low pressures (about 25% of the saturation value, at 10^{-4} mm. equilibrium pressure and 0°). The amounts of hydrogen adsorbed, at the same equilibrium pressure, show a wide spread for different temperatures, particularly in the low pressure region.

6. Extrapolation of the adsorption isotherms to high pressures leads to a saturation value of adsorption corresponding to the covering of the tungsten with 1 hydrogen molecule per 2 tungsten atoms in the metal surface.

7. The amounts of hydrogen adsorbed per 1 sq. cm. of the tungsten surface at a given temperature and pressure are identical, within the limits of experimental error, for two different powders the surfaces of which differ by the factor 3.

8. If the adsorbed amounts A are plotted against the equilibrium pressures p, in a $\log A/\log p$ diagram, the isotherms are very nearly straight lines showing different slopes $\log p/\log A$. The slopes range from 1.75 for the 750° isotherm to about 78.0 for the $-194°$ isotherm. The logarithmic isotherms converge, fanwise, toward a point of common intersection in the region of high pressures.

9. With a powder of high specific surface, measurements were carried out which reached for temperatures of 400° and above into the range of very sparse coverings of the adsorbent corresponding to less than 0.8% of the saturation value S. In this range, the logarithmic isotherms are parallel to each other, and have the common slope $(\log p/\log A) = 2$.

10. By means of the Clausius–Clapeyron equation, the differential heats of adsorption were evaluated, for increasing coverings of the tungsten surface with adsorbed hydrogen. In the "highly diluted" range of $<0.008\ S$, the adsorption heat is independent of the amount adsorbed, within the temperature range of -194 to about 530°, and amounts to about 46,000 cal./mole of hydrogen. At coverings $>0.008\ S$, the heats of adsorption decrease rapidly with the increasing covering of the surface, proportional to $Q' - \log(A/A')$; Q' and A' being constants. The entire curve of the heats of adsorption as a function of the surface covering, is shifted to lower levels at temperatures exceeding about 530°.

11. It can be shown that the measurements of J. K. Roberts of hydrogen adsorption on a tungsten wire agree qualitatively and, to a certain extent, quantitatively with the results mentioned above if it is assumed that the true molecular surface of the adsorbent wire exceeded its geometrical surface by the factor 4 5.

12. This agreement, together with other evidence, makes it very likely that the surfaces of the outgassed powders consisted practically completely of the free metal.

13. A discussion of these results, and of their bearing on views on the mechanism of adsorption, will be represented separately.

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMICAL ENGINEERING, JOHNS HOPKINS UNIVERSITY]

The Adsorption of Hydrogen on Tungsten. II

BY WALTER G. FRANKENBURG[1]

In a previous paper,[2] the adsorption of hydrogen on the surface of thoroughly outgassed tungsten powders was described, for equilibrium pressures ranging from 10^{-5} to 30 mm., and for temperatures from -194 to 750°. From the amounts A which were adsorbed at the various pressures p and temperatures T, the differential heats of adsorption Q were computed. The amounts of hydrogen adsorbed per sq. cm. of the metal surface ranged from about 1×10^{12} hydrogen molecules, at the lowest equilibrium pressures measured (1×10^{-6} to 1×10^{-5} mm.), up to about 200×10^{12} hydrogen molecules, at pressures of the order of magnitude of 30 mm. Measurements with two different tungsten powders of similar origin but with different specific surfaces (ratio 1:3) showed that the amounts of hydrogen adsorbed per unit of surface, at a given temperature and equilibrium pressure, were the same for both adsorbents, within the limits of experimental error.

Main Part of the Isotherms.—In the following discussion of these results, we shall deal first with the *main part* of the isotherms, corresponding to surface coverings from about 0.8% of the saturation value up to the highest adsorption values reached (about 35% of the saturation value). The remaining part of the measured isotherms which corresponds to the "highly diluted range" of adsorption (from the lowest coverings which were measured, about 0.25%, up to about 0.8% of the saturation value) will be discussed separately. For these very sparse surface coverings, another relationship exists between the adsorbed quantities and the equilibrium pressures than was found for the denser coverings within the main parts of the isotherms.

The discussion is greatly simplified if it is based on the "logarithmic isotherms," *i. e.*, on diagrams which show the experimental results plotted as $\log A$ against $\log p$. In such a diagram, all the

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[2] Frankenburg, THIS JOURNAL, **66**, 1827 (1944), hereafter cited as "I."

isotherms of the entire temperature range (−194 to 750°) are, within their main parts, almost straight lines, each of these lines having a different slope (see I, Figs. 4 and 5). If extrapolated toward higher pressures, the logarithmic isotherms converge, at a high pressure p_s, in one single point which corresponds to the adsorbed amount s. We want, however, to mention here that small deviations from the straightness of the experimental logarithmic isotherms exist in the sense that they become slightly flatter, in the range of higher surface coverings. This means that an extrapolation of the isotherms in the form of absolutely straight lines is not fully justified, and that it would be wrong to consider the common point of intersections of the extrapolated isotherms as the saturation values of adsorption. We shall discuss this point in detail later. For a preliminary discussion, however, matters are considerably simplified if we treat, as a first approximation, the logarithmic isotherms as straight lines, over their entire lengths, up to s, the point of intersection.

On this basis, the general equation of the main part of each isotherm is given by

$$\log p = \log p_s - \alpha(\log s - \log A) \qquad (1)$$

where p_s and s are the quantities mentioned above and α is the "slope" of every single isotherm equal to ($\log p/\log A$).[3] As the values of p_s and of s are the same for all the isotherms, the only variables depending on the temperature of the individual isotherm are the slopes α_1, α_2, etc.

Hence, for every single isotherm, eq. (1) can also be written as

$$\log p = c + \alpha_1 \log A \qquad (2)$$

α_1, the slope of the individual logarithmic isotherm measured at the temperature T_1, remains constant throughout the main part of this isotherm. The α-values of the different isotherms found in our measurements[3a] are equal to the slopes of the best straight lines which can be laid through the experimental points. They are listed as "over-all slopes," α_{OV}, in Table II, col. 2. Their values change from 1.72 ± 0.17 for the 750°-isotherm to 16.63 ± 2.5 for the 0°-isotherm, and to approximately[4] 67.4 ± 8.0 for the −194°-isotherm.

We shall now turn to the question as to how these experimental isotherms compare with the isotherms derived from the general theory of adsorption.

