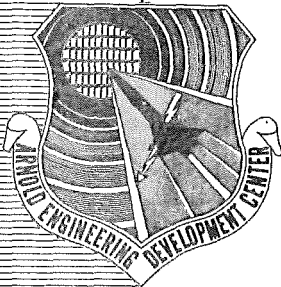


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**ENERGIES OF INTERACTION
BETWEEN GASES AND VARIOUS SURFACES**

By

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Contract AF 40(600)-909

FOREWORD

This report was prepared by the Thermodynamics Research Laboratory Department of Mechanical Engineering, under USAF Contract No. AF 40(600)-909 Project No. 7778 and Task No. 77801, "Analytical Study of Determining 'Pressure' in an Ultra-High Vacuum Chamber", with Professor S. L. Soo as Project Director. The research was administered under the Directorate of Procurement, Arnold Engineering Development Center, with Milton B. Rice, Jr., (AEK) as Contracting Officer.

The report describes a portion of the research conducted from October 1, 1960 to March, 1961.

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1. INTRODUCTION

This report supplements the study on "Kinetics of Molecules in Ultra-high Vacuum as affected by Surface Interaction" by S. L. Soo, performed under contract No. AF 40(600)-909. As far as we know, this report presents the up-to-date data on potentials of adsorption and chemisorption, and activation energies of various surfaces for gases. These data are intended for use in design for space probing and space simulation based on the kinetic theory of ultra-high vacuum.

1.1 Physical Adsorption and Chemisorption

When a clean surface of a solid or a liquid is exposed to a gas, a monomolecular layer of the gas is often formed on the surface and contaminates it. In a study of the behavior of surfaces and surface reactions, it is of considerable importance to understand the properties of such monomolecular films. Furthermore, many properties of surfaces, for example, the interchange of energy between a solid surface and a gas, depend noticeably on the presence of gas atoms or molecules adsorbed on the surface.

Adsorption is the adsorption of gas on the gas-solid interface only. This occurrence is due to the atoms in any surface being subject to unbalanced force of attraction perpendicular to the surface plane. It is called physical or van der Waals adsorption. On the other hand, many surfaces are unsaturated, and the valency requirements of their surface atoms may be not fully satisfied by bonding with nearby atoms. In adsorption such a surface will tend to form chemical bonds with a nearby phase and this process is called chemisorption or activated adsorption (See later section).

The difference between chemisorption and physical adsorption is that electron transfers take place between adsorbant and adsorbate in chemisorption, but do not take place in physical adsorption.

There are certain differences in the properties of physical adsorption and chemisorption, which can be used as experimental criteria for deciding the adsorption type.

(1) Since chemical bonds are normally stronger than physical forces of attraction, heats of chemisorption should therefore be large while heats of physical adsorption should be low. For example, heats of chemisorption of carbon monoxide and hydrogen tend to exceed some 20,000⁽¹⁾ and 15,000⁽²⁾ cal/mole respectively, whereas the heats of physical adsorption are always less than 6,000⁽³⁾ and 2,000⁽⁴⁾ cal/mole.

Although the distinction is in general valid, more recent work has shown that heats of chemisorption can be far smaller than was previously believed. For example, hydrogen values as low as 3,000 cal/mole⁽⁵⁾, ⁽⁶⁾ have been observed and in one case of carbon monoxide⁽⁷⁾ there appears to be no discontinuity in heat between the end of chemisorption and the beginning of physical adsorption on top of the chemisorbed layer.

(2) A similar criterion is the temperature range in which the adsorption proceeds. Physical adsorption occurs at the temperatures near or below the boiling point of the adsorbate at the pressure considered. Chemisorption on the other hand can usually take place at temperatures far above the boiling point.

(3) Chemisorption, being a chemical reaction, may require an appreciable activation energy. In this case it will only proceed at a reasonable rate above a certain minimum temperature. Physical adsorption on the other hand requires little or no activation energy, just as condensation of liquid from vapor requires none. It should, therefore, be exceedingly rapid at any temperature and take place as fast as the adsorbate reaches the surfaces.

(4) Chemisorption possesses a certain specificity which physical adsorption does not. This is partly because it depends upon the adsorbant surface being clean, partly because not all surfaces, even when clean, are active in chemisorption. Physical adsorption on the other hand takes place on all surfaces under the correct conditions of temperature and pressure.

In order to prevent misunderstanding of the various terms used in this article, brief definitions are given as follows:

Heat of adsorption - When a gas molecule is adsorbed on a metal surface, heat is given up. This is called the Heat of Adsorption.

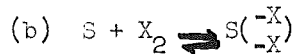
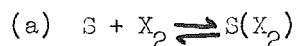
Heat of evaporation - When a gas molecule evaporates from the surface, heat has to be supplied. This is called the Heat of Evaporation

or desorption. In the case of physical adsorption, which is completely reversible and practically instantaneous, the heat of desorption will generally be equal to the heat of adsorption in quantity.

1.2 Activation Energies in Adsorption Processes

As usual in discussions of chemical kinetics, when we speak of the activation energy of a given chemical process we may, in the same sense, speak of the activation energy of the adsorption process. The consequences of this concept may be best examined by a general consideration of the adsorption of a gas at a plane surface composed of a definite number of elementary spaces. The conditions governing adsorption equilibrium at such surfaces have already been detailed by Langmuir⁽⁸⁾.

(1) Equilibrium in Processes Involving Activation Energy -- We consider the adsorption of a diatomic gas (X_2) which may be adsorbed on the surface (S) in two forms (a) as molecules, (b) as individual atoms. We may represent the two processes by means of the equations



We assume that, in a particular case, the heats of adsorption for the two processes (a) and (b) are respectively Q_a and Q_b and that Q_b is greater than Q_a . We know further that the activation energies are different and that the activation energy of process (a), E_a , is small, but that the activation energy of (b), E_b , is remarkably higher. Under these conditions the activation energies of the reverse processes of vaporization are, respectively,

$E_a + Q_a$ and $E_b + Q_b$.

The Langmuir concept of adsorption gives the time lag between condensation and evaporation. As a consequence the average time which molecules occupy the surface depends on the ratio of the rates of adsorption and desorption. Further, based on the above assumptions, the ratio is

$$\frac{A_a e^{-E_a/RT}}{B_a e^{-(Q_a + E_a)/RT}} = \left(\frac{A_a}{B_a}\right) e^{+Q_a/RT}$$

in one case, and

$$\left(\frac{A_b}{B_b}\right) e^{+Q_b/RT}$$

in the other. Since the variations in A_a and A_b , B_a and B_b are minor* as compared to the variation of the exponential for different values of Q_a and Q_b , it follows that the relative magnitudes of Q_a and Q_b largely determine the positions of the adsorption-temperature isobars for the two processes. For the case assumed, $Q_b > Q_a$, the isobar for (b) will lie above that for process (a) (Fig. 1). If the heats of adsorption for the two processes were equal, the two curves would more nearly coincide. The differences would depend only on differences in A_a , A_b , B_a , and B_b .

* In the simple Langmuir theory A_a and A_b are the rates at which molecules strike unit surface inelastically and are identical. The B factors in the evaporation process are similar to the factor C in the equation for a unimolecular reaction

$$\frac{dx}{dt} = C e^{-E/RT}$$

The variation of the C values in the available experimental data is very small.

(2) Extent of Adsorption and Temperature - By reason of the respective magnitudes of E_a and E_b , over a given range of low temperatures, the velocity of process (b) will be negligibly slow compared with that of (a). Under such circumstances the experimental results obtained will follow curve (a). As the temperature is raised there will be the normal decrease in adsorption of X_2 ; but simultaneously, there will be an increase in the velocity of process (b) so that at sufficiently high temperatures, the experimental values obtained will be due almost exclusively to the adsorption process (b). Between the two extremes of temperature, there will be a region in which the results obtained will be intermediate between (a) and (b) and determined by the relative magnitudes of Q_a , Q_b , E_a , and E_b . This intermediate stage may reveal itself by raising the values of the adsorption at a given pressure with increasing temperature. This condition is indicated by the dotted line in Fig. 1.

(3) Adsorption Equilibrium and Nature of the Activation Process - The molecular and atomic adsorption are not limited to these two processes but are applicable to any two processes of adsorption of a given molecular species producing any two forms of adsorbed product, the two processes differing in their activation energies. Dissociation of the molecule to yield atoms on the surface represents only one particular case of the general principle. It will be convenient to designate as type (a) the adsorption that occurs with low or negligible activation energies and type (b) the adsorptions involving high activation energies (i. e. chemisorption is a kind of activated adsorption). This, however, in no way imposes the restriction that the adsorptions are of any particular type, for example,

molecular and atomic. Any two adsorption processes of the same gaseous species may be involved.

(4) Activation Energy and Attainment of Equilibrium-- It is evident that because of the large activation energy, E_b , the portion of the curve (b) to the left of the dotted ascending curve cannot be experimentally realized by measurements conducted wholly at the lower temperatures involved. It is also evident that values much higher than those corresponding to curve (a) at the temperatures in question will be obtained if adsorption equilibrium is first established at higher temperatures, where both processes are occurring, and then the system be brought to the lower temperature. One can conclude from the theory that desorption of gas as far as curve (a) will not occur on cooling, that values considerably higher than those of curve (a) will be obtained and that these values will approximate to but will, in general, be somewhat lower than those for true equilibrium in the process (b) at the temperature in question.

(5) Effect of Varying Adsorbent-- Variation in the nature of the adsorbent with a given adsorbate will yield variations in the adsorption dependent on the values of Q_a , Q_b , E_a and E_b for the system in question. The discussion may be simplified if we assume that with every adsorbent the value of E_a is negligibly small. A variation in the value of E_b from case to case will involve a variation in the temperature at which the transition from adsorption along curve (a) to that along curve (b) occurs. For low values of E_b the transition will occur at low temperatures and may even result in the absence of all evidence of a transition. If E_b attains high values, the transition will take place only at elevated temperatures.

(6) Effect of Concentration of Adsorbate - The effect of increasing concentration of adsorbable gas may be indicated by again assuming that E_a is small and that the adsorption complex $S(X_2)$ is an intermediate stage in the formation of the second type of adsorption. The rate of the second stage will, therefore, be determined by the concentration of $S(X_2)$ and the activation energy E_b . The gas striking the surface will form initially complexes of type (a). Without the necessary activation energy, the molecules will re-evaporate. With increasing gas pressure, the number of molecules striking the surface increases; and therefore, the probability of a collision with the necessary activation energy present at the place of collision will increase. The adsorption complex formed will become increasingly of the type (b). While this behavior will not be exhibited by the form of the adsorption isotherm, it may be deduced from the values for the heat of adsorption at various equilibrium pressures.

