a deoxo unit, magnesium perchlorate and a charcoal trap, immersed in liquid nitrogen. Helium, for surface area measurements, was obtained from a commercial

tank and purified by passage through hot copper oxide, magnesium perchlorate and a charcoal trap immersed in liquid nitrogen. Nitrogen, from a commercial tank, was purified in a manner similar to helium with finely divided copper substituted for copper oxide.

Apparatus.—The apparatus consisted of a Pyrex glass rectangular loop, formed by 16 mm. outside diameter tubing. A large furnace with an aluminum core was located around one of the vertical arms. The metal sample was placed at the center of the heated zone of the furnace. A small glass container, filled with liquid water, was attached at the bottom of the apparatus. This container was immersed in a constant temperature bath, so that known and constant water vapor pressures could be maintained in the apparatus throughout a run. To reduce thermal diffusion effects, an electromagnetic pump, consisting of a close-fitting glass piston with a proper valve, was used in the initial phase of the research to aid in the circulation produced by convection currents. However, later experimental checks showed that convection alone was sufficient for proper circulation, and the pump was eliminated. The total volume of the system was about 300 cc., and the sample volume about 10 cc. The temperature of the furnace was controlled by a Celectray unit ($\pm 1^\circ$).

Procedure.—After placing a definite amount of metal into the apparatus, the water of the constant temperature reservoir was degassed by repeated freezing and evacuation until the residual gas pressure was no more than 1×10^{-6} mm. The water was then kept frozen during the reducing treatment of the metal samples, and subsequent evacuation. To determine the leak rate of the apparatus, and any eventual evolution of hydrogen from the sample, the system was maintained under static vacuum for periods of time up to 18 hours at 300°. No gas was evolved within the precision of the experiment. The possibility that the hydrogen measured in an equilibrium experiment could come from hydrogen dissolved during the pretreatment can be excluded on the basis of known data of hydrogen solubilities in metal.⁷ For example, at 400°, only 6.7×10^{-5} cc. STP of hydrogen dissolved in one gram of platinum. Under one atmosphere of hydrogen and for our setup, consisting of 0.4 g. of platinum and a volume of 300 cc. at room temperature, this value represents a pressure of 1×10^{-5} mm. of hydrogen, in contrast with the 3 to 50 μ actually observed. Another possible source of hydrogen, other than that originating from the reaction, can be a very firmly attached hydrogen removed by preferential adsorption of water vapor. This, however, is hardly probable since the ratio $p_{\text{H}_2}/p_{\text{H}_2\text{O}}$ increased as $p_{\text{H}_2\text{O}}$ decreased. After evacuation, the water was melted as fast as possible, the reaction volume briefly pumped out, and the temperature of the water set by the proper bath. A minimum of 12 hours was allowed for the system to come to equilibrium, this period having been independently established to be sufficient for all cases. Samples of the gas phase were then withdrawn, and analyzed for hydrogen. This was done by freezing the water with a liquid nitrogen bath and treating the non-condensable residual gases with copper oxide. By measuring the gas pressure, before and after reaction with copper oxide, it was possible to know whether hydrogen was formed by reaction (1). p_{H_2} of the system was computed from the measured value of p_{H_2} of the gas sample and known expansion volumes.

Since the initial conditions were: $p_{\text{H}_2} = 0$ and $p_{\text{O}_2} = 0$, and $p_{\text{H}_2\text{O}}$ and the reaction volumes were kept constant during a run, the amount of hydrogen formed could be used to compute the amount of surface covered, θ , with adsorbed oxygen. The value of θ can be easily obtained from the expression

$$\theta = \frac{6.30 \times 10^{23} \times V_{\text{system}} \times p_{\text{H}_2}}{2 \times Z \times T_{\text{system}}} = 1/\beta p_{\text{H}_2} \quad (4)$$

where V_{system} and T_{system} refer to different parts of the total volume of the apparatus kept at different temperatures, and Z is the total number of sites available, as derived from the total surface available. In computing values of θ by means of equation (4), the product $p_{\text{H}_2} V_{\text{system}}$ was expressed in calories. If some hydrogen is simultaneously adsorbed, it should be included in the value of θ . However, the contribution to θ due to adsorbed hydrogen must be negligible. This is a thermodynamic necessity under our experimental

(4) (a) J. A. Almquist, *THIS JOURNAL*, **48**, 2820 (1926); (b) J. A. Almquist and C. A. Black, *ibid.*, **48**, 2814 (1926).