Using simplifying assumptions, Langmuir[5] has developed the following equation for the adsorption isotherm of a gas which is adsorbed without dissociation of its molecules at the adsorbing surface

$$p = c(A/(S - A)) \qquad (3)$$

In this equation, A is equal to the amount adsorbed at the equilibrium pressure p, S is the saturation value of adsorption. The constant c contains, in addition to other factors, the quantity $e^{-Q/RT}$, or, more exactly, the expression $e^{\int(Q/RT^2)\mathrm{d}T}$, with Q being the heat of adsorption. The latter is assumed, in this derivation, to be constant over the entire range of each isotherm as well as from isotherm to isotherm. Written in logarithmic form, eq. (3) becomes

$$\log p = \log c + \log(A/(S - A)) \qquad (3a)$$

By splitting out of the constant the expression containing Q, we obtain

$$\log p = \log c' + [0.43\int(Q/RT^2)\mathrm{d}T] + \log(A/(S - A)) \qquad (4)$$

For the "linear range" of adsorption in which A/S is small (about < 0.10) compared with 1, formula (4) can be replaced, to a first approximation, by

$$\log p = \log c' + [0.43\int(Q/RT^2)\mathrm{d}T] + \log(A/S) \qquad (5)$$

By differentiating this equation over $\log A$, and remembering that Q was assumed to be constant in the Langmuir derivation, we obtain

$$\mathrm{d}\log p/\mathrm{d}\log A = \alpha_{\mathrm{lin}} = 1 \qquad (5a)$$

This means that logarithmically plotted Langmuir isotherms for a gas which is adsorbed without dissociation in the adsorbed state, ought to be parallel straight lines with the common slope $\alpha_{\mathrm{lin}} = 1$, in the linear range of adsorption.

In an analogous way, it can be shown that for diatomic gas molecules which are adsorbed as atoms on the adsorbent, the slopes of the logarithmic Langmuir isotherms in the linear range are parallel and all equal to 2

$$\mathrm{d}\log p/\mathrm{d}\log A = \alpha_{\mathrm{lin}} = 2 \qquad (5b)$$

Contrary to this, our experimental isotherms are not parallel at all but have slopes which change by a factor of about 10, between 750° and 0°. All the slopes exceed, furthermore, the value 1, and most of them the value 2. The obvious reason for this deviation from the theoretical Langmuir isotherms is that, for the hydrogen adsorption on tungsten powders, the heat of adsorption is far from being constant within the range of a single isotherm but sharply dependent upon the extent to which the metal surface is covered with the adsorbed gas. Figure 7 in our previous paper shows how rapidly the differential heats of adsorption decrease with increasing A/S. These differential heats of adsorption had been calculated by determining, from the experimental data the tangents $\mathrm{d}\ln p/\mathrm{d}T$ for each given A/S value,

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(3) More correctly, α should be called the "reciprocal slope."

(3a) The α-values found with the two powders 9798 and 9799 were averaged for this purpose.

(4) The slopes of the −194° and of the −73°-isotherms can be determined only approximately, on account of the extreme flatness of these isotherms.

(5) I. Langmuir, THIS JOURNAL, **38**, 2221 (1916); **39**, 1848 (1917); **40**, 1361 (1918). In a later publication (*J. Chem. Soc.*, 511 (1940)), Langmuir revised, in several finer details, the special kinetic picture from which he deduced originally equation (3). The same equation has also been derived thermodynamically (M. Volmer, *Z. physik. Chem.*, **115**, 253 (1925); and by statistical methods (R. H. Fowler, *Proc. Cambr. Phil. Soc.*, **31**, 260 (1935); K. J. Laidler, S. Glasstone and H. Eyring (*J. Chem. Phys.*, **8**, 659 (1940).

and by deriving the Q-values by means of the equation

$$d \ln p/dT = Q/RT^2 \qquad (6)$$

A simpler method for the calculation of the heats of adsorption is carried out as follows: We mark the values of the T_1 isotherm with the suffix 1, those of the T_2 isotherm with the suffix 2. The differential heats of adsorption $Q_{1,2}$ (between the temperatures T_1 and T_2), for a surface covering at which the equilibrium pressures p_1 and p_2 were measured at the temperatures T_1 and T_2 is then obtained, again by means of the Clausius-Clapeyron equation, as follows

$$(\log p_1 - \log p_2)/(T_2 - T_1) = 0.43 Q_{1,2}/RT_1T_2 \qquad (7)$$

Substitution of the log p values from (1) into (6) results in

$$Q_{1,2} = (\alpha_1 - \alpha_2)(\log s - \log A)RT_1T_2]/0.43(T_2 - T_1) \qquad (8)$$

As α_1 and α_2 are, to a first approximation, constants for T_1 and T_2, respectively, and as s, R, T_1 and T_2 are constants throughout, equation (8) can also be written as

$$Q_{1,2} = \gamma_{1,2} \log (s/A) \qquad (9)$$

or

$$-dQ_{1,2}/dA = \gamma_{1,2}/A \qquad (10)$$

According to this equation, the heats of adsorption decrease, *within the main parts of the adsorption isotherms*, with increasing A, proportionally to the quantity $1/A$.

For the exact numerical evaluation of Q by means of eq. (8), the slopes α_1 and α_2 have to be "comparable," *i. e.*, they have to correspond to the slopes of the T_1 and T_2 isotherms at points belonging to the same adsorbed amount A. If the experimental isotherms were ideal straight lines, each with an absolutely constant slope, these slopes could be substituted right away into eq. (8). As, however, the logarithmic isotherms show a distinct, although very slight, flattening, comparable slopes have to be selected for the correct calculation of Q. The simplest method for doing this is to operate with the slopes α_{lin} of the isotherms which correspond to the linear range of adsorption. In view of the fact that the isotherms for 200° and lower temperatures are only measured within the range of higher surface coverings, their slopes have to be reduced to the α_{lin}-slopes by calculation. The Langmuir equations, regardless of their modification by the inconstancy of the heats of adsorption, provide a theoretical basis for carrying out this calculation. The latter leads, moreover, to the evaluation of the correct saturation value S for our isotherms.

