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Physical adsorption of gases

II: Practical application of derived isotherms for monolayer and multilayer adsorption

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With 14 figures and 4 tables

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1. Introduction

In the preceding paper we showed that the process of monolayer adsorption can be represented by the equation

$$V = V_m \{1 - \exp(-ax)\} \quad [1]$$

and that of multilayer adsorption by

$$V = V_m \{1 - \exp(-ax)\} \exp(bx). \quad [2]$$

We determined also the physical meaning of a and b demonstrating some interesting features of these constants and isotherms. Evidently, the validity of the proposed equations can be estimated only when they are confronted with experimental data. In our case the possibilities of an experimental verification are varied. Apart from the fitting of experimental isotherms it is possible to calculate a and b and to compare the values thus-obtained with the expected ones, or to use experimentally found constants a and b to calculate τ_0 and δ_L whose values are known with a certain precision. Furthermore we can verify our relationships by plotting $\ln V$ versus x (this relation is explained in the next chapter), $\ln \tau$ versus $1/T$, and b versus $1/\sqrt{T}$; in all cases a straight-line dependence being expected.

Another question of importance is whether the proposed equations are capable of explaining all types of isotherms. It is generally considered that five types of isotherms exist, but in our opinion eight types (given in fig. 1) should be distinguished. Type I represents the well-known form of monolayer isotherm. Types II and III correspond to the BET isotherms for high and low C values, respectively, and their analogues for capillary condensation in porous adsorbents would be IV and V. Type VI was proposed by *Pierce and Smith* (1); it is characterized by two flexion points and a slow adsorption till relatively high pressures. These isotherms are obtained only when graphite or carbon are used as adsorbents. Type VII isotherm is known as "linear"; it is found for the

adsorption of oxygen, nitrogen, and argon on charcoal and silicagel. Finally, type VIII represents "stepwise" isotherms. It is assumed that the irregularities known as "steps" are caused by condensation phenomena.

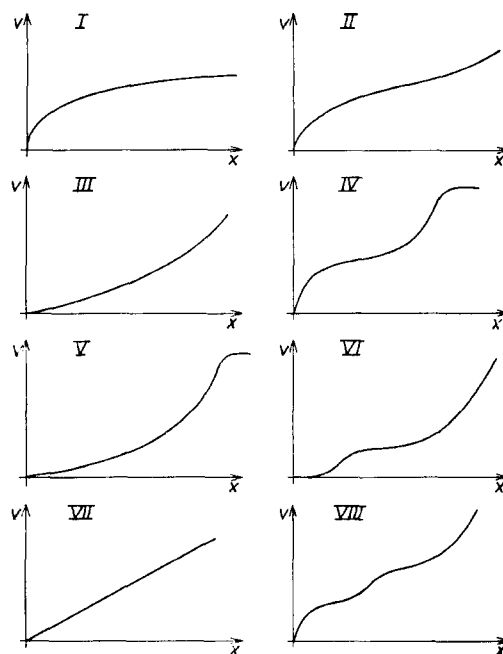


Fig. 1. Various types of isotherms

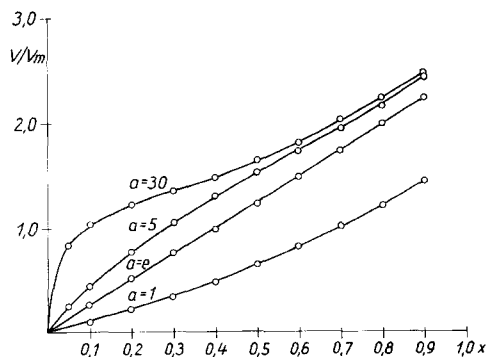


Fig. 2. Theoretical isotherms for $b = 1.0$ and different values of a

It is obvious that our equations which are not adapted to porous materials (where the number of layers is limited) cannot be applied to those adsorption processes where capillary-condensation phenomena are prevailing. Consequently, they are not capable of predicting the behavior of type IV and V isotherms. As concerns the other six types we are going to show that equation [2] can explain their form (with the exception of type VI where the process seems to be more complex). In fig. 2 the isotherm [2] is plotted versus x for some arbitrary cases. It is evident that certain familiar curves appear which will be discussed in the following chapters.

2. Type I and II isotherms

It should be emphasized, immediately, that the existence of adsorption monolayer is rather dubious and in the writer's opinion nearly impossible. The monolayer isotherm

$$V = V_m \{1 - \exp(-ax)\}$$

implies $b = 0$. From the equation derived for b in the preceding paper

$$b = \sigma \tau_{0(L)} \delta_L / \sqrt{2 \pi m k T}$$

and it is obvious that under normal conditions of adsorption b must have a definite value approaching zero only when T tends to very high values. This fact was confirmed by our investigations. Among the isotherms published up to now we could not find one that represented real monolayer adsorption.

While the very existence of monolayer-adsorption isotherms is questionable, type II isotherms are common and are frequently used to determine the surface area of powders. When examining the possibility of applying our equation to multilayer adsorption the very first impression is that the existence of three unknown factors V_m , a , and b represents a great difficulty in determining their values unequivocally. It should be admitted that the appearance of the third parameter does not simplify the problem but a closer examination reveals that in the case of type II isotherms the obtaining of V_m and b is greatly facilitated. The pronounced "knee-bends" observed with type II isotherms imply high a values (extending from 20–50) so that the term $1 - e^{-ax}$ becomes so close to one at relatively low pressures ($x \geq 0.25$) that it can be neglected. So, if $a = 20$ the error committed by neglecting e^{-ax} at $x = 0.25$ is less than one

percent. It shows that for $x > 0.25$ equation [2] can be rewritten as:

$$V = V_m \exp(bx). \quad [3]$$

Evidently, the latter equation must not be applied to type III and VI isotherms without a great precaution. In the pressure range where [3] is strictly valid

$$\ln V = \ln V_m + bx \quad [4]$$

which permits to determine unequivocally V_m and b . We shall see later that a great advantage of this treatment is the determination of adsorption parameters from the properties of higher adsorbed layers where the effects of surface heterogeneity are negligible. When V_m and b are known the constant a can be calculated from the plot $\ln(1 - Ve^{-bx}/V_m)^{-1}$ versus x , the slope being equal to a .

It should be noted that *Duncan* (2) showed that for high C values *Anderson's* equation (3) can be reduced to its simple form

$$x = \frac{1}{k} \left(1 - \frac{V_m}{V}\right) \quad [5]$$

or after a rearrangement

$$V = V_m \frac{1}{1 - kx} \quad [6]$$

starting from equation [3] it is easy to show that

$$V = V_m \exp(bx) = V_m \exp(-bx) = V_m \frac{1}{1 - bx} \quad [7]$$

and, evidently, *Duncan's* modification is analogous to [3] with intermolecular collisions neglected. *Duncan* found that k was close to 1 (which we are going to demonstrate for b) while the validity of expression [6] extended from $x = 0.25$ to $x = 0.75$ (that is exactly the region of applicability of our equation). As the lateral interaction forces are neglected at pressures exceeding 0.75 condensation phenomena cause certain deviations so that the derived equation does not hold.