(7) Effect of Non-Uniform Surface - In actual practice adsorption studies are not made with uniform surfaces but with surfaces of varied activity. This reveals itself in the case of a single process of adsorption by a steadily falling value for the heat of adsorption. The adsorption involving high heats of adsorption occur first and are succeeded by processes with lower and lower heat of adsorption. This factor introduces a constantly varying Q into the equation determining the evaporation process. When the E factor is constant, the effect of this falling Q would be to increase the rate of evaporation by increase in the term $e^{-(Q + E)/RT}$. From the analogy with the activation energy of chemical reactions at surfaces⁽⁹⁾, we know that the activation energy of adsorption processes should become larger and larger as the surface area becomes less active. This increase in E with surface covered would tend, therefore, to offset to some extent the effect of diminishing Q .

From the preceding discussions we know the extent of adsorption according to type (b) increased with increasing partial pressure of the gas, it is evident that the heat of adsorption-pressure (or amount of adsorbed gas) curve might show two descending sections corresponding mainly to types (a) and (b) with an intermediate section of transient values between. Such a possibility is shown diagrammatically in Fig. 2. It is also evident that, with suitable values for activation energies and heats of adsorption, the preliminary fall in the first portion of the curve might be eliminated, leaving a curve showing a maximum. With low values for both E_a and E_b or, alternatively at high temperatures, the curve would be entirely of the (b) type and show continuously falling values.

1.3 Heat of adsorption and Temperature

When, owing to a high value of E_b , or the low temperature of operation, the adsorption is purely of type (a), the heats of adsorption measured will be characteristic of the adsorption process (a) and the extent of the surface covered. At high temperatures, where process (b) predominates, the heats of adsorption would in the same way be characteristic of that process. For this reason one can deduce a change in heats of adsorption along with a change in temperature. Since adsorption of the type (a) is the low temperature, non-specific, non-activated type, we can in general expect low heats of adsorption Q_a . For the specific adsorption involving activation and activation energy of adsorption, with the operation of valence forces at the surface, we should in general expect somewhat higher values for Q_b . (Again we see chemisorption is the activated adsorption). It must be remembered, however, that since, for example, the activation process may involve in the case of diatomic molecule a dissociation of the molecule into atoms, there is always the possibility of Q_b becoming a small magnitude, for example, the chemical reaction $N_2 + O_2 = 2NO$;

the net heat of this reaction is -43 Kcals, as it involves the heat of dissociation of N_2 and O_2 molecules, respectively, 200 and 120 Kcals. At intermediate temperature when both adsorptions are involved, values intermediate to Q_a and Q_b would be obtained. The Q value obtained under a given set of conditions is also a function of the nature of the surface covered. It is highest with the most active areas, whether the adsorption is of the (a) or (b) type.

1.4 Extent of Saturation of a Non-uniform Surface

On a non-uniform surface, it can readily follow that the combined operation of the Q and E values may result in a set of conditions such that only on a fraction of the surface may the activating adsorption (b) occur. If the temperature be such that adsorption of the type (a) is negligibly small, it would follow that the adsorption isotherms obtained would show all the characteristics of saturation with, however, only a small fraction of the surface covered with adsorbed gas. Such a condition would be of first importance in those chemical reactions at surfaces where activation was a condition precedent to reaction.

1.5 Velocity of Evaporation and Adsorption of Molecules

The velocity of evaporation of adsorbed molecules is proportional to $e^{-Q/RT}$ where Q was the heat of adsorption. This is only true as long as the activation energy of the adsorption process is negligibly small. The correct expression for the evaporation process involves $e^{-(E + Q)/RT}$; it is evident cases might arise in which great differences in the velocity of evaporation of two adsorbed gases were obtained, even though the Q 's were identical, because the E 's were markedly different. It is also not impossible that, owing to marked differences in the values of E in two cases, the velocity of evaporation in the process with a higher Q value should be more rapid than the velocity of evaporation with the lower Q . In the reverse process of adsorption the same principles apply.

1.6 Activated Adsorption (Chemisorption)

Physical adsorption is a necessary prerequisite to chemisorption. It is the rate of collision of physically adsorbed molecules with the substrate rather than the direct impingement of gas upon the surface which limits the reaction.

On impinging upon the surface of a solid from the gas, the molecule can either suffer an elastic collision and return to the gas, or else interact weakly with the surface to become "physically" adsorbed; the fraction of the molecules following the latter course is given by the condensation coefficient. The physically adsorbed molecules will, however, again return to the gas, unless, during their sojourn on the surface, the duration of which is dictated by the ratio of the energy of desorption E_1 , to the thermal energy, kT , they form a chemical bond with the surface and become "chemisorbed."

The change of potential energy during physical adsorption and chemisorption was proposed by Lennard-Jones⁽¹⁰⁾. In Fig. 3 is shown the expected potential energy of a molecule AB as a function of its distance from a surface at which it is either physically adsorbed (curve 1), or chemisorbed as radicals A and B (curve 2). These curves show a higher heat of chemisorption, Q_b , than of physical adsorption, Q_a , and also, that when chemisorbed, the molecule lies nearer to the surface than when physically adsorbed. As the molecule approaches the surface, it initially experiences forces of physical attraction, as these are of longer range than bonding forces--that is, its energy follows curve 1. Whether it is able to switch to curve 2 and be chemisorbed is decided by whether or not it is able to reach the point P at which a transition is possible. In order to do so, it must possess an energy greater than the value E.

A molecule approaching the metal with an energy W (See Fig. 3), insufficient to reach P, might according to quantum mechanics, penetrate the barrier,

but the probability is small unless W is very nearly of the same height as the point of interaction P . The height of P above the zero energy is the "Energy of Activation" (E), necessary for a transition from the state (1) to the state (2) (corresponding to the transition from curve (a) to curve (b) in Fig. 1).

When this switch occurs the atoms A and B will both rush toward the solid along a potential field whose sum is given by curve (2) in Fig. 3. They may then give up energy to the solid (Q_b , the heat of chemisorption), and be trapped about the new equilibrium position L .

The most probable energy of translation of molecules perpendicular to the surface at a temperature T is $1/2 kT$, and so we may expect the most favorable conditions for adsorption as atoms when $T = 2E/k$. This will not necessarily be the same as the temperature of the maximum on the isobar. The kinetics of both adsorption and desorption must be worked out in detail before this maximum can be related to the energy of activation.

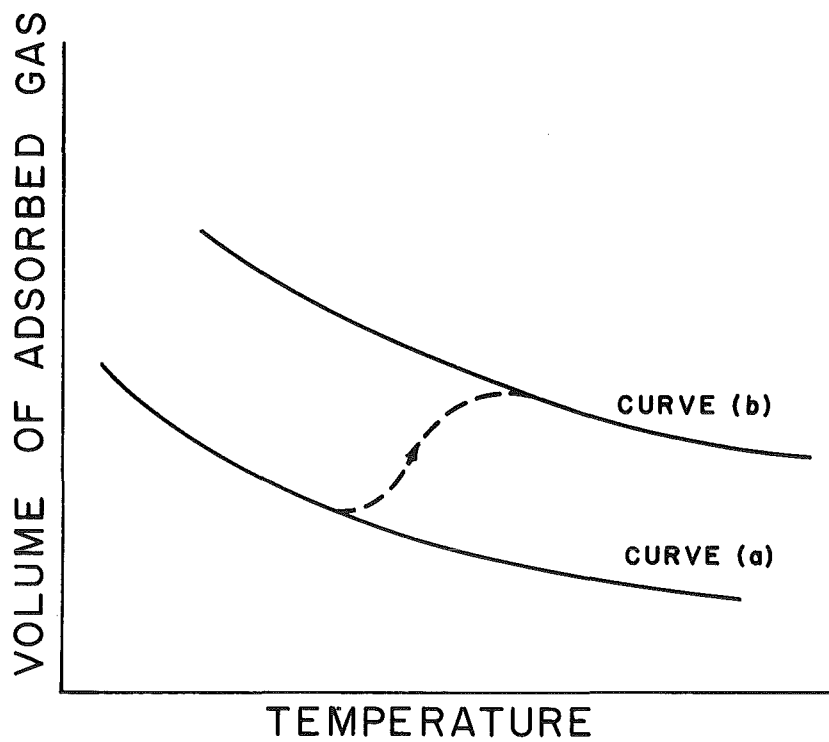


Fig. 1. Schematic representation of adsorption isobars with two activation energies for adsorption processes.

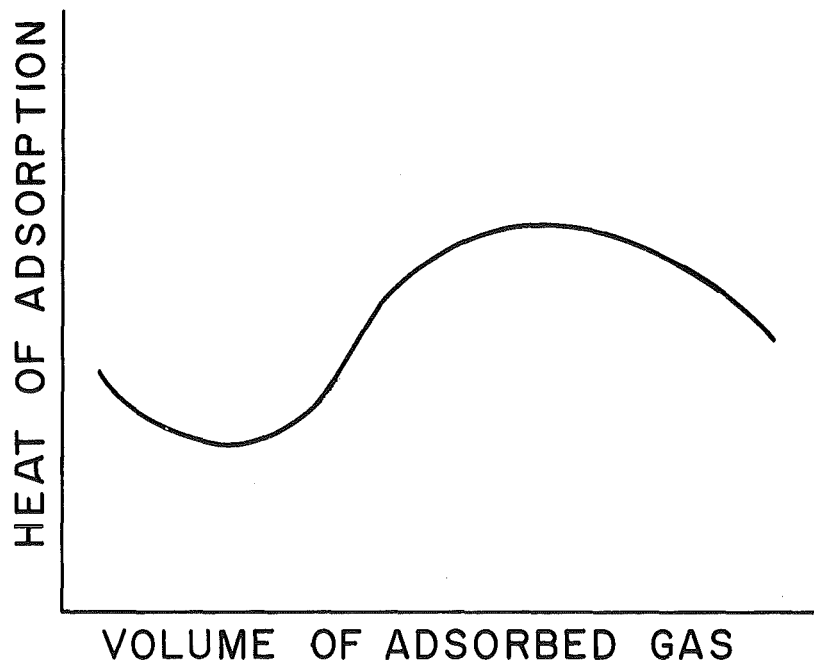


Fig. 2. Variation of heat of adsorption with amount adsorbed for two adsorption processes having different activation energies.