Substitution of the value of Q from (9) into (5), the Langmuir equation for the linear range of adsorption, results in

$$\log p = \log c'' + \left[0.43\int\left(\frac{\gamma \log (s/A)}{RT^2}\,dT\right)\right] + \log A - \log S \qquad (11)$$

α_{lin}, the slope of the isotherm in the linear range, is derived by differentiation of (11) over log A

$$\alpha_{\text{lin}} = d \log p/d \log A = [-0.43\int(\gamma/RT^2 dT)] + 1 \qquad (12)$$

For any optional point, however, of the isotherm outside of the linear range, the slope α, as a function of the adsorbed amount A_1, is derived by substituting the value of Q from (9) into the general Langmuir equation (4), and by differentiating the substituted equation over log A

$$\log p = \log c'' + \left[0.43\int\left(\frac{\gamma \log (s/A)}{RT^2}\,dT\right)\right] + \log [A/(S - A)] \qquad (13)$$

and

$$\alpha = d \log p/d \log A = [-0.43\int(\gamma/RT^2 dT)] + 1 + A/(S - A) \qquad (14)$$

Hence, if our isotherms follow in principle Langmuir's equations (with the modification that the heats of adsorption vary according to equation (9)), they ought to possess the following properties: (1) in the region of "linear adsorption," ($A/S < A/s < 0.10$), the plots of log A *vs.* log p ought to be straight lines with slopes equal to $[-0.43\int(\gamma/RT^2 dT) + 1]$. (2) For coverings of $A/s > A/S > 0.10$, the slopes ought to increase, with increasing A, by the amount $(A/(S - A))$. This agrees, at least qualitatively, with the fact that our logarithmic isotherms become flatter the closer A approaches s. In view of the appreciable limits of experimental error (see I, Table IV, col. 8), it is difficult to detect this slight flattening of the isotherms, and still more difficult to determine this effect quantitatively.

Fairly accurate values, however, for the flattening effect can be obtained by applying the method of least squares to all the experimental points measured in various runs, and by evaluating, in this way, the isothermic lines which can be laid through these points with the smallest average deviations. Thus, one can determine rather accurately the finer differences which exist between the slopes of a given isotherm in the range of linear adsorption on the one hand, and in a range lying closer to saturation, on the other hand.

TABLE I

Temp. of isotherm considered in ° C.	Slope in linear range $A/S < A/s < 0.10$, α_{lin}	Slope $\alpha_{A'}$ at a point in which amount A' has been adsorbed $\alpha_{A'}$	A' (in 10^{-7} mols H_2/g.)	$\Delta = \alpha_{A'} - \alpha_{\text{lin}}$	$S = [A'/\Delta](\Delta + 1)$ (in 10^{-7} mols./g.)
600	2.24	2.37	8	0.13	69.5
500	2.97	3.08	11	.20	66.0
400	4.02	4.35	16	.33	64.4
300	5.42	5.80	18	.38	65.4
					Av. 66.3

Table I shows, for powder 9798, the slopes α_{lin}, determined in a range in which the adsorbed amounts are smaller than 10% of s, and consequently appreciably smaller than 0.10 S (because $S > s$), and the slopes $\alpha_{A'}$ for adsorbed amounts A' which correspond to the highest surface coverings obtained at the various temperatures

TABLE II

1 Temp. in °C.	2 Measured over-all slopes α_{Ov} (averages of different powders)	3 Upper and lower limit of A/S, for measured range	4 Upper and lower limit of $A/(S-A)$, for measured range	5 Mean value M of $(A/(S-A)$, for measured range	6 Slopes $\alpha_{lin} = \alpha_{Ov} - M$	7 Av. error in det. α_{Ov} in units of slope
−194	(67.4)	(0.40 to 0.50)	(0.67 to 0.92)	0.80	(66.60)	±8.0
− 73	(24.1)	(.30 to .43)	(.43 to .76)	.60	(23.50)	±4.0
0	16.63	.22 to .40	.27 to .67	.47	16.16	±2.5
100	10.82	.15 to .35	.18 to .54	.36	10.46	±1.77
200	7.58	.087 to .30	.011 to .43	.22	7.36	±0.62
300	5.60	.020 to .25	.020 to .33	.18	5.42	± .42
400	4.17	.015 to .21	.015 to .27	.14	4.03	± .26
500	3.06	.008 to .12	.008 to .18	.09	2.97	± .18
600	2.31	.008 to .10	.008 to .11	.07	2.24	± .10
650	2.16	.008 to .09	.008 to .11	.06	2.10	± .14
700	1.85	.008 to .05	.008 to .05	.03	1.82	± .14
750	1.72	.008 to .04	.008 to .04	.03	1.69	± .17

TABLE III

CALCULATION OF THE CONSTANT γ OF THE EXPRESSION $Q = \gamma \log S/A$, FOR THE HEATS OF ADSORPTION Q, FROM THE "LINEAR SLOPES" α_{lin} OF THE LOGARITHMIC ISOTHERMS

Temperatures of the isotherms, °C. T_1	 T_2	Diff. of the linear slopes $(\alpha_1 - \alpha_2)$	Q calculated according to equation (8) $\times \log (s/A)$	Mean value of γ	Temperature dependence of γ
−194	− 73	43.0	25,000	25,100	None
− 73	0	7.34	25,500		
0	100	5.30	25,100		
100	200	3.10	25,400		
200	300	1.94	24,500		
300	400	1.39	24,900		
400	500	1.06	25,600		
500	600	0.73	22,900	Decreases with increasing temperature	Starting from 529°C. = 802°K. $\gamma' = \gamma \left(\frac{802}{T'}\right)^3$
600	650	.24	18,000		
650	700	.18	15,000		
700	750	.13	12,500		

Equations (12) and (14) show that $\alpha_{A'}$ is larger than α_{lin}, by the amount $(A'/(S - A'))$. Consequently, the difference $\Delta = (\alpha_{A'} - \alpha_{lin})$ can serve to evaluate the true saturation value S by means of the equation $S = [A'/\Delta](\Delta + 1)$ (see col. 6, Table I). The S-values derived from four different isotherms are in fairly good agreement, and yield as an average $S = 66.3 \times 10^{-7}$ mole H_2/g., for powder 9798. As the latter has a molecular surface of 7280 sq. cm./g., the saturation value amounts to 9.11×10^{-10} mole H_2/sq. cm. = 5.52×10^{14} H_2 molecules per sq. cm. A similar calculation based on the isotherms for powder 9799 leads to the value $S = 5.38 \times 10^{14}$ hydrogen molecules per sq. cm. As 1 sq. cm. of a tungsten surface contains between 10×10^{14} and 14×10^{14} tungsten atoms,[6] the surface covering at saturation amounts to one hydrogen molecule per 2 tungsten atoms, or to 1 hydrogen atom per 1 tungsten atom of the metal surface.