(5) F. H. Emmett and S. Brunauer, *ibid.*, **52**, 2682 (1930).

(6) A. E. Romanushkiina, Q. L. Kiperman and M. I. Temkin, *J. Phys. Chem. (U.S.S.R)*, **27**, 1181 (1953).

(7) S. Dushman, "Vacuum Techniques," John Wiley and Sons, Inc., New York, N. Y., 1949.

conditions (where hydrogen is never in excess), since the heat of chemisorption for hydrogen is only 18 kcal./mole on platinum and 25 kcal./mole on nickel⁸ compared to the corresponding values for oxygen chemisorption of 60 and 100 kcal./mole, and 58 kcal./mole for the heat of formation of water. Inserting the value of θ given by (4) into the equilibrium constant for reaction (1), K_1 , the latter becomes

$$K_1 = \frac{p_{H_2} \times \theta}{p_{H_2O} \times (1 - \theta)} \cong \frac{1}{\beta} \frac{p_{H_2}^2}{p_{H_2O}} \quad (5)$$

since, as it will be shown later, in the range of θ investigated, $(1 - \theta) \cong 1$. The value of β is practically temperature independent, because the contribution of the reactor volume to the total volume of the apparatus is small. In the following data, the experimental values reported are the average of at least three different measurements taken in sequences of increasing and decreasing temperatures.

Results

Nickel.—Assuming that one oxygen atom is chemisorbed for every surface nickel atom exposed, the total number of available sites, Z , is found to be equal to $1.72 \times 10^{15} \times$ weight of catalyst in g. \times surface area in $\text{cm.}^2/\text{g.}$ By computing the value of β in equation (4) for various temperatures and using the values of p_{H_2} determined experimentally, the corresponding values of θ could be determined. Typical values of

$$K_1\beta = \beta \times \theta \times p_{H_2}/p_{H_2O} \cong p_{H_2}^2/p_{H_2O}$$

are reported in Fig. 2 for $p_{H_2O} = 25$ mm. and temperature range 100 to 300°. The pressures of hydrogen corresponding to the data plotted in Fig. 2 extend from 7 to 15 μ . The slopes of a straight line drawn through the points of Fig. 1 gives the value for the enthalpy change, ΔH , involved in reaction (1). The value found is reported in the Table I together with values obtained in previous investigations, where the bulk nickel phase was involved.

Combining $\Delta H_1 = +2.2$ kcal./mole with $\Delta H_2 =$

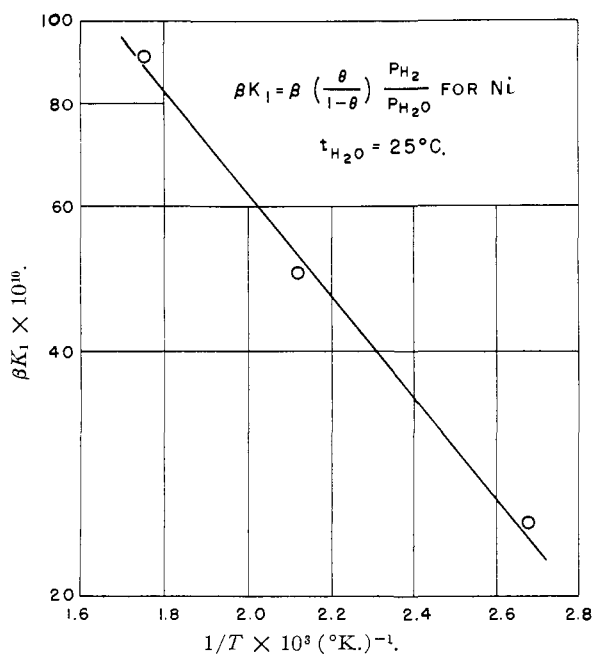


Fig. 1.—Decomposition equilibrium of water on nickel surfaces.