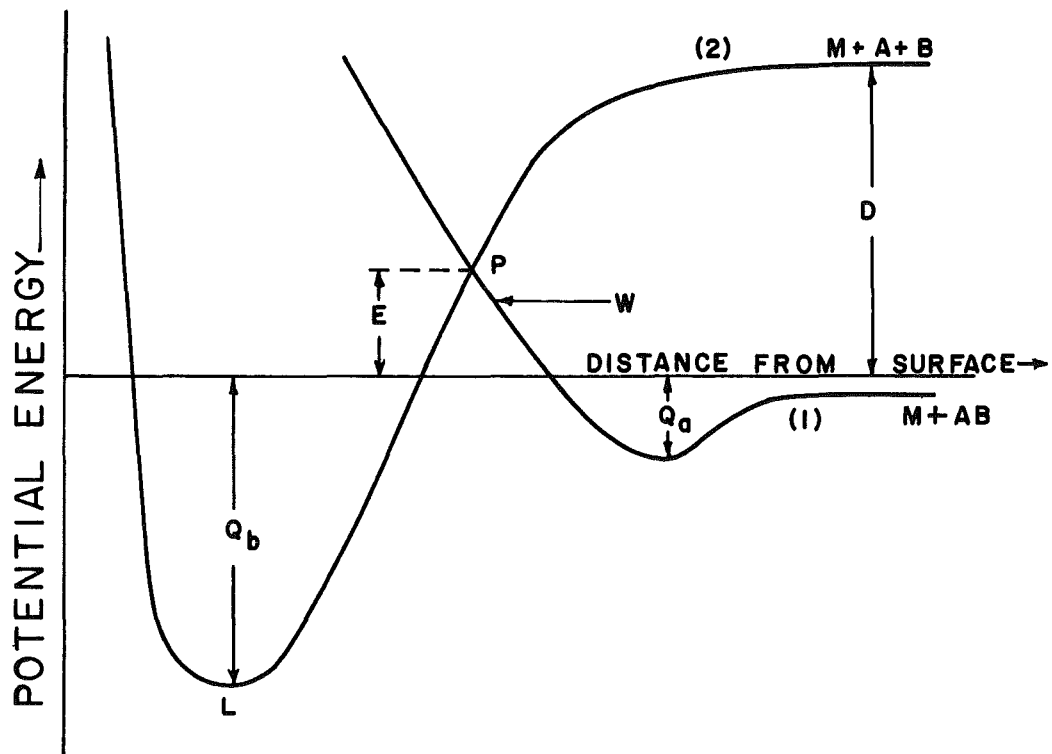


Fig. 3. The interaction of a molecule and a metal.

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2. HEATS OF PHYSICAL ADSORPTION AND EXPERIMENTAL DATA

The adsorption which is usually observed at low temperature, e.g., in the neighborhood of -180° C, is regarded as physical adsorption, in which the gas is adsorbed as molecules and held simply by residual valencies. In this type of adsorption equilibrium is reached very quickly, the heat of adsorption is low, and the amount of gas adsorbed increases with pressure, but decreases with increase in temperature. This type of adsorption is completely reversible and depends chiefly on the nature of the surfaces.

From the Langmuir isotherm, we know,

$$x = b \cdot \frac{ap}{1 + ap} \quad (2.1)$$

where x is the amount of gas adsorbed in cubic centimeters per 100 grams of metal, b is a constant and

$$a = ce^{-Q/RT} \quad (2.2)$$

Here Q is the heat of adsorption.

Theoretically, the heat of adsorption can be calculated by the Clausius-Clapeyron equation. When equilibrium is obtained, for the temperature coefficient of vapor pressure this equation can be applied in the form

$$\frac{d(\log p)}{dT} = \frac{Q}{RT^2} \quad (2.3)$$

where p is the pressure.

On integrating we obtain

$$Q = 2.303 R \cdot \frac{T_1 T_2}{T_2 - T_1} \log \frac{P_2}{P_1} \quad (2.4)$$

where p_1 and P_2 are the equilibrium values at temperatures T_1 and T_2 for a constant value of adsorption, R is the gas constant having a value of 1.99 calories, and 2.303 is the factor for conversion to naperian logarithms.

The agreement between the values determined directly by calorimeter and those obtained by calculation is generally satisfactory.

Some experimental data for a number of systems are given in the following table. These measured heats are found to vary somewhat with the amount of gas adsorbed and with the previous treatment of the adsorbent. In all cases, however, they are small compared with heats of chemical reaction.

TABLE 1
Heats of Physical Adsorption

Catalyst	Gas	Temp(°C)	Pressure (mm)(average)	Heat of Adsorption (Kcal/mole)	Ref.
Fe	H ₂	-63.9	25	4.6	1
"	"	-72.0	45	3.9	"
"	"	-78.7	22	0.7	"
"	"	-87.6	760	7.3	"
"	"	-95.0	760	2.4	"
Fe	H ₂	-183	-	1.6	2
"	N ₂	-183	-	2.05	2
		0	-	3.7	2
Ag	O ₂	-183	760	2-3	3
Hg	Kr	-34	-	2.7	4
"	Xe	-10	-	3.5	"
Cu	H ₂	-183	9	1.28	5
"	"	"	18	1.49	5
"	"	"	60	0.93	"
"	"	"	85	0.80	"
"	"	"	114	0.98	"
"	"	"	125	1.14	"
"	"	"	229	0.71	"
"	"	"	255	0.75	"
"	"	"	315	0.56	"
Cu	N ₂	-183	-	3.6	5
"	"	-78.5	-	2.1	5
Cu	C ₂ H ₂	-183	-	9.0	6
"	C ₂ H ₄	"	-	8.0	"
"	CO	"	-	5.5	6

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3. HEATS OF ACTIVATED ADSORPTION AND EXPERIMENTAL DATA

In the previous case, we have considered only the experimental results at low temperatures, and have seen that adsorption decreases with increasing temperature. As the temperature is raised still further we find, in many cases, that after the initial instantaneous adsorption is completed a further quantity of gas continued to be adsorbed very slowly. This slow adsorption which increases at higher temperatures, and after passing through a maximum falls off once more, is called the activated adsorption. The activated adsorption does not occur with all gases and all metals. As we pointed out in the previous section, its occurrence will depend on the values of activation energy of the system. The determination of the activation energy for each system will be treated later.

Processes of activated adsorption, which are reversible in the sense that the gas is recovered in its original form on desorption, can be treated in the same way as in section 2. But in many cases the molecule is dissociated on adsorption. Then the total heat is the algebraic sum of the heat of dissociation, Q_1 (a negative quantity), and the heat of adsorption of the atoms, Q_2 (a positive quantity), so that

$$Q = Q_1 + Q_2$$

The heat of dissociation can be determined from calculations on the thermal losses of the gas. Kunsman⁽¹⁾ used this method to determine the heat of dissociation for ammonia on heated filament catalysts. He found the data was satisfactory. Generally the heat of dissociation is known, for example, for hydrogen it is equal to -100 Kcal. There is, of course, a greater uncertainty as to whether any particular state represents equilibrium in cases of activated adsorption, owing to the slow character of the

process and the fact that it is often not reversible with respect to changes in temperature and pressure.

The agreement between the values determined directly by calorimeter and those obtained by calculation is generally satisfactory. For example, Ward⁽²⁾ found by direct measurement values for the heat of adsorption of hydrogen on copper varying between 9 and 14 Kcal for different samples, while Beebe⁽³⁾ obtained values between 11.5 and 13.3 Kcal by calculation from equation (2.4).

Some heats of activated adsorption, determined either by direct measurements or by calculation, for a number of metal-gas systems are given in the following tables. In several figures, the volume of gas adsorbed is expressed in m.l/100 mg of film and c.c. The coverage θ is expressed in percentage of surface area which gas covered.

TABLE 2

Heats of Activated Adsorption for Gases on Metals Cu, Au, Fe, Ag

Catalyst	Gas	Temp(°C)	Heats of Activated Adsorption (Kcal/mole)	Ref.
Cu	C ₂ H ₂	25 45	19-21	4
Cu	C ₂ H ₄	"	18.2-20.8	4
Cu	CO	-78	8.7-9.3	4
"	"	0	9-30	3
"	"	0	13-20	5
"	"	0	13.5-20.3	6
Cu	H ₂	0	18	7
"	"	25	9-14	2
"	"	25-70	4-16	8
"	"	70-95	11.5-17.5	7
"	"	25	11.5-13.5	3
Au	CO	25 45	9	4
"	C ₂ H ₂	25 45	21	4
"	C ₂ H ₄	25 45	21	4
Fe	NH ₃	25 45	45	9
"	O ₂	23	75	10
"	H ₂	-183	27	10
(θ 0.2)	CO	23	32	10
Ag	O ₂	100	54.0	11
"	"	200	54.0	11
"	"	300	54.3	11
"	"	400	54.3	11

TABLE 3

Heats of activated Adsorption for Gases on Metal W and Ni

Catalyst	Gas	Pressure (mm Hg)	Temp ($^{\circ}$ C)	Heat of Activated Adsorption (Kcal/mole)	Ref.
W	H ₂ O	60×10^{-5}	1100 ~ 1300	39	12
"	"	"	1300 ~ 1350	45 ± 1.5	"
"	"	"	1350 ~ 1450	25 ± 2.0	"
"	"	"	1450 ~ 1550	22 ± 2.0	"
"	"	"	1550 ~ 1700	31 ± 1.0	"
W	SrO	-	1720	122 ± 10	13
"	"	-	1877	141 ± 22	"
W	NH ₃	-	25-40	66	9
W	N ₂	-	23	95	10
Ni	O ₂	-	100	55.6	11
"	"	-	200	55.9	"
"	"	-	300	56.2	"
"	"	-	400	56.2	"
"	"	-	23	120	10
Ni	H ₂	-	0	14	14
"	"	-	0~35	10 - 30	15
"	"	-	25~45	12.5	16
"	"	-	0	12 - 37	17
"	NH ₃	-	25 ~ 45	37	9
"	C ₂ H ₂	-	25 ~ 45	67	9
"	CO	-	23	35	9

