Physical Adsorption on NonUniform Surfaces

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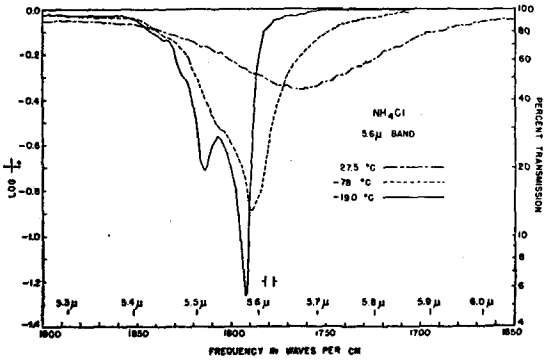

FIG. 1. 5.6μ band of NH_4Cl.

Our resolution in this region was better than 5 cm^{-1} and the reported rotational spacing was about 15 cm^{-1}.

It seems clear that the structure previously obtained was due to water vapor. Although the peaks reported do not coincide with water vapor peaks, the approximate separation is the same and we have observed that in spectra taken point by point apparent peaks are frequently obtained on the steep sides of lines in the background spectrum. Furthermore, it is noteworthy that although the band center in the bromide occurs at a frequency 50 cm^{-1} lower than in the chloride, peaks were reported at identical frequencies in both spectra.

Our data show no evidence of rotation in either phase. We have been able to interpret the major features of the low temperature infra-red spectrum of NH_4Cl on the basis of a body-centered lattice in which all NH_4^+ tetrahedra are similarly oriented, and the NH_4Br spectrum on the basis of a similar structure in two dimensions but with a screw axis replacing translation in the third dimension (i.e., space group D_{4h}^9). The splitting of the triply degenerate mode at 1400 cm^{-1} constitutes our chief evidence. These structures are both in accord with optical, piezoelectric, x-ray and Raman data obtained on these crystals.[3] The fact that the spectra of the room temperature phases of the two compounds are almost identical suggests that the room temperature modification of both salts has the same structure, in which the NH_4^+ ions are randomly distributed between the two possible orientations, and that the phase transition is a simple order-disorder transition.

Experimental work on ND_4Br is in progress and more detailed data and analysis will be published shortly.

[1] A. W. Lawson, Phys. Rev. **57**, 417 (1940).
[2] C. Beck, J. Chem. Phys. **12**, 71 (1944).
[3] A. C. Menzies and H. R. Mills, Proc. Roy. Soc. (London) **148**, 407 (1935). These data are conveniently summarized in this article. However, the NH_4Br model used by these authors does not account for the splitting of the 1400-cm^{-1} mode.

Physical Adsorption on Non-Uniform Surfaces

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November 11, 1948

IN a recent paper[1] with the above title, G. Halsey has discussed several aspects of adsorption including the BET theory and "cooperative adsorption." The writer would like to make a few comments on these two points.

Halsey makes the following statement which, it seems to the writer, may lead to some confusion: "$\cdots$ the hypotheses of the BET theory lead to substantially no adsorption beyond the first layer if $E_2=E_L$, and stepwise isotherms if $E_1>E_2>E_3\cdots>E_L$." Now actually the *hypotheses of the BET theory*[2] lead, as is well known, to multimolecular adsorption for any value of the BET constant c for p/p_0 sufficiently close to unity, and in no case to stepwise isotherms. Halsey's statement actually refers to a mixture of BET hypotheses and somewhat refined hypotheses. In summary, although the BET model assigns extremely unrealistic properties[2] to the liquid state, the model *does* lead to multimolecular adsorption. The present writer, in other words, is by no means defending the BET model, but is defending the deductions which have been made *from the model.*

Halsey discusses cooperative adsorption (i.e., adsorption in which horizontal as well as vertical interactions are taken into account so that condensation phenomena are possible[2]) and in this connection accepts the reality of stepwise adsorption near the surface—although he feels that the non-uniform nature of the surface will tend to smooth out these steps. This is a new and interesting point of view. It should be pointed out, however, that a closely related approximate *quantitative* approach to the problem of "cooperative" adsorption on a uniform surface (for mathematical simplicity) has already been given,[3] though not mentioned by Halsey in his discussion of cooperative adsorption. Stepwise adsorption was encountered in the mathematical equations and was discussed, although it was not felt that the model was sufficiently refined to come to a definite conclusion concerning the physical significance of this aspect of the approximate theory.

