Of this however it is impossible to be certain because of the small number of points and the experimental difficulties at high dilutions. In addition to this possible peculiarity of the transference numbers of the cadmium halides is the fact that all, as indicated above, pass to negative values at high concentrations. Again, while it is the general rule that values below 0.5 approach this quantity with increasing temperature, the results of Bein[6] on cadmium chloride would indicate that here too we find exceptional behavior, the values rising to markedly greater than 0.5.

Summary

Measurements at 25° of cadmium chloride and bromide concentration cells with liquid junction have been given at concentration ranges from 0.01 to 6 *M* and from 0.01 to 3 *M*, respectively.

From these data and the results from cells without liquid junction, the cation transference numbers of the salts have been calculated.

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THE HEAT OF ADSORPTION OF GASES BY SOLIDS

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Recently a number of measurements have been published for the heat of adsorption of gases by solids, showing a marked change of the heat with the amount of gas adsorbed. This change can be either a decrease[1] or an increase.[2] The first case can easily be explained by assuming the presence of spots with different affinity in the solid.[3] The spots with the higher affinity will adsorb the first part of the gas, and will in general give off larger amounts of heat. To give a more detailed description of these sensitive spots Taylor[2,4] has pointed out that the surface of metals used in adsorption experiments is very rough. The atoms lying on the top of a small hill will be bound less strongly to their surroundings than the atoms in a flat surface. Accordingly they will have more of their chemical affinity left free to bind the atoms of the adsorbed gas in analogy to an idea familiar in organic chemistry. In the case of heteropolar salts as adsorbing substance, Kossel[5] has shown by direct calculation that the

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[6] Bein, *Z. physik. Chem.*, **27**, 1 (1898).

[1] See F. Goldmann and M. Polanyi, *ibid.*, **132**, 321 (1927).

[2] H. S. Taylor, *J. Phys. Chem.*, **30**, 145 (1926); G. B. Kistiakowsky, E. W. Flosdorf and H. S. Taylor, THIS JOURNAL, **49**, 2200 (1927); W. E. Garner and D. McKie, *J. Chem. Soc.*, 2451 (1927).

[3] I. Langmuir, THIS JOURNAL, **38**, 221 (1916); **39**, 1848 (1917); **40**, 1361 (1918).

[4] H. S. Taylor and G. B. Kistiakowsky, *Z. physik. Chem.*, **125**, 341 (1927).

[5] W. Kossel, *Gott. Nach.*, 135 (1927).

electric force on the surface of a crystal is rather weak for a flat surface, stronger in a place where a new molecular layer starts above a large flat surface, forming a step, and strongest in a place where a corner is formed, or where only one or two ions project out of a flat surface. Such an explanation cannot hold in the cases in which the heat of adsorption increases with increasing adsorption, because, as we have said before, if the change in the amount of heat is due to differences in the adsorbing spots, the adsorption will start in the spots where the energy difference is highest (at least if these energy differences are above a certain limit), as we shall discuss in the second part. A possible explanation of the increase can be found in the assumption that neighboring adsorbed molecules attract each other, because one sees easily that the number of places where two or more adsorbed molecules lie close together will increase relatively stronger with the amount of gas adsorbed than the number of places with isolated adsorbed molecules. One could argue that the mutual attraction of the molecules could not amount to more than the heat of evaporation of these molecules when present in a bulk of liquefied gas, and could accordingly not account for the actual increase in heat of adsorption, which is much higher, but this argument proves to be wrong on account of a fact pointed out by DeBoer.[6] If we assume the adsorbing forces to be of an electrical nature, the molecules will be polarized (this term being used now to mean as well the orientation of molecules carrying a permanent dipole as the displacement of charges inside the molecule, which is usually meant by this term). Now this polarization of the molecules will set up much stronger forces between them than in the absence of an external field, in the same way in which two rods of soft iron which do not attract each other appreciably outside of an external magnetic field act on each other strongly if magnetized by an outside source. In the first part of the paper we intend to discuss the amount of interaction which can be produced in this way; in the second part, we are going to discuss the relation between the amount of gas adsorbed and the heat of adsorption.

Interaction of Adsorbed Molecules[7]

If the idea discussed in the introduction is proved, then it turns out that even in the case mentioned first (of a decrease of the heat of adsorption with the amount of gas adsorbed) there might be another reason for it apart from the possibility that different spots have a different sensibility. For the sake of simplicity we are going to discuss the adsorption of a gas without permanent dipoles on the surface of a heteropolar salt—for example, the adsorption of hydrogen or oxygen on the surface of rock salt

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[6] J. H. DeBoer, *Physica,* [V] **8**, 145 (1928).