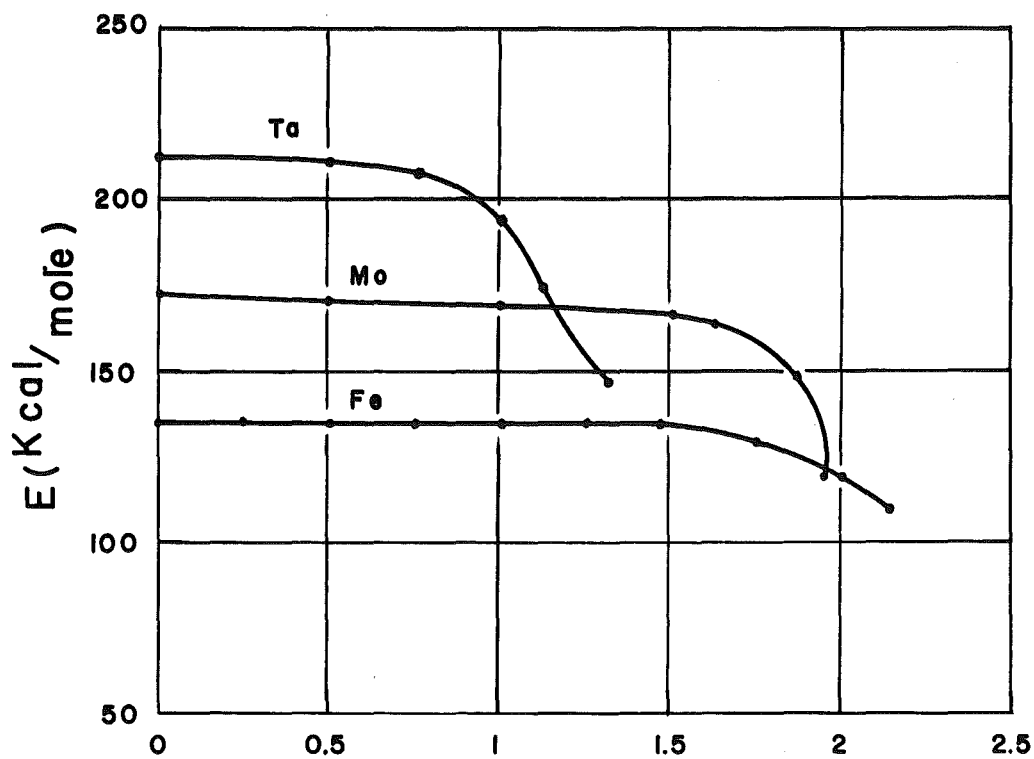
TABLE 4

Heats of Activated Adsorption for Gases on Pt, Pd, and Alloy Catalysts

Catalyst	Gas	Temp ($^{\circ}$ C)	Heat of Activated Adsorption (Kcal/mole)	Ref.
Pt	O ₂	100	26.4	11
"	"	200	26.4	"
"	"	300	26.6	"
"	"	400	26.6	"
Pt	H ₂	0	32.4	8
"	"	20	14 - 17.2	18
"	"	0	10 - 30	19
Pt	CO	0	18-35	19
Pt	SO ₂	0	15 - 37	19
Pd	CO	0 ~ 184	7 - 15	20
Pd	O ₂	250 ~ 400	24.6	21
99% Pd + 1% Ag	"	"	46.8	"
90% Pd + 10% Ag	"	"	46.1	"
70% Pd + 30% Ag	"	234 ~ 385	45.1	"
50% Pd + 50% Ag	"	250 ~ 400	45.0	"
40% Pd + 60% Ag	"	260 ~ 380	48.4	"
10% Pd + 90% Ag	"	250 ~ 400	49.1	"
Ag	"	200 ~ 300	54.0	"

TABLE 5
Heats of Activated Adsorption for Gases on Oxide and Charcoal

Catalyst	Gas	Temp (°C)	Heats of Adsorption (Kcal/mole)	Ref.
ZnCr ₂ O ₃	O ₂	25 ~ 40	42.9	22
"	CO	"	14.9	"
"	C ₂ H ₄	"	19.9	"
"	H ₂	"	49.7	23
"	C ₂ H ₆	"	28.7	"
Cu ₂ O	C ₂ H ₄	25 ~ 50	20.0	"
"	SO ₂	25 ~ 50	37.0	"
"	O ₂	25 ~ 50	55.0	"
PdO	O ₂	25	21.0	21
"	O ₂	227	24.6	"
Ag ₂ O	O ₂	25	7.3	"
"	"	227	54.0	"
MnO	O ₂	25 ~ 40	24	22
MnO	"	25 ~ 40	64.4	"
"	"	344.5	23.6	24
Charcoal	O ₂	-	72.0	25
"	Cl ₂	-	31.9	"
"	CO ₂	-	8.4	"
"	NH ₃	-	16.94	"
"	H ₂ O	-	9.46	"



Volume of O_2 adsorbed (m.l. at S.T.P./100 mg. of film)

Fig. 4 The variation of the heat of adsorption of O_2 with coverage for Ta (200), Mo (168) Fe (133); The number in parentheses refers to the mean integral heats of adsorption in Kcal/mole.

Reference: 26

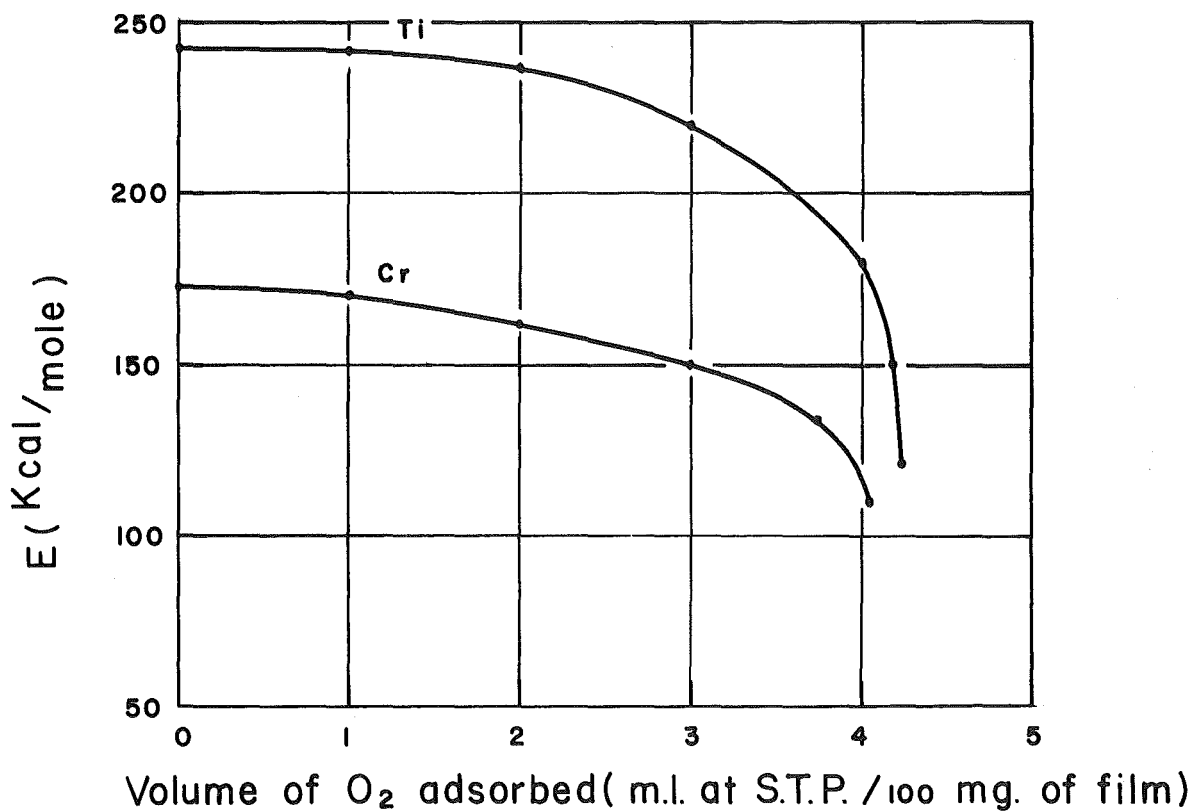


Fig. 5 The variation of the heat of adsorption of O_2 with coverage for Ti (225), Cr (162); The number in parentheses refers to the mean integral heats of adsorption in Kcal/mole.

Reference: 26

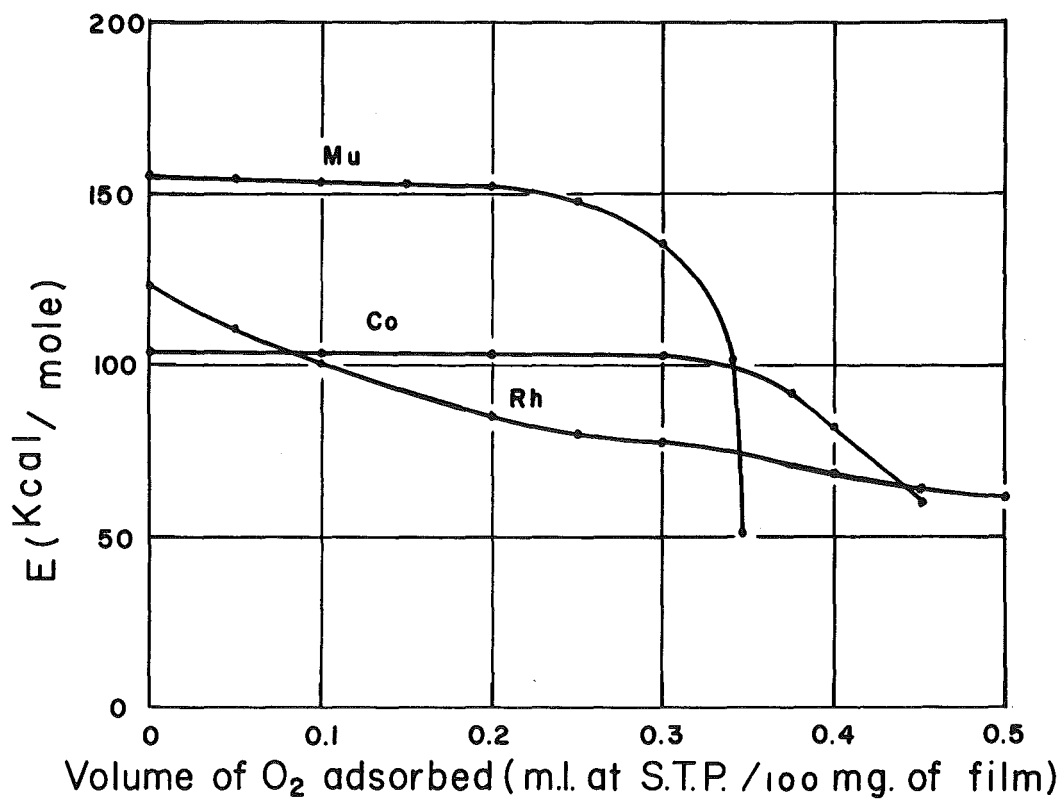


Fig. 6 The variation of the heat of adsorption of O₂ with coverage for Mn (142), Co (101) Rh (76); The numbers in parentheses refer to the mean integral heats of adsorption in Kcal/mole.