It was rather difficult to find published data which could be used in a complete analysis of our equation. In spite of a great number of reported isotherms the choice was extremely restricted due to certain shortcomings in representing data, which can be summarized as follows:

- a) isotherms traced only in a limited range of pressure,
- b) poor precision in the region of low pressures,

- c) adsorbed volumes plotted as the fraction of monolayer volume that requires the replotting of isotherms,
 d) adsorption carried out at only one temperature.

Nevertheless, we succeeded in selecting three series of isotherms which turned out to be suitable for our analysis. The first series reported by *Arnold* (4) is nearly classical when treating adsorption from gas mixtures (the adsorption of nitrogen-oxygen mixtures on anatase), the second one belongs to *Davis* and *DeWitt* (5); it treats the adsorption of *n*-butane on glass spheres, and the third series of isotherms for *n*-decane on iron powder was reported by *Basford* et al (6).

The first series was used to verify the correctness of equation [3], while the results of *Davis* and *DeWitt* and *Basford* et al. permitted a more profound analysis.

The adsorption isotherms for oxygen and nitrogen on anatase were replotted as $\ln V$ versus x (figs. 3 and 4). From the

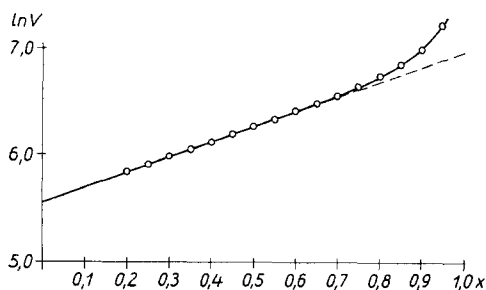


Fig. 3. Adsorption of nitrogen on anatase at 78 °K

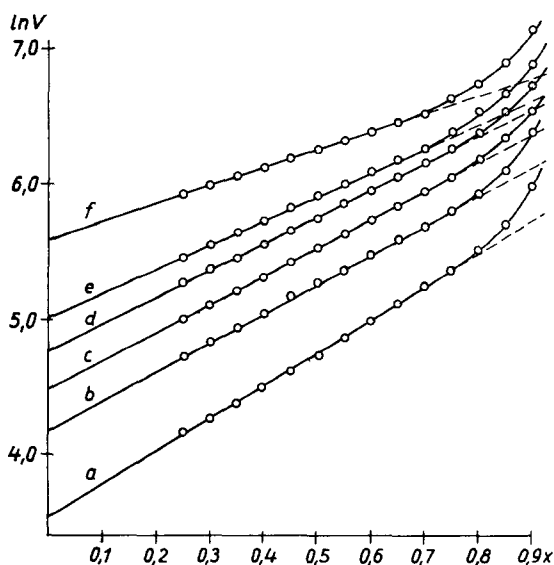


Fig. 4. Adsorption of nitrogen + oxygen mixtures on anatase: a) 15% O₂, b) 30% O₂, c) 50% O₂, d) 70% O₂, e) 85% O₂, and f) 100% O₂

plots it is evident that a straight-line dependence exists in the pressure range $x = 0.2$ to $x = 0.7$. At relative pressures higher than 0.7 the predicted values are lower than the experimental ones and this is in agreement with our model which cannot depict the condensation processes taking place when $x \rightarrow 1.0$.

In the first paper we showed that

$$b = \sigma \tau_L p_0 / \sqrt{2 \pi m k T}$$

so that it is possible to calculate τ_L when b is known. As the p_0 values are given for each gas mixture we obtained a series of average settling times corresponding to different percentages of oxygen. These values are presented in table 1.

Table 1. Calculated values of constants b and average settling time τ_L for the adsorption of nitrogen-oxygen mixtures on anatase

Percentage of oxygen	b	τ_L (sec)
0	1.36	$1.40 \cdot 10^{-9}$
15	2.44	$0.77 \cdot 10^{-8}$
30	2.18	$0.97 \cdot 10^{-8}$
50	2.08	$1.40 \cdot 10^{-8}$
70	1.98	$1.70 \cdot 10^{-8}$
85	1.80	$1.60 \cdot 10^{-8}$
100	1.32	$1.60 \cdot 10^{-8}$

The average settling times are in the range of expected values but (with the exception of values for pure gases) they should be taken with precaution as a preliminary analysis of adsorption from gas mixtures is indispensable in order to interpret the results presented here.

The isotherms of *Davis* and *DeWitt* obtained at three different temperatures (195, 225, and 273 °K) were more suitable for our analysis. In fig. 5 the plots $\ln V$ versus x are given. They result in a series of straight lines which determine the following b values: $b_{195^\circ\text{K}} = 1.70$, $b_{225^\circ\text{K}} = 1.60$, $b_{273^\circ\text{K}} = 1.60$, so that the corresponding values of τ_L and V_m can be calculated; they are given in table 2.

Table 2. Calculated values of b , τ_L , and V_m for the adsorption of *n*-butane on glass spheres

	Temperature (°K)		
	195	225	273
b	1.70	1.60	1.60
τ_L (sec)	$1.62 \cdot 10^{-7}$	$1.87 \cdot 10^{-8}$	$2.21 \cdot 10^{-9}$
V_m (cm ³)	0.30	0.29	0.27

The monolayer volumes found are lower than the BET value (0.39 cm³) and they show a less pronounced decrease with tem-

perature which we shall find with all systems investigated.