[7] Similar ideas have been developed, although in less detail, by A. Magnus, *Z. Electrochem.*, **34**, 531 (1928).

or fluorite. There will be then in general two types of spots on the surface which can adsorb, the positive and the negative ions of the lattice. Let us assume, for the sake of convenience, that one of these two will adsorb slightly more strongly than the other; for example, in the case of fluorite the calcium ions will adsorb more strongly than the fluorine ions on account of their double charge. Accordingly, first the calcium ions on the surface will be covered by adsorbed gas molecules. It might now happen that the size of the gas molecules is so large that no more gas molecules can be adsorbed between them on the fluorine ions even if we increase the gas pressure. Then, without interaction of the molecules, one would expect for a uniformly flat adsorbing surface no change in the heat of adsorption up to this saturation point; but, instead, we would get a decrease because now all adsorbed gas molecules are polarized in the same direction, all being adsorbed on ions of the same kind, and would, accordingly, repel each other, decreasing the heat of adsorption the nearer they get to each other, which means the more the surface is covered. If, on the other hand, the size of the gas molecules is such that it does not obstruct adsorption on neighboring ions of opposite sign, these adjacent gas molecules will be polarized in opposite directions, and will accordingly attract each other, increasing in this way the heat of adsorption.

Let us now assume that a molecule of the adsorbed gas gets, under the influence of an electric force E, a polarization p

$$p = \alpha E \qquad (1)$$

α is connected with the dielectric constants of the gas under normal conditions, ϵ_0, and the number of molecules N_0 contained in one cubic centimeter under these conditions is by the formula

$$\epsilon_0 - 1 = 4\pi N_0 \alpha \qquad (2)$$

The energy of an adsorbed gas molecule at 0 temperature taken negatively will then be, calculated for one mole

$$U_0 = N_L \frac{\alpha}{2} E^2 \qquad (3)$$

where N_L is the number of molecules per mole. In this formula the molecules are supposed to be so far apart that they do not act on each other. On the other hand, if we have two molecules with the polarization p_1 and p_2 at the distance r, their mutual electrostatic energy will be

$$\pm \frac{p_1 p_2}{r^3} \qquad (4)$$

with the $-$ sign in case of opposite polarization and the $+$ sign in case of polarization in the same direction. The outside fields are assumed to be parallel. They will be in general (at least approximately) at right angles to the surface, due to the symmetry at the positions of equilibrium for adsorbed molecules. If we now consider a pair of adjacent gas molecules adsorbed on two different spots suited for adsorption and situated close to each other, with the electric fields E_1 and E_2, their total energy will be (again taken with the negative sign)

$$\frac{U}{N_L} = p_1E_1 \pm \frac{p_1p_2}{r^3} + p_2E_2 - \frac{p_1^2}{2\alpha} = \frac{p_2^2}{2\alpha} \tag{5}$$

(+ sign for opposite polarization, − sign for same polarization)

Here the first and third members give the electrostatic work gained by generating the dipole p_1 in the electrostatic field E_1 (motion of a charge e over a distance l_1, $el_1 = p_1$) and the dipole p_2 in the field E_2. The fourth and fifth members are the elastic energy stored up in the distorted molecules, while the second member corresponds to the mutual electrostatic energy of the dipoles according to (4).

The strengths of the dipoles p_1 and p_2 are such that they make the potential energy to a minimum, and are accordingly given by the equations

$$\frac{\partial}{\partial p_1}\frac{U}{N_L} = E_1 \pm \frac{p_2}{r^3} - \frac{p_1}{\alpha} = 0$$

$$\frac{\partial}{\partial p_2}\frac{U}{N_L} = E_2 \pm \frac{p_1}{r^3} - \frac{p_2}{\alpha} = 0$$

or

$$p_1 = \frac{\frac{E_1}{\alpha} \pm \frac{E_2}{r^3}}{\frac{1}{\alpha^2} - \frac{1}{r^6}} \qquad p_2 = \frac{\frac{E_2}{\alpha} \pm \frac{E_1}{r^3}}{\frac{1}{\alpha^2} - \frac{1}{r^6}} \tag{6}$$

From this we get the negative energy of the pair

$$\frac{U}{N_L} = \frac{p_1E_1}{2} + \frac{p_2E_2}{2} = \frac{1}{2}\,\frac{\frac{E_1^2 + E_2^2}{\alpha} \pm \frac{2E_1E_2}{r^3}}{\frac{1}{\alpha^2} - \frac{1}{r^6}} \tag{7}$$