We can come back, now, to our purpose to evaluate the α_{lin}-slopes for all isotherms, in order to calculate Q by means of eq. (8). Table II shows the α_{lin}-values (col. 6) for all the isotherms from −194 to 750°. The calculation is based on the over-all slopes α_{Ov} (col. 2). From the range of the A/S values (col. 3) over which experimental points were determined for each single isotherm, the range of the $(A/(S - A))$ - (col. 4) values is computed. The average values M of this range (col. 5) has, according to eq. (12) and (13), to be subtracted from α_{Ov} in order to obtain α_{lin} (col. 6).

The values obtained for α_{lin} can be considered as being correct within ±10%, with the exception of the values derived from the less reliable isotherms of −194 and −73°. Column 7 shows the deviations which the over-all slopes are subjected to because of the limits of experimental errors (see 1, Table IV). It can be easily understood that, in view of these limits of error in determining the slopes, the isotherms appear to be almost perfectly straight lines although the statistical analysis of the experimental points proves that they are slightly flattened, at higher pressures.

By applying eq. (8) to the α_{lin}-values, the values of γ, and hence those of $Q = \gamma \log (s/A)$, can be evaluated. Table III contains these values and shows that γ remains constant within the temperature range from −194° to some value

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(6) Depending on whether the surface contains (100) or (110) planes of the tungsten lattice as boundary faces.

TABLE IV

Temperatures in °C. 1	Temperatures in °K. 2	Values of γ' (of the equation $Q = \gamma'$ (log S/A)) Calcd. from observed slopes 3	Values of γ' Calcd. by means of eq. (15) 4	Slopes α_{lin} of the logarithmic isotherms Observed (from Table I) 5	Slopes α_{lin} Calculated from the γ'-values by means of eq. (9) 6
529	802	25,100	25,100	betw. 2.24 and 2.97	...
550	823	22,900	23,200	2.24	...
625	898	18,000	17,800	2.17	...
675	948	15,000	15,200	1.96	...
725	998	12,500	13,000	1.76	...
1000	1273	....	6,280	...	1.26
1500	1773	....	1,890	...	1.08
2000	2273	....	1,100	...	1.013
2500	2773	....	607	...	1.002

between 500 and 600°. At higher temperatures, the γ-values drop sharply. By means of a graphical evaluation, we find that the values of γ' at temperatures $T' > (529°\text{C.} = 802°\text{K.})$ can be expressed by the formula

$$\gamma' = \gamma \left(\frac{802}{T'}\right)^3 \qquad (15)$$

Column 3 of Table IV shows the values of γ' for the temperature range from 529 to 725° derived from the observed $(\alpha_1 - \alpha_2)$ values by means of eq. (8). Column 4 contains the values of γ' for the same temperatures, but calculated by means of eq. (15). The agreement between the two sets of values is satisfactory. Equation (15) has been used, furthermore, for extrapolating some α'-values for still higher temperatures for which no adsorption measurements were made (725° to 2500°).

Table IV shows that the γ' values, and, hence, the Q values, become negligible compared with RT, at temperatures between 2000 and 2500° Column 6 lists the α_{lin}-values for the high extrapolated temperatures, calculated by applying equation (9) to the γ'-values of column 4. Obviously, the limiting values for γ' and for α_{lin}, at very high temperatures, are γ' = zero, and $\alpha_{lin} = 1.00$. This conclusion, drawn from the extrapolation of the experimental data, is in agreement with equation (12), as the latter gives for γ = zero the value of $\alpha_{lin} = 1.0$. This agreement, together with the fact that equation (12) is based on the Langmuir equation (3) which was derived for the adsorption of gas molecules which do not dissociate on the adsorbing surface, leads to the conclusion that, within *the "main range" of our isotherms* (*i. e.*, for coverings > 0.8% of the saturation covering), *the hydrogen adsorption takes place without the complete splitting of the molecular bonds of the hydrogen molecules, in the adsorbed state.* For the case that the adsorbed hydrogen would exist on the adsorbing surface in the form of single atoms, *i. e.*, as atoms which are completely independent from each other, the form (5b) of the Langmuir equation would describe the experimental data, provided that the heat of adsorption would not depend on the extent of the covering of the surface with the adsorbed atoms.

Highly Diluted Part of the Isotherms.—This contemplation of the possibility of a "true atomic" adsorption leads us into the range of high dilution of the adsorbed phase (coverings < 0.8% of saturation), the discussion of which has been postponed up to now. As the equilibrium pressures for these very low coverings are extremely small ($\leqq 10^{-6}$ mm.) at all temperatures below about 400°, reliable experimental data were obtainable only at 400° and higher temperatures, for this range of highly diluted adsorption. Nevertheless, the measurements carried out in this range yielded enough experimental points to provide adequate information about the general character of the parts of the isotherms which correspond to the very sparse surface coverings of less than 0.8% of the saturation covering of the tungsten surface. In the logarithmic plot, these parts of the isotherms (400° and higher temperatures, measured on powder 9799 as adsorbent) prove to be parallel to each other, and to possess the common slope $\alpha = 2.0$ (see I, Table V, and Fig. 5). In other words, the isotherms follow closely, in this special range, equation (5b), the Langmuir formula for "true atomic" adsorption. This indicates that, within the range of the highly diluted adsorption, (1) the heats of adsorption remain constant and are independent of the extent of surface covering below the 0.8%-covering, and that (2) *the hydrogen exists, at these high dilutions of the adsorption layer, in the form of single atoms on the tungsten surface.* Consequently, the heats of adsorption Q_{At} correspond, within this range, to the process $H_2(\text{gas}) \rightarrow 2H(\text{adsorbed})$, whereas the heats of adsorption Q of the main range are to be attributed to the process $H_2(\text{gas}) \rightarrow H_2(\text{ads.})$. At the transition point between the molecular and the atomic adsorption, *i. e.*, at about 0.8% of the saturation covering, Q is equal to Q_{At}, and the latter remains, at a given temperature, constant for all the surface coverings smaller than 0.8% of S (= 1.5% of s). By means of equation (9), we obtain

$$Q_{At} = \gamma \log (s/A) = \gamma \log (1/0.015) = 1.824\,\gamma \qquad (16)$$

The values of Q_{At} are listed in Table VI, for different temperatures, and, in addition, the heats Q_H of "atomic adsorption"[7] for the process

H(gas) → H(adsorbed) which is equal to $(Q_{\text{diss. H}_2} + Q_{\text{At}})/2$.