The calculated τ_L values were plotted as $\ln \tau_L$ versus $1/T$ (fig. 5) which permitted to determine $\tau_{0(L)}$ to be $\sim 10^{-13}$ sec and $Q_L = 5.3$ kcal/mole. These values are expected as the time of molecular fluctuations,

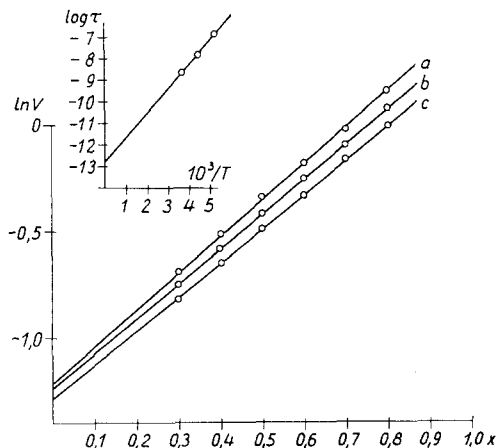


Fig. 5. Adsorption of *n*-butane on glass spheres at a) 195 °K, b) 225 °K and c) 273 °K ($\tau_{0(L)} \sim 10^{-13}$ sec $Q_L = 5.3$ kcal/mole)

that should be very close to $\tau_{0(L)}$, is 10^{-13} sec while Q_L approaches the heat of liquefaction of butane. It is not quite clear whether $\tau_{0(L)}$ is really independent of temperature and always close to 10^{-13} sec. According to *De Boer* (7) this value of $\tau_{0(L)}$ is characteristic only in the case of the supermobile adsorption, while for a two-dimensional gas $\tau_{0(L)} = h/kT$ and consequently $b = K/T^{3/2}$. Such a pronounced dependance of b on temperature we have not observed. Nevertheless, this interesting question cannot be considered as resolved. The next step in the analysis was

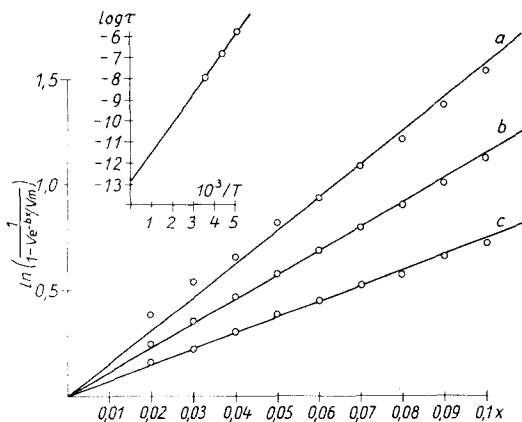


Fig. 6. Adsorption of *n*-butane on glass spheres at a) 195 °K, b) 225 °K and c) 273 °K ($\tau_0 \sim 10^{-13}$ sec $Q_a = 6.4$ kcal/mole)

to trace the $\ln(1 - Ve^{-bx}/V_m)^{-1}$ versus x plots (fig. 6) in order to determine a . These plots show observable deviations whose origin may be ascribed to two different phenomena: a) as a is not sufficiently high (see table 3) the initial part of the curve $\ln V$ versus x is slightly lowered, which combined with slightly pronounced effect of condensation at higher pressures can increase the slope giving the wrong impression of a perfect linearity. When plotting $\ln V$ versus x this represents a permanent risk that should not be underestimated and b) due to the surface heterogeneity a varies with the degree of the first-layer completion. We believe that in this case we are confronted with both the problems so that the results found should be accepted with a certain precaution.

Table 3. Calculated values of τ and a for the adsorption of *n*-butane on glass spheres

	Temperature (°K)		
	195	225	273
a	15.9	11.2	7.4
τ (sec)	$1.5 \cdot 10^{-6}$	$1.3 \cdot 10^{-7}$	$1.0 \cdot 10^{-8}$

When $\ln \tau$ is plotted versus $1/T$ a straight-line dependence is obtained as in the preceding case. From the intercept on the ordinate τ_0 is found to be $\sim 10^{-13}$ sec and $Q_a = 6.4$ kcal/mole. The difference $Q_a - Q_L$ is 1.1 kcal/mole while *Davis* and *De Witt* report (when applying three different methods of calculation) 0.9, 1.0, and 1.1 kcal/mole. It is interesting to note that all these values are lower than the experimental ones (2.0 kcal/mole at low coverages the 1.1 kcal/mole value being approached only at high degrees of coverage in the first layer). It shows that the observed inconsistencies of the BET equation, when adsorption heats and entropies are concerned, are not due to the disregard of intermolecular collisions but, probably to the role of surface heterogeneity.

When deriving our multilayer isotherm in the first paper we stated that b can be estimated with a good precision. Actually, if we assume $A \sim \epsilon_L$

$$b = \sigma \tau_{0(L)} \delta_L / \sqrt{2 \pi m k T} \quad [8]$$

and in the case $A = \epsilon_L - \frac{1}{2} kT$ the above expression should be multiplied by $e^{1/2}$. The corresponding values of b found for nitrogen are $b_{A \sim \epsilon_L} = 3.0$ and $b_{A = \epsilon_L - kT/2} = 4.7$, when the following values are applied: $\sigma = 18.6 \text{ \AA}^2$ (in the chapter devoted to

condensation phenomena we shall see that this molecular area seems to be more reliable than 16.2 Å² the molecular area of liquidlike adsorbate),

$$\tau_{0(L)} = 10^{-13} \text{ sec}, \delta_L = 2.8 \cdot 10^{10} \text{ erg/cm}^2, \text{ and } T = 78^\circ \text{K}.$$

The actual value of b is found to be 1.20 at 78 °K and quasi-independent of the adsorbent properties. The departure from the experimental value is caused, probably, by the fact that $\tau_{0(L)}$ is only approximately 10^{-13} sec and also by the uncertainty in the correlation between Λ and ε_L . In any case all these values are too high to enable the derivation of a BET-type equation.

When $\ln(V/V_m)$ is plotted versus x , curves obtained when adsorbing at one definite temperature one and the same adsorbate on different adsorbents should coincide as b is independent of the adsorbent properties.

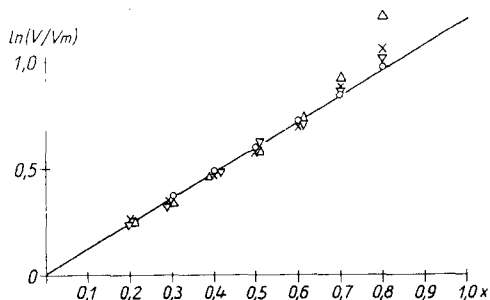


Fig. 7. Adsorption of nitrogen on — 0 egg albumin — Δ collagen — * KCl — ∇ anatase (at 78 °K)

Taking into consideration that nitrogen is still the most frequently used adsorbate we consider it useful to present its characteristic plot (fig. 7). The latter is based on isotherms obtained at 78 °K with quite different adsorbents as egg albumin (8), collagen (9), KCl (10), and anatase (11). The last isotherm (N_2/TiO_2) reported by *Harkins* and *Jura* is very precise; it gives a perfect linearity in the pressure range 0.2–0.7 and the found b value 1.20 is identical to the average one calculated from the characteristic plot. The

Table 4. Calculated $\ln(V/V_m)$ values for the adsorption of nitrogen on various adsorbents at 78 °K

x	anatase	KCl	Egg albumin	Collagen
0.2	0.24	0.25	—	0.25
0.3	0.36	0.36	0.36	0.37
0.4	0.48	0.47	0.47	0.49
0.5	0.60	0.60	0.59	0.61
0.6	0.72	0.73	0.71	0.76
0.7	0.85	0.88	0.84	0.92
0.8	1.00	1.05	0.98	1.21

logarithms of the V/V_m ratio for different adsorbents are presented in the table 4.