In the simplest case we put $E_1 = E_2$. This will hold either if the molecules are adsorbed only by a single kind of ion (negative sign, repulsion), or if the adsorbing power of both ions is about equal, as in potassium chloride, and the size of the molecules so that they can be adsorbed by neighboring ions. Then we get as energy per mole (not per pair of moles)

$$U = \frac{N_L}{2}\,\frac{E_1^2}{\frac{1}{\alpha} \mp \frac{1}{r^3}} = \frac{N_L\alpha E^2}{2}\,\frac{1}{1 \mp \frac{\alpha}{r^3}} \tag{8}$$

α and r^3 being referred to one molecule are cumbersome numbers. We introduce instead the numbers referring to 1 mole by multiplying with N_L in numerator and denominator of the fraction α/r^3, and use the equation in the form

$$U = \frac{N_L\alpha\, E^2}{2}\,\frac{1}{1 \mp \frac{N_L\alpha}{N_Lr^3}} \tag{8'}$$

The second factor gives the relative change of the heat of adsorption. To evaluate this numerically, we proceed in the following way. According to Equation 2

$$N_L\alpha = \frac{22{,}400}{4\pi}\,(\epsilon_0 - 1) \qquad (2')$$

where 22,400 is the number of cc. in a mole of a gas under normal conditions. The units in (1′) are cc. The following table gives some examples

Gas	H_2	O_2	N_2	CO	CH_4	C_6H_6
$N_L\alpha$	0.55	0.80	1.13	1.28	1.70	6.04

On the other hand, N_Lr^3 can be calculated as follows.

If we have adsorption on each ion of a rock salt lattice, N_Lr^3 will be the volume of 1 mole of ions, or half the mole volume of the salt. If adsorption takes place only on positive ions, N_Lr^3 will be four times the mole volume.

If we consider the adsorption on a metal to be of a similar nature[8] (see later), adsorption at the places where atoms sit will result in repulsion of the adsorbed molecules (positive sign). However, for a face-centered lattice like copper we would have to use half the molecular volume if we assume molecules to be adsorbed by positive ions in the lattice points, and molecules with opposite polarization adsorbed between them by electrons distributed uniformly in the space between the ions. If, on the other hand, adsorption could occur only at the lattice points occupied by metal atoms, the volume would have to be twice the molecular volume. The next table shows some examples.

	Adsorption on same kind of ions only (Repulsion between adsorbed molecules)			Adsorption on both kinds of spots (Attraction between adsorbed molecules)		
Substance	NaCl	Cu	Pt	NaCl	Cu	Pt
N_Lr^3	107.6	10.05	12.9	13.5	3.56	4.56

Calculation of (8) from the data in the two tables shows that the mutual repulsion in the first case (repulsion) could not change the heat of adsorption appreciably for a salt, and might change it by about 10% on a metal in the case of small gas molecules. On the other hand, attraction between adsorbed molecules will increase the heat of adsorption by about 10% on salts and up to 40 or 50% on metals (again for simple molecules). This number will be made somewhat larger if not only pairs but groups of more molecules are formed. For example, if there is a group of three molecules, one adsorbed by a sodium ion and two on opposite sides of it, each adsorbed by a chlorine ion, the influence is increased by a factor of about 4/3.

We have computed this change only relative to the electrostatic part of the energy of adsorption. Compared with the total energy of adsorption this fraction might be less if a large part of the energy of adsorption is due to Van der Waals forces, as Lennard-Jones[9] suggests. On the other

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[8] H. S. Taylor, "Colloid Symposium Monograph," Vol. IV, **1926**, p. 19.

[9] J. E. Lennard-Jones and Beryl M. Dent, *Trans. Faraday Soc.*, **24**, 92 (1928).

hand, it might be more if in the total heat of adsorption there is present a large negative part due to the forces of repulsion which act between the gas molecules and the adsorbing solid, and fix the position of equilibrium of the adsorbed gas molecules. These latter forces might play a more important part here than in the lattice energy of heteropolar crystals, because the force of attraction in adsorption changes more strongly with the distance than the inverse second power;[9] but, in any case, it seems that for the adsorption of carbon monoxide on copper,[2] one would not expect the rise to more than the double value.