TABLE V

HEATS OF ADSORPTION IN THE "HIGHLY DILUTED," ATOMIC RANGE OF ADSORPTION: COVERINGS OF THE SURFACE <0.008 *S*

Temp., °C.	Q_{At} (H_2(gas) → 2H(ads.)) in cal./mole H_2	Q_{H} (Hgas) → H(ads.) in cal./mole H
400, 500, up to 529	45,600	72,800
550	41,800	70,900
625	32,500	62,250
675	27,700	63,850
725	23,700	61,850
1000 (extrapolated)	11,500	55,750
1500	3,450	51,720
2000	2,010	51,005
2500	1,110	50,555

We see that the heat of adsorption Q_{H} per single hydrogen atom is, in its range of temperature independence, *i. e.*, below 529°, larger by about 50% than the heat of the combination of a single H atom with another H atom.

The fact that the heat of adsorption becomes constant, for a given temperature, at coverings below 0.008 *S*, permits a modification of our equation (9) which, without this modification, yields extremely high values for *Q*, for very small coverings (*A/s*). The modified equation (9) gives the *Q* value for a covering *A/s*, as

$$Q = Q_{\text{At}} - \gamma[\log(A/s) - \log(A'/s)] \quad (17)$$

In this equation, Q_{At} is the quantity shown in Table V for the temperature in question, *A* is the amount adsorbed, *s* = about 0.6 *S* is the amount adsorbed at the extrapolated intersection of the isotherms, and *A'* is the amount adsorbed at the "critical covering" of 0.008 *S* where the transition from the atomic to the "molecular" adsorption occurs. This equation can also be written as:

$$Q = Q_{\text{At}} - \gamma \log (A/A') \quad (18)$$

under elimination of the quantity *s*, and with $Q_{\text{At}} = \gamma\ (\log s/A')$, according to eq. (9). Equations (17) and (18) give the *Q* values for the range of adsorption covered by our measurements, *i. e.*, for coverings from about $A = 0.0025\ S$ to about $A = 0.37\ S$. For the region of higher coverings, up to $A = S$, it is questionable whether an extrapolation of these equations is permissible. Such an extrapolation would lead to Q = zero for $A = s = 0.6\ S$, and to negative values of *Q* for full saturation (for $A = S$, $Q = -5500$ cal.). It is possible, and even likely, that the equations (17) and (18) are not valid for these high surface coverings, and that *Q* decreases in this range only to such an extent that it becomes zero, at the saturation point $A = S$.

Besides the values of the differential heats of adsorption of hydrogen on a tungsten wire which were found by J. K. Roberts,[6a] several other values are given in the literature which can be compared with our results. The heats of adsorption of hydrogen atoms on tungsten (= Q_{H}, listed in Table V, col. 3) include the value of 56,000 cal./mole, given by A. Shekhter[6b] for this quantity. For 1150°, O. I. Leipunskii[6c] concludes from data on the hydrogen adsorption on tungsten that 22% of the adsorbed gas consists of atoms. No data are given as to the hydrogen pressure for which this ratio is evaluated. The slope of the logarithmic isotherm for 1150° can be found by extrapolation from our measurements to be about 1.20. By drawing an isothermic line, of this slope, through *s*, the point of intersection in our isothermic diagram, we find that the ratio of hydrogen atoms (gas adsorbed below the covering of 0.008 *S*) to the total amount of hydrogen adsorbed corresponds to 22% at an equilibrium pressure of about 210 mm., for 1150°. G. Bryce[6d] found that the rate of production of hydrogen atoms from a tungsten wire the temperature of which was varied between 1148 and 1420°K., is proportional to the square root of the hydrogen atmosphere around the wire, this pressure being varied between 3.5×10^{-3} to 4×10^{-2} mm. At these high temperatures and relatively low pressures, the covering of the tungsten surface lies, according to our measurements, completely within the range of "high dilution," *i. e.*, the adsorbed hydrogen consists exclusively of atoms the concentration of which varies proportionally to $p^{1/2}$, in agreement with Bryce's findings. The temperature dependence and the constant factor of his formula for the rate of evaporation of hydrogen atoms from the hot tungsten surface will be discussed in a separate paper dealing with the kinetic side of the hydrogen adsorption on tungsten.

The characteristic features of the hydrogen adsorption on outgassed tungsten powders can now be summed up as follows: (1) At very high dilutions (<0.8% of the surface covering at "saturated adsorption") the adsorbed phase consists of hydrogen atoms. The heat of adsorption is, within this range, independent of the concentration of the adsorbed atoms. It remains constant also over the entire temperature range from lower temperatures up to 529°. (2) Above 529° = 802°K., the heat of adsorption decreases sharply with rising temperature *T'* (in °K.), proportional to $(802/T')$,[3] but remains still independent of the concentration of the adsorbed gas, at any given temperature, within the range of high dilution of the adsorbed hydrogen. (3) If the concentration of the adsorbed hydrogen exceeds 0.8% of the value corresponding to "saturated adsorption," the pressure dependence of the isotherms indicates that attracting forces between the adsorbed hydrogen atoms come into action: the adsorbed gas behaves as is to be expected from adsorbed hydrogen molecules. (4) Together with the appearance of attracting forces

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[6a] See the discussion in I.

[6b] Shekhter, *Acta Physicochim. U. R. S. S.*, **10**, 379 (1939).

[6c] Leipunskii, *ibid.*, **8**, 527 (1939).

[6d] Bryce, *Proc. Camb. Phil. Soc.*, **32**, 648 (1936).

between the adsorbed hydrogen atoms, the differential heats of adsorption Q fall, at any given temperature, with increasing covering of the surface of the adsorbent, according to the relationship $Q = \gamma \log (s/A)$; (A = amount adsorbed with the differential heat of adsorption Q, s = about 0.6 S. (5) These heats of "molecular adsorption" show the same temperature dependence as the heats of the "atomic adsorption": they are temperature independent between −194 and 529°, and decrease above the latter temperature as described under (2) above. (6) Extrapolation of the experimental isotherms to higher pressures indicates that the saturation of the adsorption S is reached at a covering of the tungsten surface corresponding to the ratio ($2W/1H_2$) and that the decreasing heats of adsorption reach very low values, at this covering.