Reference: 26

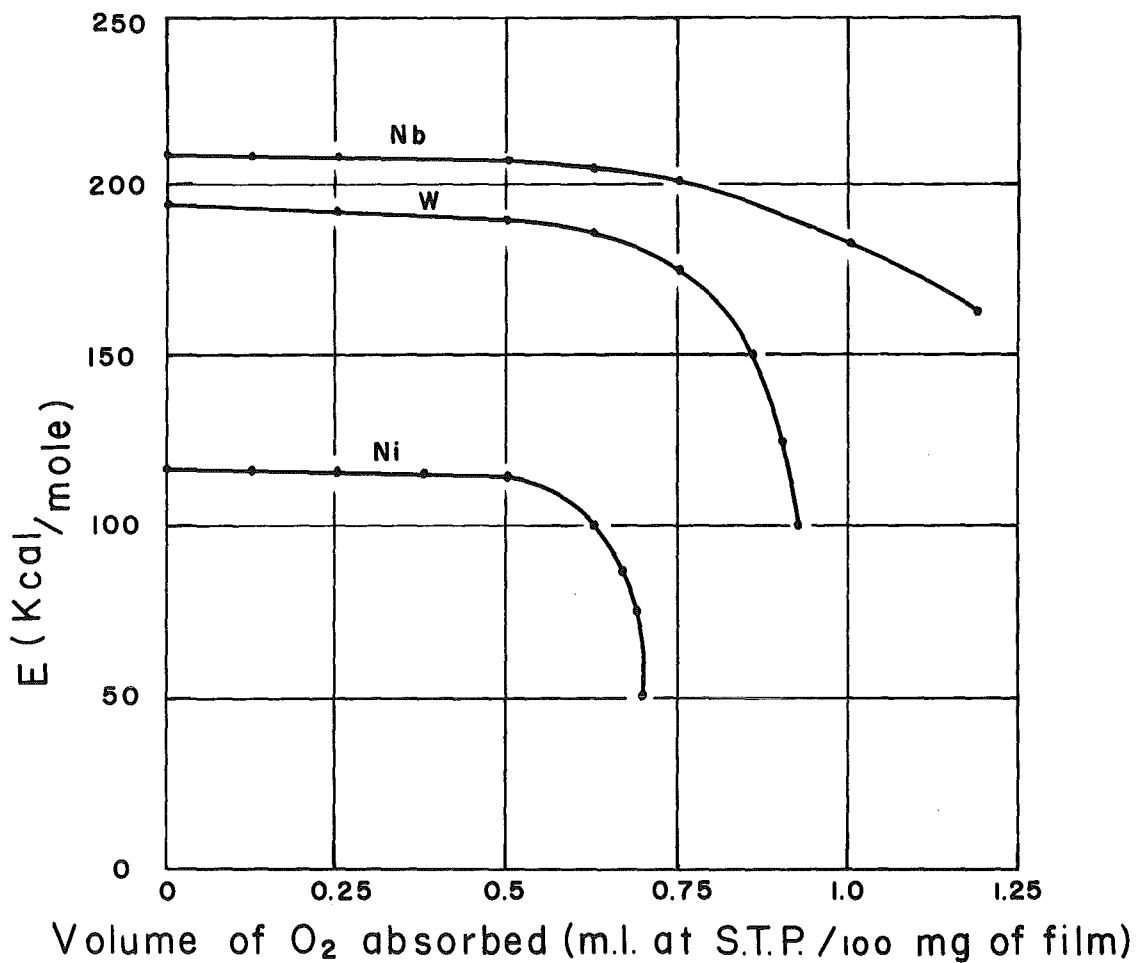


Fig. 7 The variation of the heat of adsorption of O_2 with coverage for Nb (194), W (180), Ni (105); The numbers in parentheses refer to the mean integral heats of adsorption in Kcal/mole.

Reference: 26

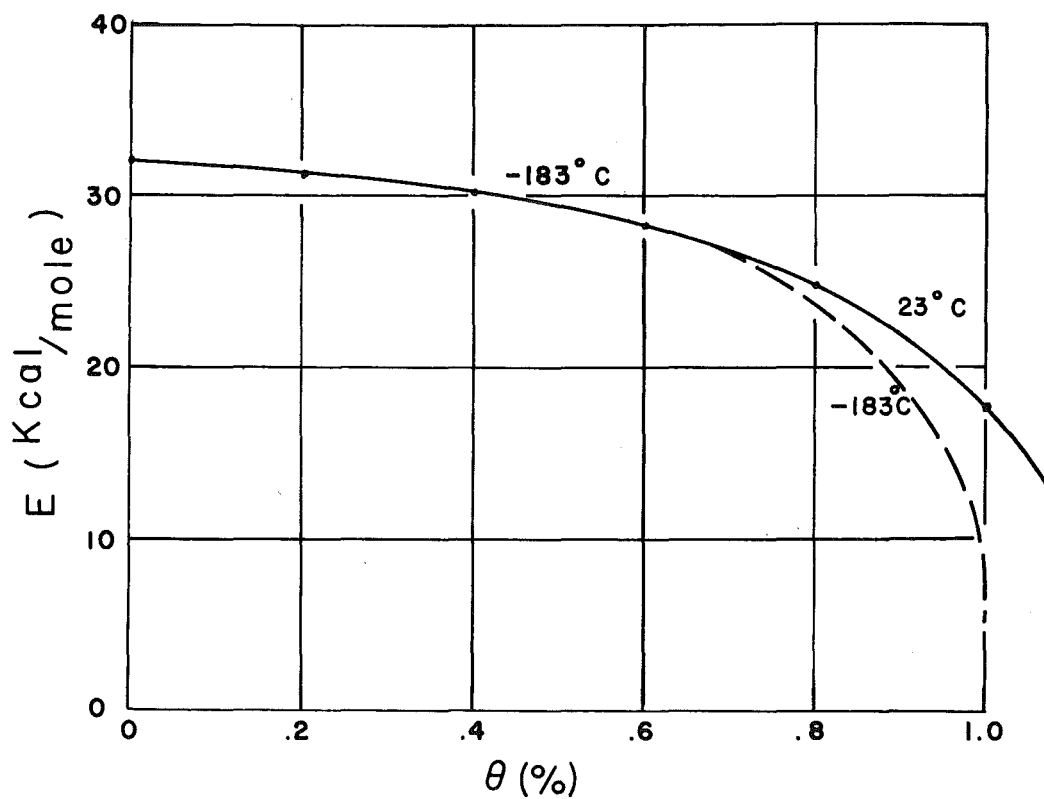


Fig. 8 Heats of adsorption of hydrogen at -183°C on evaporated nickel films (points) in comparison with the heat of adsorption at 23°C (curve) as a function of surface covered.

Reference: 27

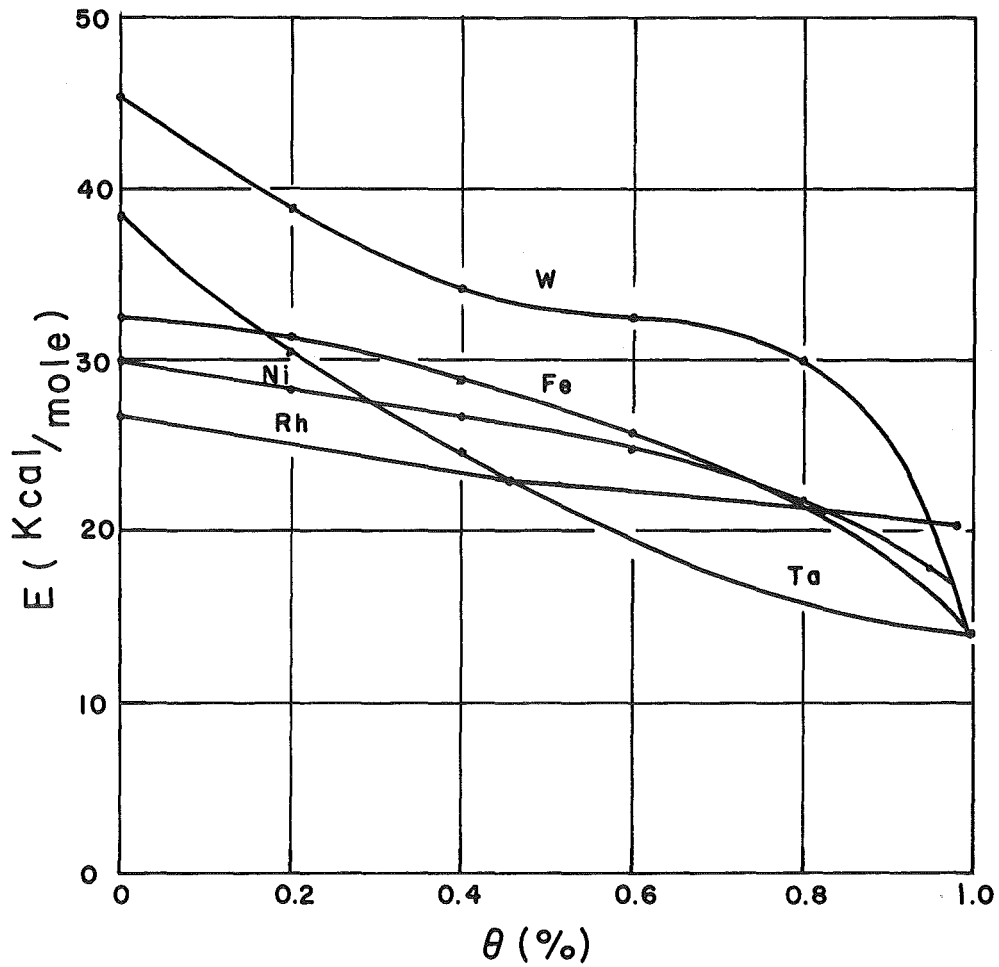


Fig. 9 The heats of adsorption of hydrogen on Rh, Ni, Fe and W as a function of fraction of surface covered where the adsorption at 0.1 mm pressure is taken to present the total coverage.