(8) "Advances in Catalysis," Vol. VI, Academic Press Publisher, New York, N. Y., 1955, Chapter by T. Kwan.

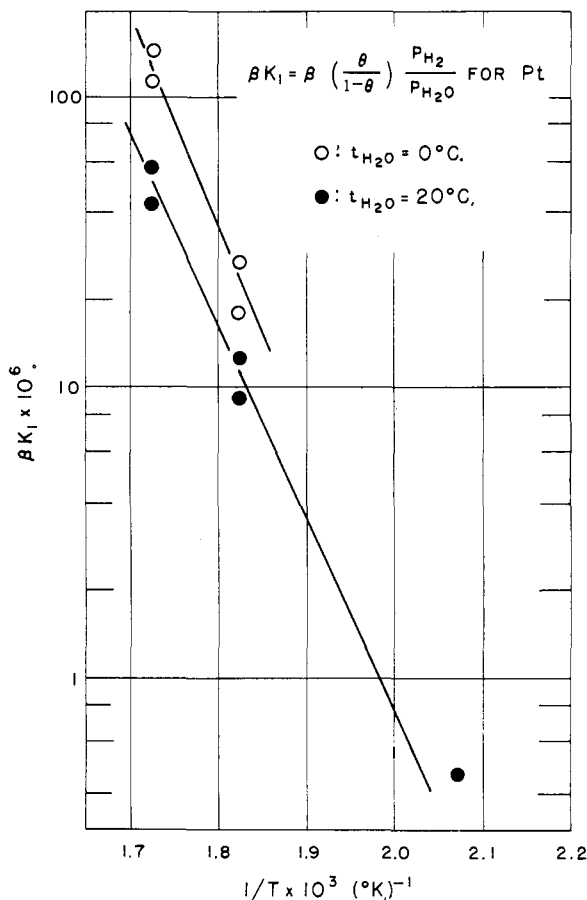


Fig. 2.—Decomposition equilibrium of water on platinum surfaces.

TABLE I
HEAT OF REACTION $\text{Ni} + \text{H}_2\text{O}(\text{g}) \rightleftharpoons \text{NiO} + \text{H}_2(\text{g})$

Temp. range (°C.)	ΔH (kcal./mole)	Source
300-600	3.6	(9)
400-600	4.2	(10)
400-1000	2.3	(11)
150-300	2.2	This research

-58.4 for reaction (2),¹² one obtains for reaction (3)

$$\Delta H_3 = -56.2 \text{ kcal./mole}$$

Similarly, by means of standard thermodynamic treatment, ΔF_3 and ΔS_3 can be computed. However, these quantities refer to different values of θ , since no attempt was made in the present work to derive an adsorption isotherm or even part of it. The results of typical calculations for nickel are reported in Table II.

It should be noted that K_3 is found to be dependent on θ and therefore on p_{H_2O} . This effect has been noted previously in thermodynamic studies of heterogeneous systems, when one of the solid phases is nearly absent. Systems for which this effect was

(9) R. N. Pease and R. S. Cook, THIS JOURNAL, **48**, 1199 (1926).
 (10) A. Skapski and J. Dawrowski, Z. Elektrochem., **38**, 365 (1932).
 (11) D. P. Bogatskii, C. A., **32**, 5688 (1938).
 (12) Thermodynamic values for reaction (2) were computed from data from Circular 500 (1952), National Bureau of Standards, Washington 25, D. C., and from heat capacities equations of O_2 , H_2 , H_2O : H. M. Spencer and J. L. Justice, THIS JOURNAL, **56**, 2311 (1934).