When examining the adsorption process in the multilayer region and after the completion of the first layer it is found that a very simple adsorption isostere can be obtained if the isosteric values are determined not for $V = \text{constant}$ but for $V/V_m = \text{constant}$. The latter represents a measure of precaution in the case where $V_m = f(T)$. Actually, we cannot ascertain this dependence, but experimental results seem to indicate a slight temperature dependence of V_m . From

$$V/V_m = \text{constant} = \exp(bx) \quad [9]$$

it follows

$$\sigma \tau_{0(L)} \exp(\varepsilon_L/kT) p/\sqrt{2\pi m kT} = \text{constant} \quad [10]$$

and

$$p = \frac{KT^{1/2} \exp(-\varepsilon_L/kT)}{\sigma \tau_{0(L)}} \quad [11]$$

the last equation representing our adsorption isostere after the completion of the first layer. When substituting p from the *Clausius-Clapeyron* equation

$$\frac{d(\ln p)}{d(1/T)} = -\frac{q_{st}}{k} \quad [12]$$

by the right-side term from the equation [11] we obtain

$$q_{st} = \varepsilon_L + \frac{1}{2} kT + K \frac{d \ln(\sigma \tau_{0(L)})}{d(1/T)}. \quad [13]$$

If σ and $\tau_{0(L)}$ are temperature independent the isosteric heat of adsorption is equal to the adsorption potential increased by $kT/2$ that points to a two-dimensional gas which has lost one degree of freedom. As $\tau_{0(L)}$ is usually associated with the entropy of translation and the activation energy for the hopping movement it should be dependent on temperature thus contributing to q_{st} . In this way q_{st} should be dependent also on the degree of localization of admolecules. As concerns the exact role of σ it is not quite clear at present.

To check the derived relationship $b = \lambda/T^{1/2}$ the data reported by *Basford* et al. for the adsorption of *n*-decane on iron powder at five temperatures (343, 353, 363, 373, and 398 °K) were replotted as $\ln V$ versus x . The chosen temperatures are relatively high and too close to each other, but it was possible to demonstrate the validity of derived expression $b = \lambda/T^{1/2}$. From the slope of $\ln V$ versus x plots (fig. 8) the b values were determined to be 1.63, 1.60,

1.57, 1.55, and 1.50 at 343, 353, 363, 373, and 398 °K, respectively. It is characteristic that even in this case the results point to $b = K/T^{1/2}$ and not to $b = K/T^{3/2}$. When the b values thus obtained are plotted versus $1/T^{1/2}$ a linear relationship is found. From the slope λ is determined to be ~ 32 while the calculated value from the equation for b is ~ 30 . As in the preceding case V_m is a variable magnitude dependent on temperature. The V_m versus T plot (fig. 8)

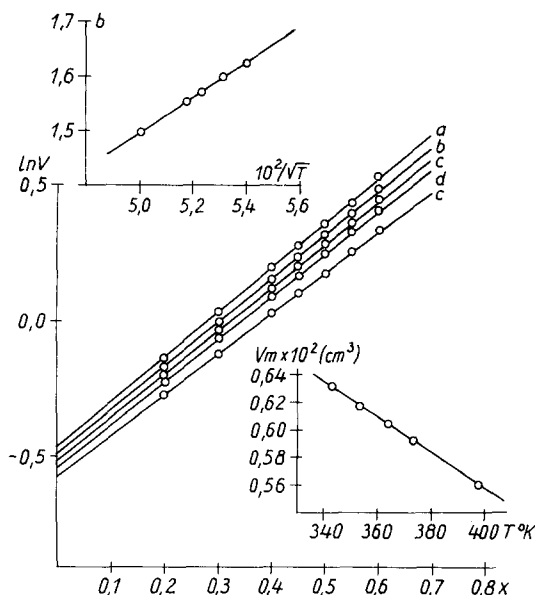


Fig. 8. Adsorption of *n*-decane on iron powder $a = 343$ °K, $b = 353$ °K, $c = 363$ °K, $d = 373$ °K, and $e = 398$ °K

might indicate a straight-line dependence but due to a relatively narrow range of temperature we cannot assert this linearity though the decrease in V_m with temperature is evident.

3. Type III isotherms

The treatment of type III isotherms is much more complex and cumbersome for a routine analysis. We are going to present results of our investigations on nearly classical isotherms of *Cameron* and *Reyerson* (12) for the adsorption of Br on silica gel. These data were replotted by *Pierce* and *Smith* (1) and we used the values thus obtained. The plot $\ln V$ versus x is given in fig. 9. It is evident that only one portion of the curve (at higher pressures) is quasi-linear. It shows that a direct application of our simplified isotherm [3] is not permissible. The constant b can be assessed in the fol-

lowing way. If two points are chosen on the isotherm

$$\ln (V_1/V_2) - b (x_1 - x_2) = \ln \frac{1 - \exp(-a x_1)}{1 - \exp(-a x_2)}$$

as a is not large (this being the presumed condition to have a type III isotherm) and if the chosen relative pressures are very small $1 - \exp(-ax) \sim ax$ so that

$$b \sim \ln \left\{ \frac{V_1 x_2}{V_2 x_1} \right\} / (x_1 - x_2). \quad [14]$$

The last equation when applied to the data of *Cameron* and *Reyerson* for $x_1 = 0.075$ and $x_2 = 0.050$ gives $b = 4.40$. As the slope of the quasi-linear portion is 4.84 we see that the possible error still rests within tolerable limits. As the equation [14] shows a tendency to lower b values 4.84 was adopted as the

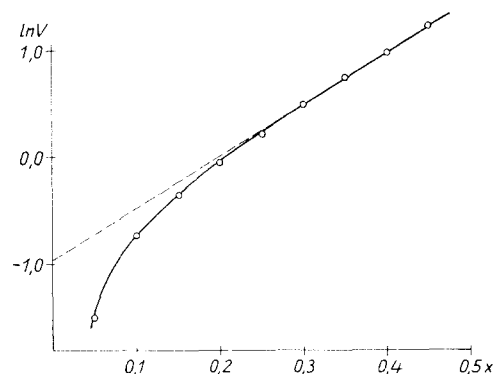


Fig. 9. Adsorption of bromine on silica gel

better value and a calculated to be 13, 13, 11, 11, and 8 at 0.1, 0.15, 0.20, 0.30, and 0.40, respectively. After a progressive correction of a and b the most probable values were found to be $a = 11$ and $b = 4.73$. By applying these two values V_m was determined to be 0.41, 0.45, 0.41, 0.41, and 0.41 cm^3 at $x = 0.05, 0.10, 0.20, 0.30,$ and 0.40 , respectively. From the intercept on the ordinate $V_m = 0.38 \text{ cm}^3$. Our monolayer volumes are quite different in comparison with those predicted by the BET theory. According to the latter for type III isotherms

$$V = V_m x / (1 - x) \quad [15]$$

so that $V_{(x=0.5)} = V_m$ and in this case $V_{m(\text{BET})} \sim 4.24 \text{ cm}^3$. Actually the proposed equation [15] is nothing else but a disguised form of our isotherm [2] with neglected intermolecular collisions

$$V = V_m (1 - e^{-ax}) / e^{-bx} \sim V_m a x / (1 - b x) = V_m x / (1 - x) \quad [16]$$

when $a = b = 1$. As it was shown in the preceding paper the BET constant C_{BET} is analogous to our $C = a/b$ so that the BET assumption (for type III isotherms) $C_{\text{BET}} = 1$ implies $a = b$ and as the very derivation of the BET equation is based on $b = 1$ it follows automatically that $a = b = 1$.