General Discussion

In many cases, changes of the differential heats of adsorption with increasing covering of the adsorbent surfaces—as found for the system tungsten/hydrogen—have been explained by the assumption of a heterogeneous nature of this surface ("active points"). This explanation can also be applied to the system described here. Doing so, we reach the following conclusions:

A relatively small part of the metal surface has a structure which favors the adsorption of hydrogen in atomic form whereas, on the remaining part of the surface, the gas is adsorbed in the form of molecules. The number of surface sites of various "adsorptive power" varies according to the formula $N = N_0 e^{-E/f}$, where N designates the number of surface sites exerting an adsorptive power of E or greater than E, f the average adsorptive power of the entire surface, and N_0 the total number of adsorbing sites present on the metal surface. This formula corresponds to a "Maxwell distribution" of the potential energy among all the surface sites. This statistical distribution of the surface activities, if expressed in form of the equation $E = f \log (N_0/N)$ is very similar to our equation $Q = \gamma \log (s/A)$ for the variation of the differential heats of adsorption.

If we make the assumption that the heats of adsorption of the gas molecules are equal—or at least proportional—to the amount of surplus energy E of the surface sites, and that the surface sites are covered with the adsorbed gas in a succession corresponding to their decreasing adsorptive capacities, the variation of the differential heats of adsorption, with increasing surface covering, would be traced back to that of the energetic structure of the surface of the adsorbent tungsten specimen. In this hypothetical picture, it is tacitly assumed that the final energy content of the adsorbed gas molecules is identical over the total surface, regardless of the prior activity of the various adsorbing sites; otherwise no parallelism would exist between the activity of the surface centers and the differential heats of adsorption. The following inferences can be derived from this "active surface hypothesis": (1) The variation of the energy content of the surface sites extends over a large part of the total surface (at least 40%) of the adsorbent, contrary to the usual picture that the "active spots" on an adsorbent or on a catalyst comprise only a small fraction of the total surface. (2) The activity distribution of the surface sites follows Maxwell's law of the energy distribution among the molecules of a gas. (3) The surfaces of two different tungsten powders of considerably different particle sizes possess, qualitatively and quantitatively, the same activity characteristics per unit of surface area. (4) Prolonged heating of the powders at 750° in a high vacuum or in hydrogen does not result in any appreciable change of the activity characteristics of the surfaces of the powders.

These conclusions represent a picture of surface structures which deviates in some respects from the usual conception of "active surfaces" such as has been developed especially by H. S. Taylor and his collaborators.[7] Nevertheless, it seems not to be impossible that the tungsten powders used in our experiments represent actually exceptional systems. They have been prepared from tungstic oxides by reduction with hydrogen at temperatures (900 to 1200°) far below the temperature at which the atoms of metallic tungsten acquire a high enough mobility to arrange themselves into a more ideal lattice. It is conceivable that this method of preparation leads to a "frozen Maxwell equlibrium" of the newly formed tungsten atoms, and that the formation of a corresponding scale of active sites is well reproducible, even when powders of different particle sizes are prepared.

In order to decide whether the unusual variation of the differential heats of adsorption derived from our measurements is actually caused by an exceptional surface structure of the powders used as adsorbents, adsorption measurements ought to be made with the same powders after they have been subjected to a drastic heat treatment at temperatures high enough to attribute a certain mobility to the tungsten atoms, giving them a possibility to "smooth out" the surface irregularities. Such a treatment would result in an appreciable decrease of the total surface of the powders, and in a corresponding diminution of their adsorptive capacities per unit of weight. The main question, however, is whether the characteristics of the adsorption per unit of surface area, particularly whether the variation of the differential heats of adsorption with increasing surface covering would be considerably modified by such a treatment of the powders. As we had to interrupt our work, measurements of this kind could not be carried out. J. K. Roberts[8]

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[7] See, *e. g.*, the survey given by Hugh S. Taylor in "Twelfth Report of the Committee on Catalysis," 1940, J. Wiley & Sons, Inc., New York, N. Y., p. 41.

[8] See discussion in I.

found in his experiments with a tungsten wire as an adsorbent, a similar decrease of the differential heats of adsorption with increasing surface covering as found by us for the powders. This might indicate that the characteristic features of the hydrogen adsorption on tungsten do not depend on the surface characteristics of the metal specimen used as adsorbent. For a conclusive decision of this important question, it would be, however, preferable to use the same experimental method for adsorption measurements on tungsten surfaces prepared by different procedures.

An experimental decision on this point would be particularly desirable because there is also the possibility that the characteristic features of the hydrogen adsorption on tungsten, as they have been found in our experiments, are not caused by the heterogeneous nature of the surfaces of our powders, but that they represent a peculiarity inherent to the adsorption system hydrogen/tungsten, independently of any structural properties of the surfaces. In this case, the experiments suggested above would lead to the result that, even with "smoother" tungsten surfaces, the variations of the heats of adsorption with changes of the surface covering and of the temperature would remain practically identical with those observed on the original powder samples.

Several authors[9] have already proposed explanations for other adsorption systems in which the differential heats of adsorption decrease with increased concentration of the adsorbed molecules, by attributing this effect to repulsive forces between the adsorbed particles. According to these authors, these forces come into play whenever the average distance between the adsorbed molecules falls below a certain limit. An explanation of this kind is not sufficient to account for our experimental findings because, in our system, the decline of the heats of adsorption with increasing surface covering is most pronounced at the sparse coverings of a few per cent. of saturation, where the distances between the adsorbed particles are large, and diminishes with increasing covering. For this phenomenon, another explanation has to be offered.