We have to justify now our assumption that the adsorption forces in the case of metals are of the same nature as those in heteropolar salts. The newer development of the electron theory by Sommerfeld[10] has removed the difficulties which adhered to the older form of the theory, and has again made reasonable the old assumption that a metal is built up as a lattice of positive ions with the free electrons distributed approximately uniformly[11] between them. In this case there will be an electrostatic field on the surface of the metal of a type very similar to the one on the surface of a crystal like rock salt. However, it seems somewhat doubtful to the author whether the same idea can be applied to carbon (charcoal). If so, in this case the distance between neighboring atoms is $1.5 \cdot 10^{-8}$ cm., and the repulsing forces due to adsorbed molecules polarized in the same direction would require the introduction of 2.04 cc. as the value for $N_L r^3$ in (8), giving a very strong decrease of the heat of adsorption with the amount of gas adsorbed. If, on the other hand, adsorption on spots of opposite character could be possible, this could not be in the middle of the line between two atoms of carbon on account of the short distance but would have to be in the center of the ring formed by each group of six atoms in graphite. In this case the number to be inserted in (8) would have to be ~ 2 cc. To account in this way for the curve given by Polanyi[1] one would, therefore, explain the initial decrease of the heat of adsorption as due to the fact that gradually less sensitive spots come into action. The increase after the minimum would be due to the formation of pairs or larger groups with mutual attraction. The final sharp maximum with corresponding quick fall might mean the covering of much less sensitive places.

Thermodynamic Consideration of the Increase in the Heat of Adsorption.—The foregoing discussion might alleviate a difficulty which seems connected with the experimental result that the heat of adsorption increases. From the thermodynamical standpoint it is clear that the processes which will first take place are the ones where the decrease in free

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[10] A. Sommerfeld, *Z. Physik*, **47**, 1 (1928).

[11] H. Bethe, *Ann. Physik*, **87**, 55 (1928); J. E. Lennard-Jones and H. J. Woods, *Proc. Roy. Soc. London*, **120**, 727 (1928).

energy is largest, while the experiment shows that at the same time the decrease in total energy is relatively small, and will be much larger for later processes of adsorption. This difficulty has been pointed out by the author to Dr. Kistiakowsky and Dr. Taylor, and has been mentioned by them.[2] R. E. Burk,[12] in his recent report on contact catalysis, states that it is perfectly possible that a large change in free energy is connected with a small change in total energy due to a large difference in the chemical constants. While this is quite true in principle, the difficulty in the present case rests just on the numerical values which seem possible from a kinetical standpoint, and it might be of interest to discuss the question here in general.

In any physical or chemical equilibrium the probability that a molecule will be in a certain state is proportional to[13]

$$ve^{+U/RT} \tag{9}$$

Here U is the negative potential energy in this state calculated for 1 mole, while v is the "average available volume" in the phase space which belongs to this state. Here we have assumed that the classical theory holds, the temperature being high enough to insure equipartition for the kinetic energy.

v is a product, each factor belonging to one degree of freedom. The connection between (9) and the free energy, μ, is given by

$$e^{-\mu/RT} = ve^{+U/RT} \tag{9'}$$

where μ is the free energy of the system per mole. Some additional members referring to the kinetic energy are left out due to the fact that we have left out the corresponding *factors* in v. If we now want absorption to occur first at places with smaller heat of adsorption ($+U$), these places must have a correspondingly higher v. If the logarithm of (9′) is taken this statement is equivalent to the usual statement that a small change of the total energy might be overcompensated by a large change in the chemical constants (or the specific heats). To compensate for an increase in the heat of adsorption, there must be a factor 10 in v for each increase of about 1400 calories at room temperature, as $e^{-1400/RT}$ is about $^1/_{10}$th. We have therefore to discuss next the factor v.

(A).—When a gaseous molecule is bound, the three degrees of freedom of translation go over into three degrees of oscillation around the position of equilibrium. The corresponding factors in v are

$$\left(\frac{1}{\nu}\sqrt{\frac{kT}{2\pi m}}\right)^3 \tag{10}$$

Accordingly, for a given gas these factors are in the ratio ν_2^3/ν_1^3 for two different positions. From our knowledge of infra-red vibration it would

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[12] R. E. Burk, *J. Phys. Chem.*, **32**, 1601 (1928).