Our analysis does not confirm the BET assumption $C_{\text{BET}} = 1$ as the actual ratio $a/b = 2.34$ and as $x_f = (2/a) \ln(C - 1)$ this isotherm should possess the flexion point at $x \sim 0.075$. If one examines, carefully, the replotted data of *Cameron* and *Reyerson* it is evident that the curve shows a diminutive but still observable concavity in its initial portion. This concavity terminates between $x = 0.05$ and $x = 0.10$ when the isotherm becomes convex.

The same treatment was applied to an adsorption isotherm reported by *Pearce* and *Smith* (13) for NH_3 on graphite NC-1. It represents the case of an extremely weak adsorption. After a profound analysis the most probable values of a and b are found to be 9.3 and 4.5, respectively, so that $C = 2.06$. It is not quite clear whether adsorption is possible when $C < 2$.

4. Type VI and VII isotherms

Two isotherms belonging to type VI were examined. One for the adsorption of H_2O on Mogul carbon black, reported by *Emmett* and *Anderson* (14) and the other for the adsorption of CH_3OH on graphite NC-1 reported by *Smith* and *Pierce* (1). Both isotherms are characterized by an initial convex portion of the curve which becomes concave at medium pressures and regains its convexity when $x \rightarrow 1.0$. It should be stressed that these isotherms are rare and known only for carbon and graphite adsorbents. *Pierce* and *Smith* showed that they cannot be represented by the BET isotherm while obeying an empirical equation

$$V = V_0 + Ax/(1 - Bx). \quad [17]$$

The first isotherm (H_2O /Mogul carbon black) was replotted as $\ln V$ versus x (fig. 10) both for original samples and those degassed at 1000° . The plots are characterized by a relatively abrupt change in the b value so that two linear portions result. The intercepts on the ordinate give two different monolayer volumes for each isotherm, one corresponding to a small but very active surface area and the other that should be related to a large but less active portion of the surface. For

non-degassed samples the surface of the active portion is $\sim 30 \text{ m}^2/\text{g}$; after heating the active portion is nearly negligible and the total surface area is substantially reduced. The constant b is approximately 9 and 0.7 and 13 and 1.4 for the original and degassed samples, respectively. The same results were found for the adsorption of CH_3OH on graphite. Two linear portions can be distinguished which indicate again that a small part of the surface possesses strong adsorption forces (1/50 and 1/100 of the total surface area at 0° and 29°C , respectively).

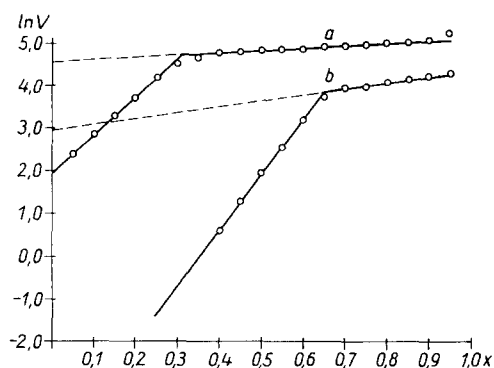


Fig. 10. Adsorption of water on Mogul carbon black - a) original sample - b) sample degassed at 1000°

It is interesting to note that according to *Young* et al. (15) the surface of graphon, a highly graphitized carbon, would contain a small area of hydrophilic sites (1/1500 of the total surface) which might be an oxygen surface complex, while the rest of the surface is hydrophobic and homogeneous. In our case the area of presumed hydrophilic sites significantly higher but it is normal to expect that this area will be smaller with highly graphitized and "oxygen free" graphon. Nevertheless, there are two phenomena which look rather peculiar. The first peculiarity is the fact that the beginning of the second portion marks, at the same time, the end of the rapid adsorption process (this transition is very sharp). It is possible that the slow process exists in the whole range of pressure it being not detectable at lower pressures due to the rapid adsorption. If we accept the existence of hydrophilic sites with strong adsorption forces it is not quite clear why the process terminates so abruptly. Even, more curious are relatively high values which we must attribute to b belonging to the first portion of our $\ln V$ versus x plots. In the writer's opinion a plausible explanation might be given by a recent paper by *Harris* et al. (16). They showed that under certain

conditions graphite adsorbents could be slightly delaminated the resulting separations between the graphite layers being smaller than 10 Å. The heat of adsorption in such crevices must be substantially higher than that on the bare surface. If the appearance of these crevices is common to graphite adsorbents this might explain both a small surface area of these "active sites", the abrupt termination of the adsorption process on these sites, and the observed high values of b .

As concerns type VII isotherms known as linear according to fig. 2 it seems that they represent nothing else but a special case when $a \sim e$ and $b \sim 1.0$. Evidently, their linearity is only apparent as it was emphasized by Young and Crowell in their monograph (17) so that they do not merit a special attention.

5. Condensation phenomena and type VIII isotherms

There exist isotherms which cannot be classified in either of the previously mentioned groups. They possess certain irregularities known as "steps" presumably due to condensation phenomena. When examining in the first paper the constant b we showed that it was independent of the attractive potential between molecules in the higher layer. Consequently, condensation processes should not affect its value, the slope of $\ln V$ versus x plots, and the way of building up molecular piles. On the contrary, as during condensation a certain contraction of the layer must take place, it should give the impression of an "increasing surface area". It is interesting to see whether experimental results confirm our hypotheses.