It seems that the features of hydrogen adsorption on tungsten can be described adequately if it is assumed that the configurations of the adsorbed hydrogen molecules depend upon their concentration on the adsorbing surface. More specifically, this hypothesis postulates that the adsorbed hydrogen molecules exist in states ranging from that of a "normal" hydrogen molecule (corresponding to H_2 in the gas phase), over the states of an increasingly "stretched" configuration (with increased H–H distances, and correspondingly weaker binding forces between the atoms) to, finally, completely separated hydrogen atoms.[9a] This picture has the advantage of explaining better the transition from the "molecular" to the "atomic" adsorption, by assuming a gradual change from the one form of the adsorbed phase into the other. The "active surface hypothesis" has to accept the coexistence of the two forms of adsorption, without suggesting any explanation for this fact. The alternative assumption that the adsorbed hydrogen, depending upon its surface concentration, exists in states intermediate between the molecular and the atomic form offers, in addition, an approach to the question of what causes the high negative temperature coefficient of the heats of adsorption, above 529°. On the other side, it has to be emphasized that the explanation of the decrease of the heats of adsorption with the specific configurations of the adsorbed hydrogen molecules involves the unusual assumption that the forces which act on the particles of the adsorbed phase reach over considerably larger distances than do the forces between the same particles in a free state. This fact indicates that the *adsorbent surface participates in the spread of the forces between the adsorbed particles* by acting, in some way, as a "transmitter" of these forces. This conclusion is not new: the forces between adsorbed molecules and the adsorbing surfaces have been repeatedly attributed to the action of electric "image forces" which result from a local concentration of metal electrons, under the influence of the electric charge or the electric moment of the adsorbed particle.[9b] In a quantitative way, this idea has been worked out into a theory of the thermionic and photoelectric emission of electrons and of adsorbed ions and atoms such as K, Na, Cs and Th from tungsten surfaces.[10] According to this theory, strong electric fields are built up, opposite to the adsorbed atoms. It is only a short step from this picture to the assumption that similar fields of electrons are concentrated, within the metal surface, opposite to the adsorbed hydrogen atoms. The energy which is set free by the action of this "cloud of electrons" on the polarized or ionized hydrogen atoms, is, according to this hypothesis, equal to the heat of adsorption.

This picture is susceptible of a quantitative evaluation, if the following simple assumptions are made: In the metal surface, a limited number

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(9) Compare, *e. g.*, M. Polanyi, *Trans. Faraday Soc.*, **28**, 316 (1932); A. Magnus, *ibid.*, **28**, 386 (1932); J. K. Roberts, "Some Problems in Adsorption," Cambridge University Press, 1939.

(9a) In a similar form, this idea has been already expressed in connection with qualitative data on catalysts, by R. E. Burk, *J. Phys. Chem.*, **30**, 1134 (1926); **32**, 1601 (1928).

(9b) Compare, for similar considerations: J. E. Lennard Jones, *Trans. Faraday Soc.*, **28**, 333 (1932), and R. C. L. Bosworth (*J. Proc. Roy. Soc. N. S. Wales*, **74**, 538 (1941)). The latter author calculated theoretically the energy of interaction between an adsorbed H-atom and its "electrical image" in an ideal metal surface, to 15,200 cal./mole. See also: A. Frumkin, *Z. physik. Chem.*, **141A**, 141 (1929); **155**, 71 (1931); *Trans. Faraday Soc.*, **28**, 273 (1932).

(10) Z. A. Becker, *Trans. Am. Electrochem. Soc.*, **55**, 153 (1929); *Phys. Rev.*, **28**, 341 (1926); W. H. Brattain and J. A. Becker, *ibid.*, **43**, 428 (1933); I. Langmuir and I. B. Taylor, *ibid.*, **40**, 483 (1932). Further literature in: O. W. Richardson, "Emission of Electricity from Hot Bodies," Longmans, Green & Co., 2nd ed., 1921; and A. L. Reimann, "Thermionic Emission," J. Wiley & Sons, Inc., New York N. Y.. 1934

of electrons, k, is available to form "electron clouds," under the influence of the electrical image forces around each adsorbed hydrogen atom. At very low concentrations of the adsorbed atoms, the size of the individual clouds is determined only by the maximum amount of electrons which can be gathered in each cloud. Thus, the clouds are independent of each other, and the heats of adsorption remain constant, within this range. As soon, however, as the concentration of the adsorbed hydrogen atoms exceeds the critical value A_{crit} of 0.008 S (about 1 H per 125 W atoms), the individual clouds start to overlap each other. As a consequence of this overlapping or merging of adjacent electron clouds, a certain fraction β of the electrons within each cloud comes under the *simultaneous* influence of two neighboring adsorbed hydrogen atoms. These shared electrons, in a first step toward "molecule" formation, build up a loose "resonance" binding force between the two adjacent hydrogen atoms, and do thus not act any more as cloud electrons.

At concentrations of the adsorbed particles above A_{crit}, the number of electrons per cloud is equal to $k/2A$ per hydrogen atom. Thus, with the heat of adsorption Q being proportional to the number of cloud electrons, we get

$$\frac{-\mathrm{d}Q}{\mathrm{d}A} = c\beta k/2A \qquad (19)$$

which leads to

$$Q = C - \frac{k\beta}{2}\ln A$$

We see that this equation has the same form as our empirical equation (18).

Besides interpreting the transition from the purely atomic to the molecular adsorption, this picture of electrical, far-reaching adsorption forces explains, at least qualitatively, the high negative temperature coefficient of the heats of adsorption above the critical temperature of 802°K. = 529°C.

The sharp decline of the heats of adsorption with increasing temperature, above 802°K., indicates that within this temperature range the specific heat of the adsorption complex (hydrogen adsorbed on the tungsten surface), per mole of adsorbed hydrogen, is by far larger than the specific heats (per mole) of the two components tungsten and hydrogen in the separated state. The temperature coefficient of γ is illustrated by equation (16). Within the range of 802°K. to about 1050°K., the decrease of γ can also be expressed as

$$\gamma' = 24{,}900 - 133(T' - 802)^{0.86} \qquad (20)$$

with γ' being the value of γ at the temperature $T' > 802$°K. The temperature coefficient of γ' and of the adsorption heat Q is, in this range, consequently equal to

$$-\frac{\mathrm{d}\gamma'}{\mathrm{d}T'} = \frac{114}{(T' - 802)^{0.14}} = [C_{(\text{H absorbed on W})} - (C_{\text{H}_2} + C_{\text{W}})] \qquad (21)$$

As $(C_{\text{H}_2} + C_{\text{W}})$, the sum of the molar specific heat of hydrogen and of the atomic specific heat of tungsten, amounts to about 11 cal./degree, at these temperatures, the "specific heat of the adsorption complex" ranges, per mole of adsorbed hydrogen, from about 96 cal./degree at 810°K. to about 64 cal./degree, at 1050°K.