[13] K. F. Herzfeld, *Physik. Z.*, **22**, 186 (1921); **23**, 95 (1922); "Kinetische Theorie der Wärme," Braunschweig, 1925.

seem improbable that the ratio of frequency for different positions could be larger than 2:1. A similar conclusion can be reached if we assumed that the potential energy of the molecule is given by an expression like $\frac{A}{r^m} - \frac{B}{r^n} = U$. A simple calculation shows that the frequency is given by

$$4\pi^2 M\nu^2 = \frac{mn}{r^2} U$$

This formula also makes it improbable that for a given substance the frequency might vary more than two-fold. This means that these three degrees of freedom could, at the utmost, be responsible for a change in v by a factor 8, which would compensate an energy difference of 1250 calories. (As in general the higher energy will correspond to a higher frequency, the change in v is in the right direction.)

(B) **Internal Vibrations.**—Burk suggests that the internal vibration of the molecule might be affected. Considering the strength of the internal forces compared with the strength of the adsorption forces, it seems improbable that the change in frequency of the internal vibration would be more than, let us say, 12%. Each internal degree of freedom will produce a factor similar to one of the three factors in (10). Accordingly, one would expect at the utmost compensation for 60 calories for each internal degree of freedom. The same will be true for an influence upon the vibration of the molecules of the adsorbing solid. It seems to the author, therefore, that this part can be neglected.

(C) **Rotations.**—If we have to deal with a gas molecule which is not monatomic, this gas molecule will have rotational degrees of freedom, two in number for a diatomic molecule or a straight molecule like carbon dioxide, three for all other molecules. For the adsorbed molecule it might be that on all spots adsorbing these rotations will be changed into oscillations of the axis of the molecule around an equilibrium direction. In this case we get in v again factors of the form (10). There will be two of them for a straight molecule, three for a more complicated one. This will mean for the ratio of the two v's for two different spots a ratio of $(\nu_2/\nu_1)^2$ or $(\nu_2/\nu_1)^3$. In numbers this might make a factor of four or eight, if we assume again that the frequencies cannot be changed more than by a factor of two. Accordingly, this might compensate for 800 or 1250 calories. We might get a stronger effect if we assume that in one of the spots the molecule might turn freely, while in the other one it might only be allowed to oscillate. For example, it might be that on adsorption at a flat plane a molecule might turn freely around an axis perpendicular to this plane, while if adsorbed in a corner and accordingly fixed by more than one spot it might be forced to oscillate only.

To make an estimate for this case, consider a permanent dipole in a homogeneous electric field, E. This dipole will either rotate or oscillate around the field according to the strength of the field. A short calculation shows that Expression 9′ takes the form

$$v_0 \frac{kT}{pE}\left(e^{+pE/kT} - e^{-pE/kT}\right)$$

where v_0 is the value of v for the rotation of a free molecule and p is the moment of the permanent dipole. If pE, the amount of potential energy at absolute zero, is sufficiently large compared with kT, this takes the form

$$v_0 \frac{kT}{pE} e^{U/RT}$$

showing that here we have in fact a factor kT/pE smaller than that appearing before the e-power with the larger energy. This formula is essentially no different from the formula just mentioned above because we have to deal here with vibrations around a given axis in two dimensions, in which case, according to our previous reasoning, we should have a factor proportional to $(\nu_2/\nu_1)^2$ and, on the other hand, pE is proportional to $\sim \nu^2$. But the factor which we find here cannot be much smaller than $^1/_{10}$th (corresponding to $NpE \sim 6000$ small calories), and would accordingly compensate for about 1400 small calories (for half this amount, if there were only one degree of freedom; for 1.5 the amount if there were all three degrees of freedom of rotation).

(D) A Majority of Spots with Low Heat of Absorption.—If we assume that there are two kinds of spots, one with a low heat of absorption, U_1 (number of these spots per square centimeter, N_1), and one with high heat of absorption, U_2 (number of these spots per square centimeter, N_2), we will get for the ratio of molecules adsorbed on these two kinds (n_1, n_2) if we make assumptions similar to Langmuir's

$$\frac{n_2}{N_2 - n_2} = \frac{n_1}{N_1 - n_1}\frac{v_2}{v_1} e^{(U_2 - U_1)/RT} \tag{11}$$

We call $n = n_1 + n_2$ the total number of molecules adsorbed and introduce the abbreviation

$$A = \frac{v_2 N_2}{v_1 N_1} e^{(U_2 - U_1)/RT} \tag{12}$$

Then a rather complicated calculation shows that the (differential) heat of adsorption will be given by

$$U_1 + (U_2 - U_1)\frac{1}{1 + \dfrac{AN_1N_2}{[(1 - A)n_2 + AN_2]^2}} \tag{13}$$

The slope of this curve is shown to be

$$\frac{(U_2 - U_1)\, 2N_1N_2A(1 - A)}{\left[(1 - A)n_2 + AN_2 + \dfrac{AN_1N_2}{(1 - A)n_2 + AN_2}\right]^3} \tag{13′}$$