The first example is the adsorption of Ar on BN reported by Pierotti (18) and carried out at 76 °K. From the plot $\ln V$ versus x (fig. 11) it is evident that two linear portions exist. One at $x = 0.2-0.35$ and the other at $x = 0.50-0.65$. The BET monolayer volume is 5.30 cm^3 while we find from the first linear portion $V_m = 5.05 \text{ cm}^3$ and from other $V_m' = 5.50 \text{ cm}^3$. From the plot $\ln(1 - Ve^{-bx}/V_m)^{-1}$ versus x a is assessed to be ~ 38 (it should be noted that at $x < 0.075$ the points do not fit the straight line passing through the origin, as it should be expected, as the a values are higher). Nevertheless, even 38 represents a relatively high value which might explain the

enhanced condensation at $x = 0.35-0.50$. Before and after condensation b has the same value 1.20 and the observed change in the slope between $x = 0.35$ and $x = 0.50$ should be entirely ascribed to the contraction in the first layer.

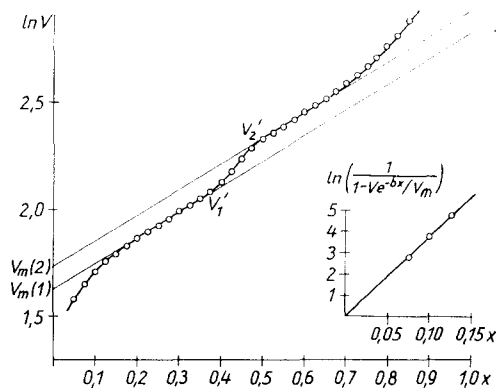


Fig. 11. Adsorption of argon on BN at 76 °K ($V_{\text{BET}} = 5.30 \text{ cm}^3$, $V_m = 5.05 \text{ cm}^3$, $a = 38$, $b = 1.20$)

The other example is, even, more convincing (fig. 12). It represents the adsorption of nitrogen on BN (18). In this case three linear portions exist at $x = 0.1-0.2$, $x = 0.35-0.55$, and $x = 0.67-0.72$. The corresponding "monolayer volumes" obtained by extrapolating each linear portion are $V_{m(1)} = 5.26 \text{ cm}^3$, $V_{m(2)} = 6.05 \text{ cm}^3$, and $V_{m(3)} = 6.70 \text{ cm}^3$.

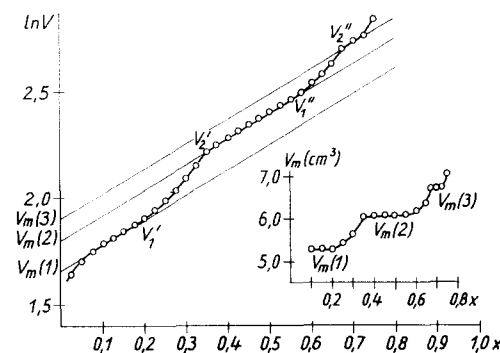


Fig. 12. Adsorption of nitrogen on BN ($b = 1.20$)

If we assume that the first step corresponds to the first-layer condensation (it is quasi-impossible to attribute this phenomenon to the second-layer contraction) it is obvious that $V_{m(1)}$, that is usually found from the $\ln V$ versus x plots and practically identical to the BET monolayer volume, represents the maximum volume of compressed gas which can be accommodated on the given surface at a definite temperature before condensation and not the volume of liquidlike

adsorbate. As it cannot be attributed to the liquid state all calculations of the surface area based on the molecular area of liquidlike adsorbate should be considered as erroneous.

If the first step reflects condensation in the first layer $V_{m(2)}$ might be associated with the monolayer volume of liquidlike adsorbate. Naturally, it is not quite certain whether the first layer after condensation corresponds exactly to the presumed liquid state due to strong attractive forces on the adsorbent surface. Nevertheless, this value is certainly closer to the monolayer volume of liquidlike adsorbate than $V_{m(1)}$.

Such an interpretation of experimental results can be verified. If our assumptions are correct the observed increase in volume during the first step $V_2' - V_1'$ should be equal to the resulting piling-up of ad-molecules on the surface corresponding to

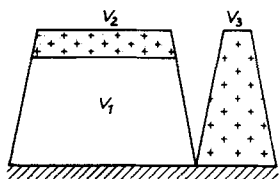


Fig. 13. Building up of the molecular pyramid

$V_{m(1)}$ + the molecular pyramid on the newly covered surface corresponding to $\Delta V_m = V_{m(1)} - V_{m(2)}$. From fig. 13 it follows that $V_2' - V_1' = V_2 + V_3$. For the adsorption of Ar on BN the experimental values are $V_{m(1)} = 5.05 \text{ cm}^3$, $V_{m(2)} = 5.46 \text{ cm}^3$, $V_2'(x=0.475) = 9.80 \text{ cm}^3$, $V_1'(x=0.375) = 8.06 \text{ cm}^3$, and $b = 1.20$. So $V_2' - V_1' = 1.74 \text{ cm}^3$ while

$$V_2 + V_3 = V_{m(1)} \{e^{1.2 \cdot 0.475} - e^{1.2 \cdot 0.375}\} + \Delta V_m e^{1.2 \cdot 0.475} = 1.73 \text{ cm}^3$$

so that the presumed relationship is completely satisfied. In the case of nitrogen adsorption on BN $b = 1.20$, $V_{m(1)} = 5.26 \text{ cm}^3$, $V_{m(2)} = 6.05 \text{ cm}^3$, $V_{m(3)} = 6.70 \text{ cm}^3$, and for the first step $V_2'(x=0.35) = 9.20 \text{ cm}^3$ and $V_1'(x=0.2) = 6.70 \text{ cm}^3$ so that $V_2' - V_1' = 2.50 \text{ cm}^3$

$$V_2 + V_3 = 5.26 \{e^{1.2 \cdot 0.35} - e^{1.2 \cdot 0.2}\} + 0.79 e^{1.2 \cdot 0.35} = 2.53 \text{ cm}^3.$$

As concerns the second step it should be realized that the surface available to adsorption is both before and after the step the same. The observed increase in volume $V_{m(3)} - V_{m(2)} = 0.65$ corresponds to the fictive creation of a new molecular pyramid which can be separated from the initial one. The found values are $V_2'' = 14.90 \text{ cm}^3$ and $V_1'' = 12.00 \text{ cm}^3$ so that $V_2'' - V_1'' = 2.90 \text{ cm}^3$

$$V_2 + V_3 = 6.05 \{e^{1.2 \cdot 0.675} - e^{1.2 \cdot 0.575}\} + 0.65 e^{1.2 \cdot 0.675} = 2.99 \text{ cm}^3.$$