Reference: 28

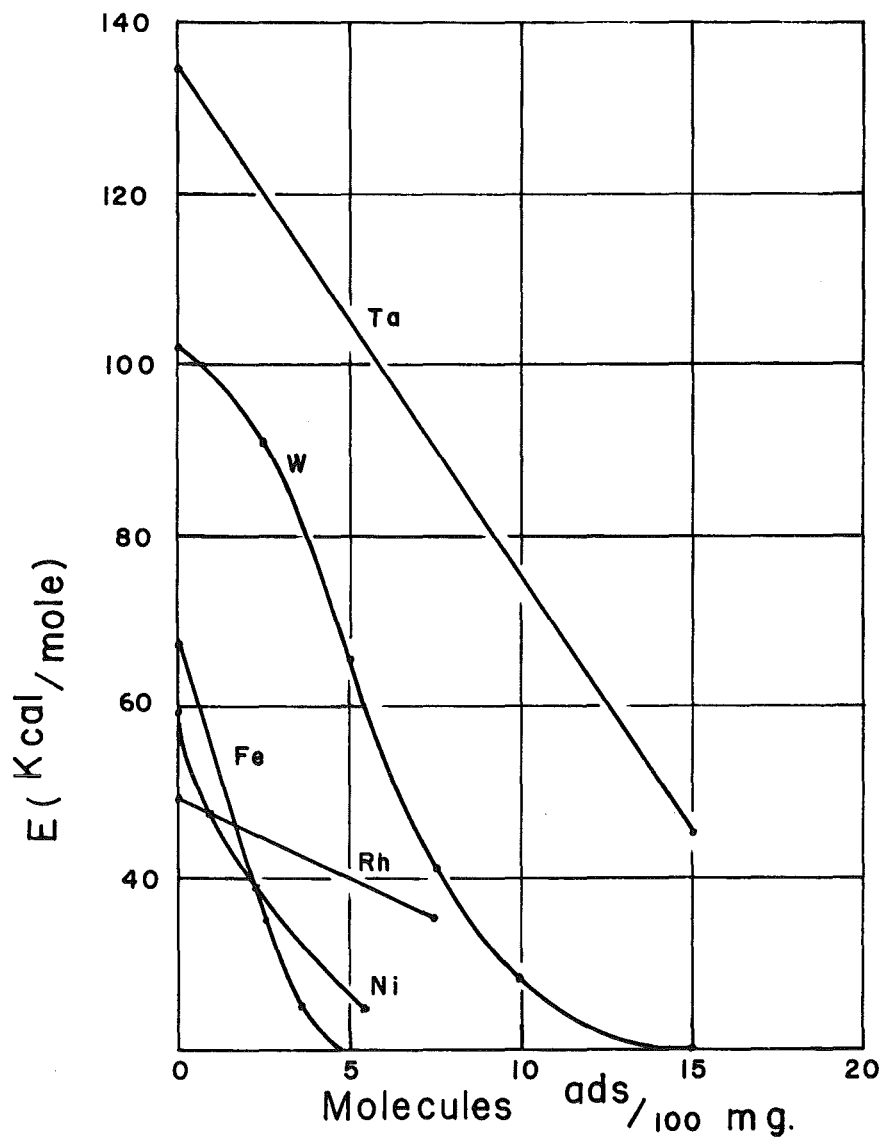


Fig. 10 The heats of adsorption of ethylene as a function of number of molecules adsorbed for 100 mg of film. All films were high vacuum evaporated.

Reference: 28

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4. ACTIVATION ENERGIES OF DESORPTION AND EXPERIMENTAL DATA

The activation energy of desorption E' is related to the heat Q and activation energy E of adsorption by the equation

$$E' = Q + E \quad [4.1]$$

Since adsorption is always exothermic, E' is appreciable even in the limiting case where $E = 0$. Desorption is therefore always activated.

Usually E' varies markedly with θ . With the non-activated adsorptions, the activation is due solely to the change of Q and θ : Q falls as θ increases, and so therefore does E' . As a result desorption is more rapid from concentrated layers. For example, if Q falls from 40 to 10 Kcal/mole with increasing θ , the resulting change in desorption velocity at 250 °C is a factor

$$e^{(40,000-10,000)/2 \times 523} = 10^{13}$$

With activated chemisorptions, the effect is likely to be smaller because E seems to increase with θ , and this to some extent offsets the fall in Q .

In order to measure true desorption velocities and hence activation energies, the desorbed molecule must not be allowed to strike the surface again before being removed from the system. If it does, it may be re-adsorbed. With powders and evaporated films this condition is not easily fulfilled, and quantitative measurements of E' have mainly been made using metal filaments. The most important application of such measurements is to the case of non-activated chemisorptions. Here $E' = Q$ and the temperature coefficient of desorption velocity gives the heat of chemisorption.

Activation energies of desorption have been given in the following table and figures for several systems.

TABLE 6

Activation Energies of Desorption for Gases on Tungsten

Metal	Gas	$\theta(\%)$	Activation Energies of Desorption (Kcal/grm atom)	Ref.
W	O ₂	0.2	147	3
"	Th	0.5	177	2
"	Na	0.00	32	4
"	"	0.13	28.5	"
"	"	0.27	27	"
"	"	0.40	23	"
"	"	0.54	20	"
"	"	0.67	17	"
"	Cs	0.00	65	1
"	"	0.01	64	"
"	"	0.10	60	"
"	"	0.20	57	"
"	"	0.30	53	"
"	"	0.40	50	"
"	"	0.50	48	"
"	"	0.60	45	"
"	"	0.70	43	"
"	"	0.80	42	"
"	"	0.90	41	"
"	"	1.00	40	"

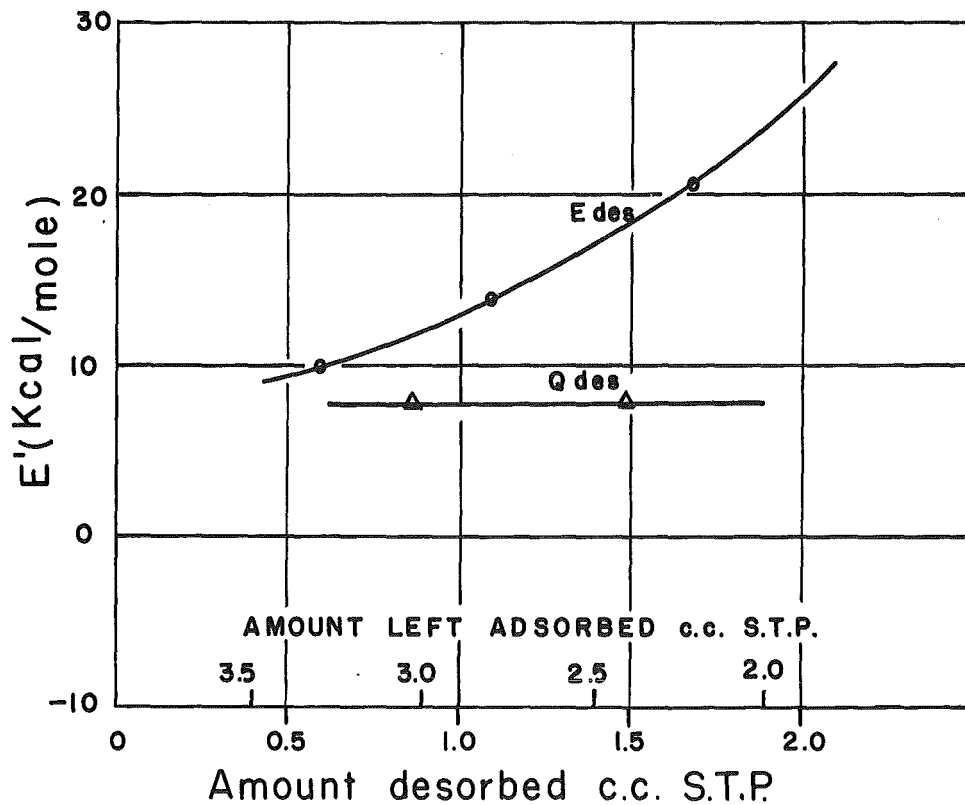


Fig. 11 The activation energies of desorption for hydrogen on ZnO(I) at high coverage. The amount adsorbed and the equilibrium pressure at room temperature before desorption were 3.99 c.c. and 29.5 mm Hg. respectively. Figures indicates the temperature interval where E' was determined.

Reference: 5

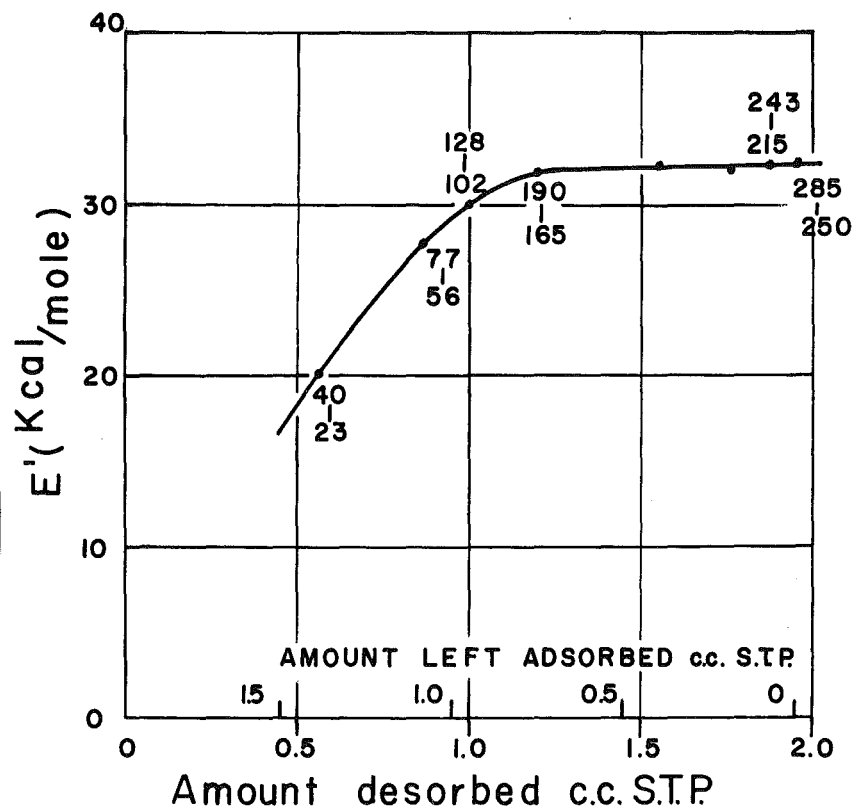


Fig. 12 The activation energies of desorption for hydrogen on ZnO(II) catalyst. The amount adsorbed before desorption at room temp. was 1.98 c.c. Figures indicates the temp. interval where the activation energies is determined.