Accordingly this expression will have the sign of $1 - A$, and will be positive (rising heat of adsorption) if A is smaller than 1, which means that the larger heat of adsorption of spots No. 2 can be compensated not only by a smaller volume v_2 but also by a smaller number of spots N_2. But if this is so, then the resulting curve will not have the form given by Taylor and Kistiakowsky,[2] because if one calculates now the next differential quotient, which measures the curvature of the line, it turns out to be given by the following expression, which appears multiplied with essentially positive factors (even powers)

$$(U_2 - U_1)\,\frac{A\,\frac{N_1}{N_2} - \left[A\left(1 - \frac{n_2}{N_2}\right) + \frac{n_2}{N_2}\right]^2}{A\left(1 - \frac{n_2}{N_2}\right) + \frac{n_2}{N_2}}$$

A discussion of this expression shows that with A smaller than 1 this expression is positive, which means a line curving upward, while in the experimental curve the slope is steadily decreasing with an increase in the amount adsorbed. It is not quite out of the question that such a form could be explained if we assume more than two different kinds of spots present,[14] but from the present assumption it would follow that N_1 large compared with N_2 does not explain the experimental facts.

(E) Formation of Pairs.[15]—We consider now the effect of the attraction between two neighboring molecules. To simplify the formulas we assume that there will always be two adjoining spots on the adsorbent at which adsorption might take place. For example, in the case of a heteropolar salt as adsorbent there might be always pairs of ions sticking out scattered over a plane surface. We call N the number of these double spots per square centimeter, n the total number of adsorbed gas molecules per square centimeter, n_2 the number of pairs, and n_1 the number of adsorbed gas molecules occupying alone a spot which could hold two. We have, therefore, $n = n_1 + 2n_2$. Furthermore, we use the abbreviation

$$B = 4\,\frac{v_2}{v_1}\,e^{(U_2 - U_1)/RT} \tag{14}$$

We now compare the probabilities that a newly adsorbed molecule will either form a pair with one already adsorbed or will stay single. In the first case it will have to go in an empty place, the neighbor of which con-

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[14] In fact, Kistiakowsky's calculations can be formally explained in this way. He gets a curve of the appropriate form by writing for the heat of adsorption

$$\Sigma_i N_i\,\frac{(W_i - w)\,e^{W_i/RT}}{1 + n^r k_i\,e^{W_i/RT}} : \quad \Sigma_i\,\frac{N_i\,e^{W_i/RT}}{1 + n^r k_i\,e^{W_i/RT}}$$

If we write now $W_i - w = N_i$, $e^{W_i/RT} = v_i\,e^{U_i/RT}$, $v_i = e^{W/RT}\,k_i$, $N'_i = N_i/k_i$. This can be put into the form

$$\Sigma_i U_i\,\frac{N'_i v_i\,e^{U_i/RT}}{1 + n^r v_i\,e^{U_i/RT}} : \quad \Sigma_i\,\frac{N'_i v_i\,e^{U_i/RT}}{1 + n^r v_i\,e^{U_i/RT}}$$

but then we have again the difficulty of explaining the large differences in the v's which would be given by the expression $v_i = k_i\,e^{W/RT}$.

[15] See also J. Frenkel, *Z. Physik*, **26**, 117 (1924).

tains already one adsorbed molecule. There are n_1 such places per square centimeter. On the other hand, if it should stay single it will have to go to a spot formed by two ions on which there is not yet any adsorbed molecule. There are $N - n_1 - n_2$ such spots. We get, therefore, the equation of our adsorption isotherm

$$\frac{n_2}{n_1} = \frac{n_1}{N - n_1 - n_2}\frac{B}{4} \tag{15}$$

Eliminating n_2 and calling the fraction x, which gives the amount adsorbed in terms of the saturation amount, $x = n/2N$, a short calculation gives the formula

$$n_1 = \frac{N}{B - 1}\left(\sqrt{(B - 1)4x(1 - x) + 1} - 1\right) \tag{16}$$

From this we get for the differential heat of adsorption

$$U_2 - (U_2 - U_1)\frac{1 - 2x}{\sqrt{(B - 1)4x(1 - x) + 1}} \tag{17}$$

From this it follows that for a very small amount adsorbed (x negligible) the differential heat of adsorption will be U_1, as in this case all molecules will be single. With increasing amount adsorbed the relative amount of pairs will increase. For x very small the formula will be $U_1 + (U_2 - U_1)2Bx$, giving an increase in heat of adsorption. If B is comparatively large, we will have in the middle part of the range (x neither too small nor too close to 1) approximately the formula