By assuming that the first layer is in the liquid state after condensation it is possible to calculate the molecular area of nitrogen σ which according to the derived theory is identical to our cross-section of interaction. It is not difficult to show that $\sigma_L n_L = \sigma n$, where n and n_L are the number of accommodated ad-molecules on the same surface before and after condensation. As

$$n_L = V_{m(2)} N / V_M \quad n = V_{m(1)} N / V_M$$

where V_M is the molar volume and N the Avogadro number. It follows

$$\sigma_L V_{m(2)} = \sigma V_{m(1)}.$$

If we accept the commonly used molecular area of liquid nitrogen 16.2 \AA^2 it is not difficult to show that $\sigma = 18.6 \text{ \AA}^2$. This value is in agreement with our hypothesis in the first paper that the molecular area should be slightly higher than $\pi D^2/2$ due to the existence of a sphere of attraction around each molecule. It is interesting to note that in a recently published paper *Pierce and Ewing* (19) came to the same conclusion on the basis of their results for the localized adsorption of benzene on a graphite surface. The proposed value is 19.4 \AA^2 slightly higher than that based on our calculations. But it should be emphasized that *Pierce and Ewing* use the point *B* estimate to determine the monolayer volume of adsorbed benzene. As we showed in the first paper the monolayer volume thus determined is always slightly higher than the real V_m . If it had been possible to calculate the exact monolayer volume it is highly probable that the proposed values would be closer. On the other hand it is not excluded that the density of the condensed nitrogen layer is slightly higher than that of liquidlike adsorbate due to strong attractive forces of BN so that our proposed area 18.6 \AA^2 is a little lower in comparison with the real value. Anyhow we concur the conclusion of *Pierce and Ewing* that the actual molecular area of nitrogen is

closer to 19 Å² than to 16 Å² as it has been considered.

6. Discussion

It is very difficult to draw some definite conclusions when introducing a new theory that is frequently in contradiction with some generally-accepted ideas and based on experimental results which we consider, in spite of an apparent agreement with the theory, insufficient. Therefore we shall limit our discussion to a few questions of special interest.

The general form of our multilayer isotherm is given by

$$V = V_m \{1 - \exp(-ax)\} \exp(bx) \quad [18]$$

and it corresponds to the model of mobile layers without lateral interaction. We saw that this model worked rather well in the pressure range $x = 0.2-0.7$. A further generalization of the equation to include the surface-heterogeneity and condensation phenomena should lead to a more general form

$$V = V_{m(x,T)} \{1 - \exp[-a_{(x,T)}x]\} \exp[b_{(T)}x] \quad [19]$$

where the second-term constant $a_{(x,T)}$ should reflect the surface heterogeneity phenomena which practically disappear with the completion of the first layer and $V_{m(x,T)}$ the effect of lateral forces on the condensation process in the layers. The third term seems to be correct so that no further improvements are necessary. Future efforts should be made in this direction.

As concerns the monolayer volume V_m there is a strong evidence that this magnitude cannot be considered as independent of temperature and pressure. Nevertheless, we believe that at lower pressures preceding the condensation process V_m may be considered as nearly constant when the range of applied temperatures is not so extended.

According to the kinetic theory of gases σ is temperature dependent as well, but it is highly probable that small variations in temperature are not capable of influencing its value significantly. As the range of temperatures applicable to the adsorption of one adsorbate is usually limited to 50–100° σ might appear as a quasi-constant value.

The most intriguing problem is related to the settling time τ and especially to τ_0 . If we were able to obtain the exact values of τ_0 the degree of localization of admolecules and their behavior might be better understood. It could be used, also, for determining σ with

a good precision from the constant b values. The earlier presented experimental results seem to indicate a total independence of τ_0 on temperature leading in all cases to values close to 10⁻¹³ sec. This is in contradiction with the conclusion of *De Boer* (7) that $\tau_0 = 10^{-13}$ sec represents only a special case of the "supermobile" adsorption.

We shall apply the *De Boer* treatment which he used to derive an expression for τ_0 . It should be emphasized that the derivation is unimpaired by the fact that it is based on the *Langmuir* model. As the *Langmuir* isotherm represents nothing else but a degenerated form of our monolayer equation obtained by the substitution of e^{ax} by $1 + ax$, the constant a from the *Langmuir* isotherm is identical with our constant a . Consequently, τ_0 as derived from the *Langmuir* constant a must be necessarily the same if a figures in the exponential expression. *De Boer* considers that the adsorbate loses one degree of freedom during the adsorption and behaves as a two-dimensional gas which leads to

$$\tau_0 = \frac{h}{kT} f_z \frac{f_{tr}^a}{f_{tr-j}^a} \frac{f_{rot}^a}{f_{rot}^g}, \quad [20]$$

where f_z is the partition function of the vibration of the adsorbed molecules perpendicular to the surface, f_{tr}^a and f_{tr-j}^a are the partition function of the hindered and free two-dimensional translation, respectively, and f_{rot}^a and f_{rot}^g the partition function of the rotation of adsorbed and free gas molecules, respectively. If we introduce [20] into [13] considering that σ is quasi-independent of temperature

$$q_{st} = \epsilon_L + \frac{1}{2} kT + k \frac{d}{d(1/T)} \left\{ \frac{h}{kT} f_z \frac{f_{tr}^a}{f_{tr-j}^a} \frac{f_{rot}^a}{f_{rot}^g} \right\}. \quad [21]$$

It is quite common to consider the perpendicular vibrations of admolecules as simple harmonic oscillations so that

$$f_z = 1/(1 - e^{-h\nu/kT})$$

and

$$q_{st} = \epsilon_L + \frac{3}{2} kT - \frac{h\nu}{e^{h\nu/kT} - 1} + k \frac{d}{d(1/T)} \left\{ \frac{f_{tr}^a}{f_{tr-j}^a} \frac{f_{rot}^a}{f_{rot}^g} \right\}. \quad [22]$$

The approximation $h\nu \ll kT$ is frequently used for adsorbed molecules which leads to

$$\tau_0 = \frac{1}{\nu} \frac{f_{tr}^a}{f_{tr-j}^a} \frac{f_{rot}^a}{f_{rot}^g} \quad [23]$$

and

$$q_{st} = \varepsilon_L + \frac{1}{2} kT + k \frac{d}{d(1/T)} \left\{ \frac{f_{tr}^a}{f_{tr-f}^a} \frac{f_{rot}^a}{f_{rot}^a} \right\}. \quad [24]$$

The last two equations show that in the case of a two-dimensional gas, when the translatory motion and rotation of adsorbed molecules are not seriously hindered so that $f_{tr}^a = f_{tr-f}^a$ and $f_{rot}^a = f_{rot}^a$,

$$\tau_0 = 1/\nu$$

and

$$q_{st} = \varepsilon_L + \frac{1}{2} kT.$$

It is possible to show that τ_0 varies with temperature but slightly when $h\nu \sim kT$, so that it may be considered as nearly constant. So, if we accept $\nu = 10^{13} \text{ sec}^{-1}$ the following values are found for τ_0 : 2.1, 2.4, and $2.7 \cdot 10^{-13} \text{ sec}$ at 273, 225, and 105 °K, which explains the observed constancy of τ_0 for the adsorption of *n*-butane. At very low temperatures when the lateral displacement of admolecules is substantially hindered by the existing energy barrier the whole problem becomes more complex.