Reference: 5

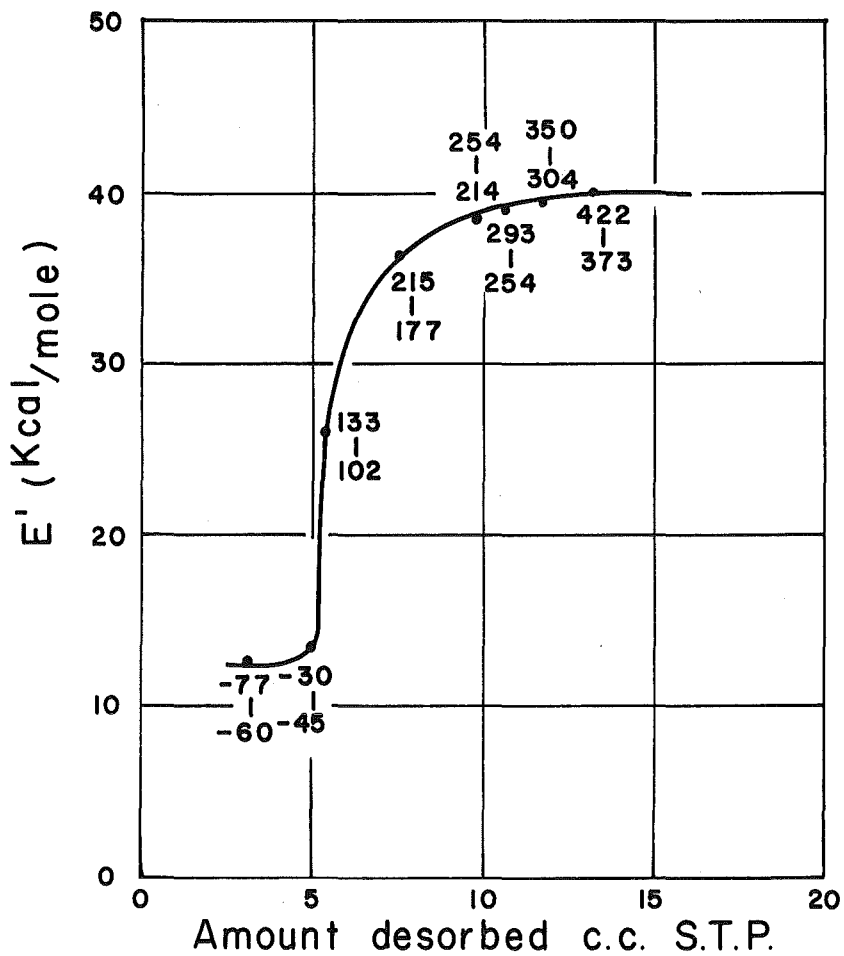


Fig. 13 Activation energies of desorption for CO chemisorbed on ZnO. The amount adsorbed at room temp. before desorption was 15.81 c.c. Figures indicate the temp. interval where the E' was determined.

Reference: 6

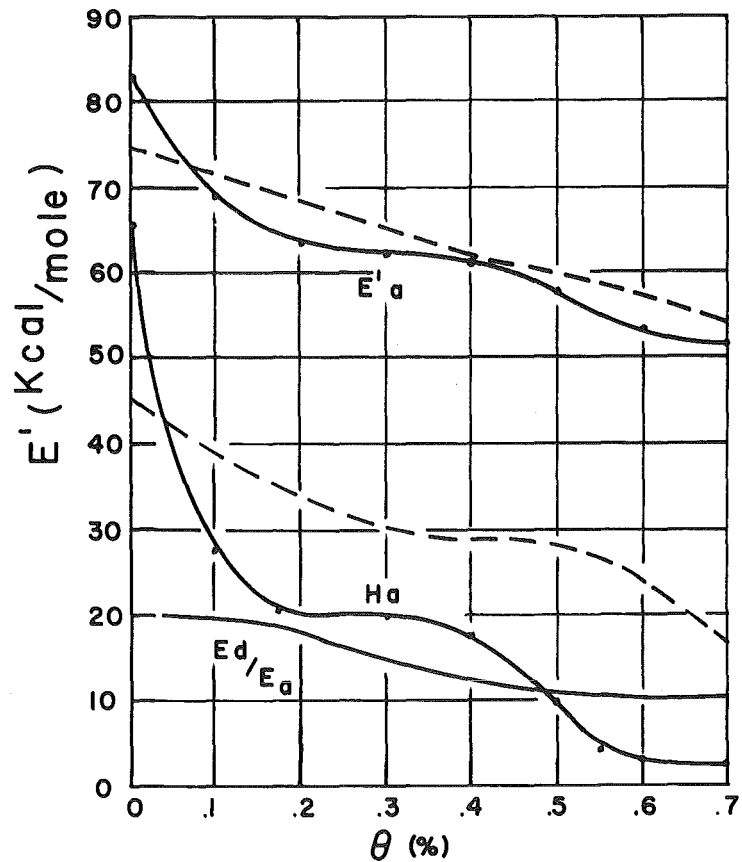


Fig. 14 Activation energies of desorption for Hydrogen on Tungsten. Solid lines for field emission tip, dotted lines for evaporated films, E_d/E_a ratio of activation energy for surface diffusion to binding energy of hydrogen atoms.

Reference: 7

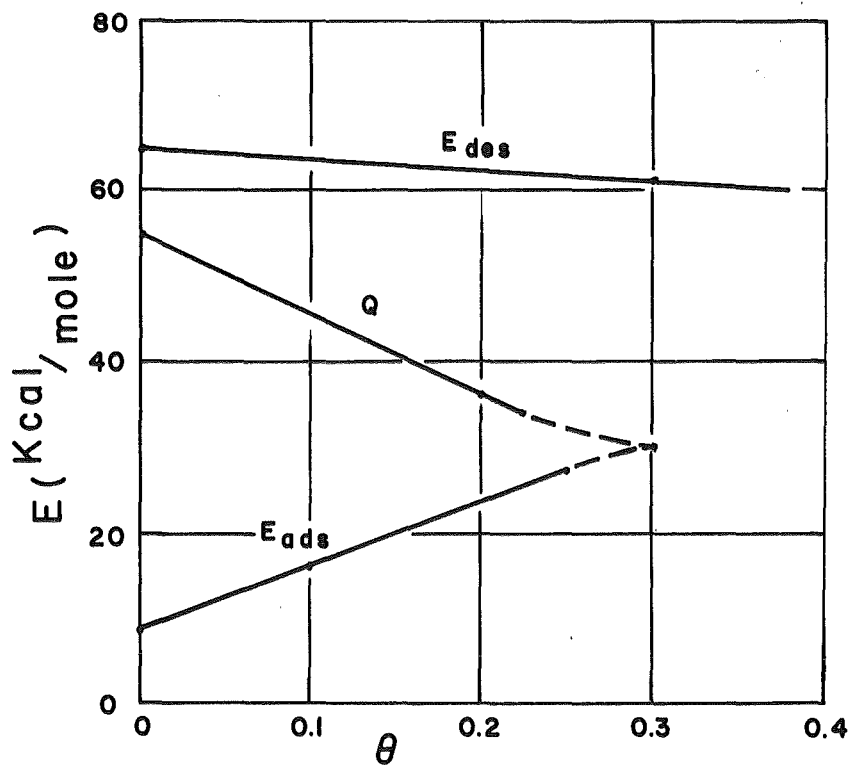


Fig. 15 The variation of activation energies of desorption for H_2 on Fe catalyst at standard condition.

E_{des} = Activation energies of desorption

E_{ads} = Activation energies of adsorption

Q = Heat of Chemisorption = $E_{des} - E_{ads}$

Reference: 8

References (for Sec. 4)

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5. ACTIVATION ENERGIES OF ADSORPTION AND EXPERIMENTAL DATA

The activation energy of the adsorption process can be calculated by means of the Arrhenius equation.

$$\frac{d(\log k)}{dT} = - \frac{E}{RT^2} \quad [5.1]$$

where k^* is the reaction velocity constant and E the energy of activation, equation [5.1] can only be applied in cases where the kinetics of the adsorption process may be deduced.

The activation energy of a simple reversible adsorption like hydrogen on a metal, may be calculated in the following way. The rate of condensation is given by $k_1 p(1-\theta)$ and the rate of evaporate by $k_2 \theta$.

Therefore the rate of adsorption is

$$- \frac{dp}{dt} = k_1 p(1 - \theta) - k_2 \theta$$

if θ is small this becomes

$$- \frac{dp}{dt} = k_1 p - k_2 \theta$$

and

$$\therefore \frac{dp}{dt} = k(p - p_e)$$

where P_e is the equilibrium pressure and k is the velocity constant. By drawing tangents to the isothermal curves of $\log (p - p_e)$ against time at points of equal adsorption, the velocities at two different temperatures may be determined, and the activation energy is given by Arrhenius' equation.

*The values of k are determined in many papers in catalysis for several systems. Some data in the following tables are converted from the k values and these results are very satisfactory with the real experimental data.

in the form

$$E = 2.303 R \frac{T_1 T_2}{T_2 - T_1} \cdot \log \frac{t_1}{t_2} \quad 5.2$$

where t_1 and t_2 are the times taken for the adsorption of a given amount of gas at temperatures T_1 and T_2 .

When the activation energy of desorption and heat of activated adsorption are determined, activation energy can be calculated from equation 4.1 too; i.e., $E = E' - Q$

It might reasonably be believed that the activation energy is associated with the separation of the atoms composing the molecule. For example Pace and Taylor⁽¹⁾ have found that the value of E is the same for both hydrogen and deuterium on nickel, and they therefore concluded that the activation is mainly associated with the surface.

Some activation energies, determined either by direct measurements or by calculation for a number of gas-metal systems are given in the following tables.

SUMMARY

The concept of activation energy for adsorption processes is of great importance in the general problem of reactivity at surfaces. It has been shown that the only essential distinction between "physical adsorption" and "activated adsorption" or between "reversible" and "irreversible" adsorption processes are adsorptions normally with small heats of adsorption and small activation energies and that so called "activated" or "irreversible" adsorptions involved moderate or large energies of activation, frequently with high heats of adsorption. The velocities of these latter processes are

indeed extremely slow. In general, these types of adsorptions with higher energies of activation are important in the surface activity of high vacuum technology. In this article most values of activation energies corresponding to different temperatures are given because the temperature is the main factor in determining what type of adsorption can take place. On the other hand we must remember variation of adsorption with pressure is important too.

Some surface-potential data for gases chemisorbed on different metals are also given. Based on those data and methods, activation energies and work functions can be determined.