$$U_2 - (U_2 - U_1)\frac{1 - 2x}{2\sqrt{Bx(1 - x)}}$$

Finally, at the upper end, when $1 - x$ is very small, we get $U_2 + (U_2 - U_1)$ $2B(1 - x)$, a final linear increase ending up with a value $2U_2 - U_1$. The final differential heat of adsorption is much larger than half the heat of adsorption of one pair ($^1/_2\ 2U_2$) because, if we form one pair by adding one molecule at a place where another sits, we get not only the heat of adsorption U_2 of the newly added molecules, but we increase also the heat U_1 of the first molecule to U_2. (This is the same thing Polanyi[1] calls the heat of compression developed in the substance already adsorbed by further adsorption.) Roughly the curve which gives the heat of adsorption as a function of the amount adsorbed would look like Fig. 1. Unfortunately, it seems difficult to get this into agreement with the first part of the experimental curve. If we assume that U_1 is 5000 cal., and $U_2 - U_1 = 6000$ cal., we

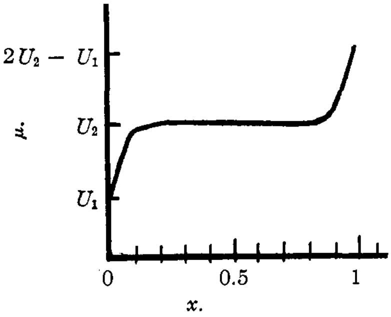

Fig. 1.—Heat of adsorption depending on the amount of gas adsorbed, if there is formation of pairs of molecules or dissociation.

have adjusted starting and end-point to the values 5000 and 17,000. From what we have seen before, this will make $B = 400$ even if we make v_1/v_2 equal to 100, which is the best we can do. This will give us for $x = {}^1/_{10}$th the differential heat of adsorption 10,600, and for $x = {}^9/_{10}$th, the value 11,400. In other words, there will be a very steep rise from 5000 to 10,600 during the adsorption of the first tenth of the gas; then only a rise of 800 more calories during the next ${}^8/_{10}$ths, and finally again a steep rise of 5600 calories during the last tenth of adsorption. The only way in which this could be smoothed out would be to make B smaller, but this would again necessitate making v_2/v_1 smaller, and as stated before there seems to be no way to do it. The decrease of the heat of adsorption beyond the maximum will, in any case, have to be explained by the presence of a different kind of adsorption spots, which are not included in N and which might be the spots on the plane surface. The inclusion of these in a way similar to (D) or to Kistiakowsky[14] might make somewhat smoother transitions in the first part of the curve, but would probably necessitate a higher value for $U_2 - U_1$, offsetting this advantage.

(F) **Dissociation.**—We have finally to consider the possibility advocated by Taylor and Kistiakowsky that on the spots with the lower heat of adsorption the molecules might be dissociated (into atoms for diatomic molecules, into other parts for larger molecules). In this case the lower heat of adsorption would be due to the energy necessary to dissociate the adsorbed molecule. If we again call N the number of available spots, assume furthermore that such a spot can be occupied either by a molecule (number n_2), or an atom (number n_1) we get the following equations for the adsorption

$$n_2 + \frac{n_1}{2} = n \quad \text{and} \quad \frac{n_2}{N - n_2 - n_1} = \frac{n_1^2}{(N - n_2 - n_1)^2}\,\frac{C}{4} \tag{18}$$