TABLE II
ADSORPTION THERMODYNAMICS OF OXYGEN ON NICKEL SURFACE

Temp. (°K.)	$\theta \times 10^4$	ΔH_3^a (kcal.)	ΔF_3^a (kcal.)	ΔS_3^a (cal./deg.)	K_3
373	12	-55.6	-41.2	-38.6	13.1×10^{23}
473	17	-55.9	-37.2	-39.5	16.0×10^{17}
573	5.3	-56.2	-32.4	-41.5	22.4×10^{12}
573	22	-56.2	-33.7	-39.2	72.6×10^{12}

^a Per mole of surface oxide, assumed to be NiO.

observed include: Ni-NiO,⁹ Co-CoO,¹³ Fe-FeO.⁴ Detailed investigations in the case of Co have shown that the ratio p_{H_2}/p_{H_2O} increased as p_{H_2O} decreased. It was also found that this behavior did not hold when the oxide phase dissolved into the metal.

Platinum.—Oxygen chemisorption on platinum was assumed to occur with the formation of a surface compound of composition PtO. A value of $Z = 1.0 \times 10^{15}$ sites/cm.² was computed and used for polycrystalline platinum. Typical values of the product βK_1 at different temperatures and two different p_{H_2O} 's are reported in Fig. 2. A summary of typical thermodynamic quantities computed from smooth curves (Fig. 2) is presented in Table III.

TABLE III
ADSORPTION THERMODYNAMICS OF OXYGEN ON PLATINUM

Temp. (°K.)	$\theta \times 10^4$	ΔH_3^a (kcal.)	ΔF_3^a (kcal.)	ΔS_3^a (cal./deg.)	K_3
473	3.7	-26.4	-36.9	+20.1	2.44×10^{15}
473	6.8	-26.4	-36.2	+18.7	1.30×10^{14}
573	15	-26.6	-38.0	+19.9	3.17×10^{14}
573	24	-26.6	-37.1	+18.3	1.42×10^{14}

^a Per mole of surface oxide, assumed PtO.¹⁴

Silver and Gold.—In view of past observations^{3,16,17} the adsorption site for silver was considered as two silver atoms per oxygen atom adsorbed, and consequently the number 0.22×10^{15} sites/cm.² was chosen in computing θ . Typical values of K_1 as a function of temperature are reported in Fig. 3. Computed thermodynamic quantities for silver are reported in Table IV.

TABLE IV
ADSORPTION THERMODYNAMICS OF OXYGEN ON SILVER

Temp. (°K.)	$\theta \times 10^4$	ΔH_3^a (kcal.)	ΔF_3^a (kcal.)	ΔS_3^a (cal./deg.)	K_3
473	4.26	-54.0	-40.1	-32.5	1.20×10^{18}
473	5.67	-54.0	-39.1	-34.6	4.06×10^{17}
573	6.02	-54.3	-37.2	-32.6	6.21×10^{13}
573	8.22	-54.3	-36.0	-34.7	2.22×10^{13}

^a Per mole of surface oxide, assumed Ag₂O.

(13) P. H. Emmett and J. F. Schultz, *THIS JOURNAL*, **51**, 3249 (1929).

(14) There is some evidence that PtO₂ is, at least in the bulk phase, thermodynamically more stable than PtO.¹⁵ If this is also the case for the surface, K_1 becomes equal to $p^3_{H_2}/\beta p^2_{H_2O}$, but, in the calculation of ΔH_3 following Hess' law, the new value of ΔH_3 is very slightly different from the value computed from equation 5. Since the ratios p_{H_2}/p_{H_2O} used in this work corresponded to p_{O_2} 's $\sim 10^{-30}$ mm. we believe that the most logical assumption for the composition of the surface compound is PtO.

(15) L. Brewer, *Chem. Revs.*, **52**, 1 (1953).

(16) A. F. Benton and L. C. Drake, *THIS JOURNAL*, **56**, 255 (1934).

(17) T. H. Butner, E. R. Funk and H. J. Udin, *J. Phys. Chem.*, **56**, 657 (1952).