TABLE 7

Activation Energies for Gases on Metals W, Ni, Rh

Catalyst	Gas	Pressure (m.m. Hg)	Temp (°C)	Activation Energies (Kcal/mole)	Ref.
W	O ₂	10 ⁻¹ 10 ⁻³	127	17	2
"	"	"	227	22	"
"	"	"	327	22	"
"	O ₂	-	227	19	36
"	H ₂	10 ⁻¹ 10 ⁻³	127 ~ 227	7	3
"	"	"	227 ~ 327	10.2	"
"	"	-	-23	9	36
"	C ₆ H ₂	-	-69 ~ -48	11	4
"	C ₃ H ₈	-	-82 ~ -24	9.0	"
"	i-C ₄ H ₁₀	-	-80 ~ -27	7.9	"
Ni	H ₂	-	127 ~ 227	8.8	3
"	C ₆ H ₁₂	-	-35 ~ 0	10.8	4
"	Decahydro- naphthalene	-	45	<10.0	5
"	Cyclohexane	-	25 ~ 45	13.7	5
"	C ₃ H ₈ (2°H)	-	-47 ~ 0	10.4	4
"	i-C ₄ H ₁₀ (3°H)	-	-47 ~ 0	9.0	"
Rh	C ₆ H ₁₂	-	-48 ~ 0	10.4	4
"	C ₃ H ₈	-	-25 ~ -16	13.3	"

TABLE 8

Activation Energies for Gases on Metals Cu, Pt, Pd

Catalyst	Gas	Temp (°C)	Activation Energies (Kcal/mole)	Ref.
Cu	$\text{CH}_3\text{-CH} = \text{O}$	261	12.8	6
"	$\text{CH}_3\text{CH}_2\text{CH} = \text{O}$	252	12.2	7
"	$(\text{CH}_3)_2\text{C} = \text{O}$	250	16.35	8
"	$\text{C}_6\text{H}_{10} = \text{O}$	250	14.0	9
Pt	Piridine	25 \approx 45	19.9	5
"	Decahydro- naphthalene	"	19.0	"
"	Cyclohexane	25 \approx 50	18.0	"
Pt	C_6H_{12}	0 \approx 31	12.0	4
Pd	Piridine	25 \approx 45	16.2	5
"	Cyclohexane	"	15.3	5
"	C_5H_{10}	00 \approx 37	14.2	4
"	C_6H_{12}	18 \approx 82	13.0	4
"	$(\text{CH}_3)_2\text{CH}_2 \text{C} = \text{NH}$	292	9.14	4
"	$(\text{C}_2\text{H}_5)_2\text{N}-(\text{CH}_2)_3\text{C} = \text{NH}$ CH ₃	302	11.4	10

TABLE 9

Activation Energies for Gases on Catalysts ZnO

Catalyst	Gas	Pressure (mmHg)	Temp. ($^{\circ}$ C)	Activation Energies (Kcal/mole)	Ref.
ZnO	H ₂	50 ~ 70	14 ~ 98	5.5 ± 1.5	11
"	"	"	98 ~ 140	7.5 ± 1.0	11
"	"	"	140 ~ 210	11.0 ± 1.5	11
"	"	"	210 ~ 260	14.5 ± 1.5	11
"	"	0.1 ~ 0.2	80 ~ 148	6.3 ± 1.0	11
"	"	"	148 ~ 202	13.0 ± 1.0	11
"	"	"	202 ~ 246	15.0 ± 1.0	11
"	CO	0.2 ~ 0.4	56 ~ 92	5.5 ± 1.0	12
"	"	"	92 ~ 127	7.5 ± 1.0	12
"	"	"	127 ~ 167	11.5 ± 0.7	"
"	"	"	167 ~ 205	16.5 ± 0.7	"
"	C ₂ H ₄	-	25 ~ 50	25.2	13
"	(CH ₃) ₂ CO	-	340	11.4	14
"	"	-	342	12.28	"
"	"	-	345	12.5	"
"	"	-	348	15.0	"
"	"	-	344	17.6	"
"	"	-	346	19.4	"
"	"	-	341	26.8	"

TABLE 10

Activation Energies for Gases on Oxide Catalysts

Catalyst	Gas	Temp (°C)	Activation Energies (Kcal/mole)	Ref.
Ni-Al ₂ O ₃	C ₆ H ₆	236	15.6	15
"	CH ₃ C ₆ H ₅	245	15.6	16
"	(CH ₃) ₂ C ₆ H ₄	245	14.7	17
"	CH ₃ (CH ₂) ₄ C=NH CH ₃	300	9.37	18
"	[(CH ₃) ₂ CH] ₂ C=NH	302	8.68	10
Pt-asbestos	H ₂	230	18.2	19
Cr ₂ O ₃ -asbestos	C ₆ H ₆	415	28.4	20
"	CH ₃ C ₆ H ₅	472	25.8	20
"	C ₁₀ H ₈	425	32.3	21
"	CH ₃ C ₁₀ H ₇	448	33.9	21
CuO	O ₂	0 to 300	7.0	22
"	"	300 to 400	23.0	22
Cu ₂ O ₃	CO	25 to 40	21.0	13
Oxide Catalyst	CH ₃ CH=O	342	17.7	23
"	CH ₃ CH ₂ CH=O	342	15.6	"
"	CH ₂ =CH-CH=O	352	17.5	"
"	(CH ₃) ₂ C=O	336	12.8	"
"	CH ₃ (CH ₂) ₂ -CH=O	341	16.3	"
"	(CH ₃) ₂ (CH ₂) ₂ -CH=O	342	12.9	"
"	C ₆ H ₅ CH ₂ CH=O	349	18.0	"

TABLE 11
Activation Energies for Gases on Oxide With Different Impurities

Catalyst	Gas	Temp (°C)	Activation Energy (Kcal/mole)	Ref.
NiO + 0.01 mole % WO ₃	CO	180-220	6.5	24
" + 0.01 mole % Cr ₂ O ₃	"	160-220	7.9	"
" + 1 mole % NiCl ₂	"	160-220	8.2	"
" + .01 mole % CO ₂ O ₂	"	160-220	8.9	"
NiO	"	180-250	13.7	"
NiO + 0.01 mole % Ag ₂ O	"	180-250	14.9	"
NiO + 1 mole % Ag ₂ O	"	225-260	17.5	"
NiO + 0.01 mole % Li ₂ O	"	230-280	18.0	"

TABLE 12
Activation Energies for I₂ on S₂O₈²⁻ in the presence of different impurities

Catalyst (mole)	Gas	Activation Energies (Cal/mole)	Ref.
S ₂ O ₈ ²⁻	I ₂	12,863 ± 60	25
S ₂ O ₈ ²⁻ + 0.02 mole NaCl	"	12,983 ± 34	"
" + 0.04 NaCl	"	12,955 ± 48	"
" + .01 NaCl	"	12,759 ± 65	"
" + 0.02 KCl	"	12,926 ± 72	"
" + 0.04 KCl	"	12,744 ± 90	"
" + 0.1 KCl	"	12,590 ± 18	"
" + 0.01 MgCl ₂	"	13,278 ± 60	"
" + 0.02 MgCl ₂	"	13,187 ± 37	"
" + 0.00333 LaCl ₃	"	14,357 ± 131	"
" + 0.000333 Co(NH ₃) ₆ Cl ₃	"	12,121 ± 130	"

TABLE 13
Activation Energies for Gases on Glasses

Catalyst	Gas	Temp (°C)	Activation Energy (Kcal/mole)	Ref.
SiO ₂	He	200-150	4.77	26
"	"	150-1000	5.24	26
"	"	"	5.42	27
"	"	"	5.79	28
"	Ne	-	9.58	27
"	H ₂	-	8.64	28
"	"	-	7.75	29
"	"	-	8.14	30
"	N ₂	-	22.0	28
"	"	-	25.2	30
Pyrex	He	-	5.35	31
Porcelain	Air	-	35.7	32

TABLE 14
Activation Energies of Gases on Charcoal, Diamond

Catalyst	Gas	Temp (°C)	Volume Adsorbed (x10 ³ cm ³ at N.T.P.)	Activation Energies (Kcal/mole)	Ref.
Charcoal	H ₂	20.4	-	2.5	33
"	N ₂	77.3	-	4.4	"
"	A	87.3	-	4.2	"
"	CO	83.1	-	4.8	"
"	CH ₄	111.7	-	5.5	"
Diamond	O ₂	-	35	4.3	34
"	"	-	59	12.0	"
"	"	-	73	18.0	"
"	"	-	93	23.0	"

TABLE 15
Activation Energies Changed at Various Pressure

Gas-Metal	Pressure	Activation Energy (Kcal per mole)	Ref.
H ₂ -D ₂	12 (cm)	13.8	35
"	25 (")	12.8	"
"	40 (")	12.3	"
"	60 (")	12.3	"

TABLE 16
Surface Potential Data for H₂ Chemisorbed on Metals

Gas-Metals	S. P. volts	Method	Ref.
H ₂ -Fe	-0.19	Photoelectric	37
"	-0.43	Diode	38
"	-0.47	Capacitor	39
H ₂ -Co	-0.33	Diode	38
H ₂ -Ni	-0.1	Photoelectric	40
"	-0.12	"	37
"	-0.35	Capacitor	41
"	-0.35	Diode	38
"	-0.39	Photoelectric	42
"	-0.40	Capacitor	43
"	-0.50	F. E. M.	44
H ₂ -Cu	-0.33	Diode	45
"	-0.36	"	38
H ₂ -Ag	-0.34	"	38
"	-0.49	Capacitor	43
H ₂ -Au	-0.18	Diode	38
H ₂ -W	-0.48, -0.65	Capacitor	46, 47
"	-0.50	Diode	46
"	-0.55	F. E. M.	48
"	-1.04, -1.26	Diode	49
H ₂ -Ta	-0.44	Photoelectric	40
"	-0.43	"	37
H ₂ -Pt	-0.14	Capacitor	50
"	-0.15	Diode	50

TABLE 17
Surface Potential Data for O₂ Chemisorbed on Metals

Gas-Metal	S.P. volts	Method	Ref.
O ₂ -Ni	-0.55	Capacitor	51
	-1.40	Diode	52
	-1.60	Capacitor	53
O ₂ -Cu	-0.68	"	54
O ₂ -Ag	-0.60	"	51
O ₂ -W	-1.60	Diode	55
	-1.70	"	56
	-1.70	F. E. M.	57
	-1.71	Diode	58
	-1.74	Diode	59
	-1.89	"	60
	-1.90	Capacitor	61
	-1.90	F. E. M.	62
O ₂ -Pt	-1.2	Magnetron	63

TABLE 18
Surface Potential Data for N₂ Chemisorbed on Metals

Gas-Metals	S.P. Volts	Method	Ref.
N ₂ -W	-0.50	Capacitor	64
	-1.38	Diode	65
N ₂ -Ta	-0.38	Photoelectric	66

TABLE 19
Surface Potential Data For CO chemisorbed on Metals

Gas-Metals	S.P. volts	Method	Ref.
CO-Fe	-1.33	Capacitor	67
	-1.64	Diode	68
	-1.15	Photoelectric	69
CO-C ₆₀	-1.48	Diode	68
CO-Ni	-1.35	"	68
	-1.20, -1.35	Capacitor	67
CO-Cu	+0.28	"	67
	+0.30	Diode	67
	+0.30	Diode	68
CO-Ag	+0.31	"	68
CO-Au	+0.92	"	68
CO-W	-0.86	Photoelectric	70
CO-Ta	-0.67	"	60

TABLE 20
Surface Potential Data for Alkalies adsorbed on Tungsten

System	S.P. Volts	Method	Ref.
W-Na	+2.8	Diode	71
W-K	+2.9	"	71
W-Cs	+3.0	Thermionic	72
	+2.8	Diode	73
	+2.8	Photoelectric	74
W-Ba	+2.4	Thermionic	75
	+1.9	"	76
W-Sr	+2.2	"	76
W-Th	+1.7	Diode	77

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