where C is an abbreviation for

$$C = 4\,\frac{v_2}{v_1^2}\,e^{(U_2 - U_1)/RT} \tag{19}$$

Here v_1 is the corresponding volume for one adsorbed atom; accordingly, v_1^2 is the volume for both atoms, U_1 is the heat developed by adsorption and subsequent dissociation into two atoms. If we again call x the ratio of the total amount adsorbed to the saturation amount $\left(\text{this time } x = \frac{n}{N}\right)$, we again get Equation 16, only with C instead of B. In the same way we get for the differential heat of adsorption, Equation 17 with C instead of B, and all of the subsequent discussion remains unchanged. The only task left is to discuss the numerical value of C, which amounts to discussing the ratio v_2/v_1^2. Now, as we said before, we can divide v_2 into two factors, $v_2 = v_2'v_2''$. Here v_2' is due to the oscillation of the molecule as a whole around its position of equilibrium, and accordingly the discussion under (A) applies. It follows that if we write for v_2/v_1^2 the expression $v_2'/v_1 \times v_2''/v_1$, the first factor will be 8 to 10 at the best.[16] v_2'', on the other hand, is due to the motions of the adsorbed molecules around a certain direction, as stated in (C), and this motion might either be an oscillation or a free rotation. In the first case the ratio will be $(\nu_1/\nu_2)^3$, or again a factor of 10 at the best. In the latter case we get for this ratio $8\pi^2\nu_1^2I/kT$, where I is the moment of inertia. With a frequency of $\nu_1 = 10^{13}$ (wave length, 30μ), and a moment of inertia of 10^{-40}, this would make a factor 20, with a wave length of 100μ ($\nu_1 = 3 \times 10^{12}$) and $I = 10^{-41}$, as in the case of hydrogen, the value would be 0.2. So it seems impossible to expect for v_2/v_1 anything smaller than 0.01, but probably the value will be much larger; accordingly for the same difference $U_2 - U_1$ measured experimentally, C will be at least as large as B. Accordingly, the interpretation of the effect as dissociation into atoms will lead to even greater difficulties than the assumption of formation of pairs discussed under (E).

Thermodynamical Comparison of Two Gases with the Same Heat of Adsorption

From what we have said before it will now be easy to answer the question under what conditions the amount of gas adsorbed on the same adsorbent under the same external pressure will be different for two gases with approximately the same heat of adsorption, or in other words, comparing the two gases when the same amounts are adsorbed, under which conditions the equilibrium pressure will be different. The equilibrium pressure will be inversely proportional to the expression (9′). If we have the same U, it will be inversely proportional to v. First of all, as far as the vibrations of the molecule, as a whole, are concerned (A of the preceding part), it is merely a question of how different the forces can be for the same energy; here, too, we might assume that these forces will surely not vary more than the ratio 1:4, giving at the utmost the factor 8. As far as the influences are concerned which are mentioned in (C), it seems possible that if one molecule is rotating freely, and the other one only oscillating around one direction, the latter might have a vapor pressure 20 times as great as the former. It might be that if we compare a mole-

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[16] Here the ratio is not really $(v_1/v_2)^3$ because the two things compared have not the same masses, but is $(m_1v_1^2/m_2v_2^2)^{3/2}$, or the ratio of the quasi-elastic forces to the third power, which is really the expression to which our discussion applies, but probably in this case it will be $m_1v_1^2$ which will be greater than $m_2v_2^2$, because the forces which bind the atom to the adsorbent are greater than the forces which bind the molecule, in spite of the fact that U_2 is larger than U_1. U_1 is not the heat liberated if we adsorb two atoms out of the gaseous state, but the heat liberated if we first adsorb a molecule and then dissociate it in the adsorbed state. For a detailed discussion see, for example, M. Polanyi, *Z. Elektrochem.*, **27**, 142 (1921). From what we have said before it is more probable that v_2'/v_1 is 10 than $^1/_{10}$th.

cule without permanent dipole, like H_2, with a molecule with permanent dipole, like H_2O, these conclusions might apply. Finally, if we compare molecules which dissociate with molecules which do not and adsorb only very small amounts, we might expect for the dissociating molecules a vapor pressure lower than that for the non-dissociating. This follows in the manner shown. The vapor pressure p_1 of the first kind will be proportional to $(n_1^2/N^2)v_1^2e^{(U_1/RT)}$ if so little is adsorbed that practically all is dissociated and only a small part of the surface covered. On the other hand, the vapor pressure of the non-dissociating type, p_2, will be proportional to $(n_2/N)v_2e^{(U_2/RT)}$. If, then, $U_1 = U_2$, and the same amount of moles, $n = n_2 = 2n_1$, is adsorbed, we find

$$\frac{p_1}{p_2} = \frac{n}{4N}\frac{v_1^2}{v_2}$$

The latter factor has been discussed in the last section of the preceding part while the first factor is small compared with one and proportional to the amount adsorbed.

Summary

In the first part it is shown that the increase in heat of adsorption with the amount of gas adsorbed can be explained by the interaction of the dipoles in neighboring molecules which are set up if we assume that the adsorption is mainly due to electric forces. In this case the interaction can be much stronger than the usual heat of evaporation would lead us to expect.

In the second part the thermodynamical difficulty connected with an increase in heat of adsorption is discussed. It is shown that the best explanation seems to be the formation of groups of adsorbed molecules sticking together.

Finally, the equilibrium pressures of different gases with the same heat of adsorption are compared.

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