It seems that there is no reason to consider τ_0 and $\tau_{0(L)}$ as two different magnitudes (that is also confirmed by the analysis of the *n*-butane adsorption data), so that our a/b ratio given in the first paper [27] becomes

$$a/b = \exp \{ (\varepsilon_a - \varepsilon_L) / kT \}. \quad [27]$$

A good agreement between the experimentally determined a/b ratios and the calculated ones is found for the adsorption of *n*-butane when the $\varepsilon_a - \varepsilon_L$ value proposed by Davis and DeWitt 0.9 kcal/mole is applied. Our value 1.1 kcal/mole is too high; as the values of a and b are not so precise the found agreement should be considered as satisfactory.

It is well-known that when the Gibbs adsorption isotherm is applied the surface tension of the adsorbed film as determined

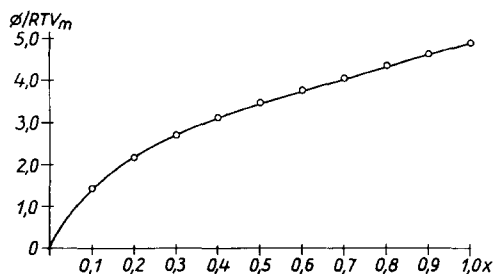


Fig. 14. Surface tension of the spreading film as a function of the equilibrium pressure

from the BET equation becomes negative at $p = p_0$. This discrepancy is ascribed to the total disregard of interaction forces. We are going to show that when using our multilayer isotherm the found surface tension values are acceptable in the whole region of relative pressures in spite of disregarded lateral interaction. When substituting V from the Gibbs equation

$$d\Phi = RTV d(\ln p)$$

by $V_m(1 - e^{-ax})e^{bx}$ the final expression for the spreading pressure is

$$\Phi = RTV_m \{ \ln C - 1/x + E i(bx) - E i| - (a - b)x \} \quad [28]$$

where $C = a/b$ and Ei is the exponential function. The calculated Φ/RTV_m ratios as a function of x are given in fig. 14; it is evident that Φ increases with x giving finite values of the surface tension in the whole pressure interval.

Summary

Theoretically derived isotherms for monolayer and multilayer adsorption are used to interpret some earlier published experimental data. A satisfactory agreement is found in nearly all cases. To check the validity of the theoretical constant b it is plotted versus $1/\sqrt{T}$ and this results in a straight-line dependence as it is foreseen by the theory. The b values found for the adsorption of *n*-butane on glass spheres are used to calculate the average settling times τ_L at different temperatures and subsequently $\tau_{0(L)}$ which is estimated to be $\sim 10^{-13} \text{ sec}$. It seems that the constant b is quasi-independent of the adsorbent properties which permits to obtain a characteristic plot for nitrogen isotherms.

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Elektrisch induziertes Streulicht in Kaolinsuspensionen

Von H. H. Käs und R. Brückner

Mit 8 Abbildungen in 9 Einzeldarstellungen

(Eingegangen am 7. Juli 1969)

1. Einführung

Unter der Wirkung eines homogenen elektrischen Feldes ändert sich die Lichtstreuung von Suspensionen wegen der teilweisen Ausrichtung der suspendierten Teilchen. Mit Hilfe dieses Effektes können Teilchenparameter wie Größe, Form, Rotationsdiffusionskonstante, elektrische Polarisierbarkeit und elektrische Momente bestimmt werden. Hierzu ist im wesentlichen die Kenntnis der Abhängigkeit der gestreuten Lichtintensität vom Winkel zwischen elektrischem Feldvektor des einfallenden und gestreuten Lichtstrahles und die Feldstärkeabhängigkeit der Streulichtintensität erforderlich.

Derartige Messungen wurden an organischen Substanzen von C. Wippler (1, 2), C. Wippler und H. Benoit (3), M. L. Wallach und H. Benoit (4), S. Stoylov (5) und an Wyoming-Bentonit von B. R. Jennings und H. G. Jerrard (6) durchgeführt.

Beim Studium der elektrisch induzierten Doppelbrechung und des elektrisch induzierten Dichroismus in Suspensionen fanden H. H. Käs und R. Brückner (7, 8) spezifische Elektrolytabhängigkeiten und charakteristische Ein- und Ausschwingmechanismen der untersuchten Effekte. Da der Ausrichtungsmechanismus der suspendierten Teilchen im elektrischen Feld für alle elektrooptischen Effekte der gleiche bleibt, ist es von Interesse, die sich hieraus ergebende Vermutung zu prüfen, ob die in (7) und (8) beschriebenen Erscheinungen auch bei elektrisch induziertem Streulicht auftreten. Diese Messungen sollen durch bisher nicht durchgeführte Messungen der Polarisationsrichtung und der Temperaturabhängigkeit ergänzt werden. Elektrolytabhängigkeit und Einschwingvor-

gänge erlauben dabei Einblicke in die Vorgänge an der Phasengrenzfläche flüssig-fest.

Als Untersuchungsbeispiel wird Kaolin gewählt, da einmal an Kaolin-Suspensionen noch keine Messungen des elektrisch induzierten Streulichtes vorliegen, zum anderen wegen der ausgeprägten Plättchenstruktur deutliche Effekte erwartet werden können und der Anschluß an die gemessenen Effekte in (7) und (8) gewährleistet ist.

2. Theoretische Betrachtung

Erste theoretische Untersuchungen wurden von C. Wippler (9) durchgeführt und von S. Stoylov (10) erweitert. Für den experimentell interessanten Fall eines elektrischen Wechselfeldes ($E = E_0 \cos \omega t$) (im Gleichspannungsfeld stören elektrophoretische Erscheinungen) wird die von A. Peterlin und H. A. Stuart (11) abgeleitete Verteilungsfunktion der Hauptachsen der suspendierten Teilchen auf die verschiedenen Raumrichtungen bei Anlegen eines elektrischen Feldes zugrunde gelegt. Die Differentialgleichung wird für die Grenzfälle gelöst, daß entweder nur ein induziertes oder nur ein permanentes elektrisches Moment der suspendierten Teilchen vorliegt.

H. H. Käs und R. Brückner (12) berechneten den allgemeineren Fall der Verteilungsfunktion für gleichzeitiges Vorliegen von induziertem und permanentem elektrischem Moment. Eine Verallgemeinerung der Theorie von C. Wippler ist mit Hilfe dieser Ergebnisse ohne weiteres möglich. Hiernach sollten zusätzlich zu der von C. Wippler erhaltenen Gleichlichtkomponente des Streulichtes und einer phasenverschobenen Kom-