Several runs were devoted to trying to obtain adsorption data on gold in the temperature range 568 to 653°K. Under these conditions, hydrogen pressure readings of the order of 1 to 5×10^{-6} mm. were recorded. These were considered too low to be of any significance and disregarded. Thus, within the limits of the sensitivity of our apparatus, no oxygen chemisorption could be measured on gold powder.

Discussion

The values of the heats of chemisorption reported in Tables II to IV are consistent with values previously obtained calorimetrically and by direct oxygen chemisorption (isosteric heats). Thus, on nickel films a value of 130 kcal./mole of O₂ at room temperature¹⁸ and a value of 92 kcal./mole O₂ at 0° on nickel powder were found.¹⁹ The data on platinum are much sensitive to the method of preparation of the metal.

Values from 100 to 58 kcal./mole O₂ were found in the low coverage range²⁰ but a value of 60 was reported to be constant over a wide coverage range.²¹ A value of 11.5 kcal./mole for the formation of a compound PtO_{1.33} on platinum black at 675°K. was also found.²² Values between 100 and 200 kcal./mole O₂ were recently obtained electrochemically.²³ The chemisorption of oxygen on silver previously has been studied in the same temperature range used in this work. At 183° and $\theta \approx 1$, values of 23 to 15 kcal./mole O₂¹⁶ were found, and it was noticed that there was always some oxygen adsorbed that could not be pumped off, but could only be removed by hydrogen reduction. This indicates the existence of a very strongly bound residual oxygen. This fact recently was confirmed also at higher temperatures.¹⁷ At 1200°K., an oxygen pressure of approximately 1×10^{-5} atm. was found in equilibrium with the chemisorbed layer ($\theta \cong 1$). This value is very different from the calculated equilibrium value of 1.7×10^4 atm. for bulk Ag₂O at the same temperature. An extrapolation of the data obtained in the present investigation to 1200°K. gives

$$P_{O_2} = 2 \times 10^{-4} \text{ atm. at } \theta = 6 \times 10^{-4}$$

This represents an agreement of one order of magnitude. Considering the large difference in temperature and surface involved, this can be considered a satisfactory agreement.

Oxygen chemisorption on gold powder was in the past found to occur at temperatures as low as room temperature.²⁴ It is doubtful whether actual chemisorption was observed in that case. With the present method, only chemisorption reactions can be observed and clearly differentiated from other physical adsorption or solution processes.

(18) "Advances in Catalysis," Vol. II, Academic Press, Inc., New York, N. Y., 1950, Chapter by O. Beeck.

(19) W. W. Russell and O. C. Bacon, *THIS JOURNAL*, **54**, 54 (1932).

(20) G. B. Taylor, G. B. Kistiakowsky and J. Perry, *J. Phys. Chem.*, **34**, 799 (1930).

(21) E. B. Maxted and N. Hassid, *Trans. Faraday Soc.*, **29**, 693 (1933).

(22) S. M. Ariya, M. P. Morozova, G. S. Markevich and A. A. Reikhardt, *J. Appl. Chem. (URSS)*, **23**, 1455 (1953).

(23) A. I. Shlygin and M. A. Kerdivarenko, *Referat. Zhur. Khim.*, No. 37489 (1954); *C. A.*, **49**, 10098 (1955).

(24) A. F. Benton and J. C. Elgin, *THIS JOURNAL*, **49**, 2426 (1927).

Surface oxidation of gold was detected at temperatures higher than those used in this investigation. Thus, at 450° an oxide film was formed in air and detected by means of chemical analysis. At lower temperature, however, the test became less positive.²⁵ It is interesting to compare the heats of oxygen chemisorption obtained in the present work with the heats of formation of bulk oxides. This is done in Table V.