This abnormal high value leads to the following conclusion: A considerable number of "particles" belonging to the adsorbent possesses potential thermal degrees of freedom which do not come into action at temperatures below 802°K. They are, however, coupled with the adsorbed hydrogen in such a way that they start to take up thermal energy, above 802°K. As one degree of freedom corresponds to an energy uptake of roughly 1 cal./degree, the number of particles coupled with a single adsorbed hydrogen atom amounts to a value between 20 and 100, according as to whether 3 or 1 degrees of freedom are ascribed to each particle. The large number of the particles coupled with each adsorbed hydrogen atom seems to be related to the other conclusion drawn from the decline of the heats of adsorption with increasing surface covering, that the "sphere of influence" of each adsorbed hydrogen atom reaches over a relatively wide distance. The facts that the capacity of the particles responsible for the high specific heat of the adsorption complex to take up thermal energy starts suddenly at a certain temperature,[11] that this uptake involves the simultaneous action of an entire cluster of the particles, and that the binding forces between adjacent hydrogen atoms appear as soon as these clusters overlap each other, indicate that the particles are subjected to quantum rules. This makes it likely that they are identical with the "free" electrons of the tungsten surface. It has to be left to the theoretical physicists to decide to what extent this picture is compatible with the present theory of the behavior of electrons in metals, and in metal surfaces.

The quantitative study of the hydrogen adsorption on tungsten leads thus to a somewhat unusual picture of the mechanism of this adsorption system. This mechanism, however, will deserve a closer discussion only provided that the adsorption equilibria established between hydrogen and the tungsten powders used as adsorbents in our experiments will be found to exist for the system tungsten–hydrogen universally, independent of the special surface structure of the metal. Only when this latter question has been decided by further experiments in a positive sense, will it be proved that the new picture of a special adsorption system presented here has a solid foundation. In this case, some of our present views on the nature of surface forces as well as on the mechanism of heterogeneous catalytic processes might have to be revised in some points.

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[11] F. S. Goucher, *Phil. Mag.*, [5] **48**, 229 (1924), found that sudden changes occur in the thermal expansion coefficient and in the electrical resistance of tungsten, at about 580°.

Summary

1. The equilibria in the adsorption system hydrogen/outgassed tungsten powder, the measurement of which was described in a previous paper, are discussed, in relation to the general theories of the adsorption of gases on metallic surfaces.

2. It is shown that a theoretical derivation of the measured adsorption equilibria can be based on Langmuir's formula for adsorption isotherms with the modification that the latter formula has to be adapted to the rapid decrease of the differential heats of adsorption with increasing covering of the tungsten surface with adsorbed hydrogen.

3. A detailed discussion of the slopes of the experimental "logarithmic isotherms," in combination with the theory underlying Langmuir's formula, leads to the evaluation of the saturation value S of the adsorption (1 adsorbed hydrogen molecule per two tungsten atoms in the surface), and to the conclusion that the adsorbed hydrogen exists on the surface in form of atoms, at all surface coverings $<0.008\ S$, and as "molecules," at all surface coverings $>0.008\ S$.

4. Q, the differential heat of adsorption of the hydrogen molecules, decreases, at a given temperature, according to $Q = C - c \log A$ (A = adsorbed amount). It is further temperature independent, for a given surface covering, from low temperatures up to 529°; at temperatures above 529° a sharp decrease with increasing temperatures takes place.

5. These changes of the heats of adsorption with surface covering and temperature can be explained by either a very heterogeneous nature of at least 40% of the total surface of the tungsten powders (corresponding to a "frozen Maxwell equilibrium" of the surface tungsten atoms), or by the assumption that the adsorbed hydrogen molecules exist on the tungsten surface in different states, varying from a widely stretched configuration, at low concentrations of the adsorbed phase, to molecules with the normal H–H distance, at coverings close to saturation. The forces between two widely separated hydrogen atoms of the stretched adsorbed molecules are, according to this picture, due to the fact that clouds of electrons of the adsorbent metal participate as components of the adsorption complex hydrogen–tungsten. Whereas these clouds attract the hydrogen atoms as independent units, as long as the atoms are widely separated, they start to overlap each other as soon as the distance of the adsorbed hydrogen atoms falls below a certain value. The electrons of the overlapping clouds which are shared by two adjacent hydrogen atoms, act as binding electrons, bringing about a kind of molecular bond between the two hydrogen atoms. This hypothetical picture leads, under simple quantitative assumptions, to a variation of the heats of adsorption which is in agreement with the experiment, and seems to provide an explanation for the sharp drop of the heats of adsorption, at temperatures above 529°.

6. A decision in favor of this picture, against the explanation based on a heterogeneous nature of the tungsten surface, requires further experimental work with tungsten surfaces of widely different structures.

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Ionization Constants of Butylamine, Piperidine and Triethylamine in Methanol

BY JOHN R. SCHAEFGEN, MELVIN S. NEWMAN AND FRANK H. VERHOEK

The concentration ionization constants of butylamine, piperidine, and triethylamine in methanol were determined in connection with an investigation of the methanolysis of pseudo *l*-menthyl *l*-*o*-benzoylbenzoate.[1] The procedure used involved (a) the determination of the concentration ionization constants, K_A, of the conjugate acids of the amines by the method of Kolthoff and Guss,[2] using brom cresol purple as the indicator; and (b) a conversion of these values of K_A to the basic concentration ionization constants, K_B, by use of the ion product constant of methanol.

Procedure and Materials.—The protolysis equilibrium measured may be written

$$B + HIn^- \rightleftarrows BH^+ + In^-$$

where HIn^- represents the acid form of brom cresol purple and In^- the basic. The maximum absorption of the basic form in methanol occurs at 583 mμ.[3] Solutions of amine, amine salt, and indicator were mixed and the absorption of the resulting solution at 583 mμ was determined with a Beckmann Quartz Spectrophotometer. If the amine and amine salt solutions were mixed first and the indicator solution added, the absorption was found to decrease slowly with time. If the three solutions were mixed at the same time the absorption increased to a maximum in five to ten minutes and then decreased very slowly. The magnitude of this change in an experiment with 1.28×10^{-3} M butylamine and 5.67×10^{-3} M butylammonium ion was as follows: after 3.6, 5.6, 9.0, and 12.4 minutes the extinction was 1.271, 1.275, 1.267, 1.264. Values of the protolysis constant K, obtained by extrapolating to zero time, when the indicator was added after the amine buffer had come to equilibrium, and those values obtained by using the maxi-

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[1] Schaefgen, Newman and Verhoek, forthcoming publication in THIS JOURNAL.

[2] Kolthoff and Guss, THIS JOURNAL, **60**, 2516 (1938).

[3] The absorption maximum for the acid form occurs at 417 mμ; the isobestic point at 476.5 mμ. See Brode, "Chemical Spectroscopy," John Wiley and Sons, Inc., New York, N. Y., 2nd ed., 1943, p. 249.