TABLE V

HEATS OF FORMATION OF SURFACE AND BULK OXIDES OF NICKEL, PLATINUM, SILVER AND GOLD

Oxide	ΔH surface ^{a, b}	ΔH bulk ^{a, c}
NiO	-55.4 ± 1.0	-58.0 ± 0.5
PtO	-26.5 ± 1.0	-17.0 ± 0.5
Ag ₂ O	-54.0 ± 1.0	-7.3 ± 0.1
Au ₂ O ₃	?	Metastable

^a In kcal. per mole of oxide. ^b Temperature range 200–300°. ^c From ref. 13, temp. 25°.

Two important facts emerge from an inspection of Table V. First, the sequence of the relative stabilities for bulk oxides is not similar to that for surface films. Second, large discrepancies in heat values between surface and bulk are shown by platinum and silver, but not by nickel. Since the electronic structure of platinum is more similar to that of nickel than to that of silver, it is clear that oxygen bonding upon chemisorption does not directly involve electrons derived from d bands, as is known to be the case for hydrogen. It is interesting to note that silver and platinum are better oxidation catalysts than nickel. Furthermore, the relationship between K_3 and θ differs between nickel on one hand and platinum and silver on the other. For nickel as θ increases, the value of K_3 increases. This fact would indicate that mutual interaction is predominant. This can be taken as suggestive of the formation of "patches" or "small islands" of nickel oxide on the nickel surface, even at very low values of θ . These "patches" show all the thermodynamic characteristics of the bulk nickel oxide phase. This conclusion is supported by the observation that electron diffraction from a nickel film with adsorbed oxygen produced a pattern similar to that of nickel oxide.¹⁸ The behavior of nickel surfaces is in striking contrast with that of platinum and silver surfaces. In these latter cases, it was found that the value of K_3 decreased as θ increased. This would indicate that surface heterogeneity predominates. We are unable, at the present time, to offer an explanation for the difference in surface behavior among these three metals. Clearly, the factors which determine surface properties of metals toward oxygen are not directly related to electronic configurations controlling metal bonding.

(25) P. A. Thiessen and H. Schutz, *Z. anorg. allgem. Chem.*, **243**, 32 (1939).

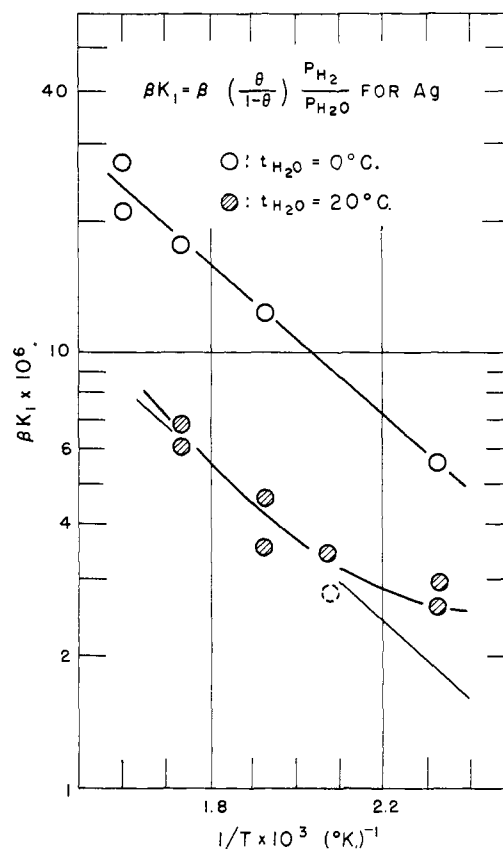


Fig. 3.—Decomposition equilibrium of water on silver surfaces.

Conclusion

An attempt has been made to characterize oxygen chemisorption on nickel, platinum and silver by means of the adsorption equilibrium function. This function has been derived by means of adsorption-chemical reaction equilibria of water vapor on the above metal surfaces. This approach has proved quite fruitful in giving the over-all energy behavior of the surfaces concerned. This behavior can be considered in respect to that of the bulk phase and in regard to the behavior of different parts of the same surface. This method, therefore, is particularly suited for studying the contribution of the solid phase to the nature and energy content of the adsorbent-adsorbate bond involved in chemisorption and catalytic systems.

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PHILADELPHIA, PA.