[1] G. Halsey, J. Chem. Phys. **16**, 931 (1948).
[2] These can probably be outlined most clearly in terms of a statistical mechanical model. See: (1) T. L. Hill, J. Chem. Phys. **14**, 263 (1946), Eqs. (3)–(5), (28) (29), and Fig. 1; (2) J. Chem. Phys. **15**, 767 (1947), Eq. (18).
[3] T. L. Hill, J. Chem. Phys. **15**, 767 (1947).

A New Equation for the Non-Stationary Shock Wave

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November 2, 1948

IN analogy to the "Stoßpolare" of Busemann[1] for the stationary shock wave of two dimensions I found an equation for the non-stationary shock wave of one dimension.

We start from the well-known hydrodynamic equations

$$(w-\mu)\rho=(\rho-\bar{u})\bar{\rho}, \tag{1}$$

$$(w-u)^2\rho+p=(w-\bar{u})^2\bar{\rho}+\bar{p}, \tag{2}$$

$$\frac{a^2}{u-1}+\frac{(w-u)^2}{2}=\frac{\bar{a}^2}{u-1}+\frac{(w-\bar{u})^2}{2},$$

where w is the speed of the shock wave, u the velocity of the gas, ρ the density, p the pressure, a the velocity of sound, and $a^2/u-1=i$, the enthalpy of a perfect gas; the bar refers to the quantities behind the shock wave. By

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dividing (2) by (1) one obtains

$$\bar{u}=\mu\pm\left(\frac{1}{u}\left[-(a^2+\bar{a}^2)+\left((\bar{a}^2+a^2)^2-\frac{4u^2}{u-1}\left[\frac{1}{u}-\frac{1}{u-1}\right](a^2-\bar{a}^2)^2\right)^{\frac{1}{2}}\right]\right)^{\frac{1}{2}},$$

where use has been made of the relation $a^2=up/\rho$. For large values of $\bar{a}(\bar{a}\gg a)$ we have the limiting relations (if $u=0$)

$$\frac{\bar{u}}{\bar{a}}=\left(\frac{1}{u}\left[1+\left(1-\frac{4u^2}{u-1}\left[\frac{1}{u}-\frac{1}{u-1}\right]\right)^{\frac{1}{2}}\right]\right)^{\frac{1}{2}};\quad \frac{w}{\bar{a}}=\frac{\bar{u}}{\bar{a}}\cdot\frac{u+1}{4}.$$

If $k=1.40$ (air), we have

$$\bar{u}/\bar{a}=1.89(w/\bar{a})=2.27\frac{w}{\bar{u}}=1.20.$$

A comprehensive publication of this topic will appear in Helvetica Physica Acta. Since sometimes the opinion is expressed that there is no limiting law for w, it might be of interest to point out that there is such a limiting relation.

[1] Lectures in the department of aerodynamics, Aachen 1929.

The High Frequency Factors of "Unimolecular" Reactions

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November 18, 1948

IT was shown by Polanyi and Wigner[1] that the frequency factor of unimolecular reactions should be of the order 10^{13} sec.$^{-1}$. The further elaboration of this subject[2] introduced various coefficients (e.g., the transmission coefficient, the quantum restrictions, and so on), which may account for the changes in the magnitude of the frequency factor, and in particular enable us to explain the low values of this quantity. Indeed, a review of the experimental data shows that the frequency factors of the "true" unimolecular reactions are preferentially of the order of 10^{12}–10^{14} sec.$^{-1}$, and the data obtained for reactions in which molecules are decomposed by the breaking of one bond only[3] are especially illuminating.

It was claimed, however, that in some "unimolecular" reactions (these include decomposition of some explosives) the frequency factors attained values as high as 10^{24} sec.$^{-1}$.* As the treatment mentioned before does not offer any explanation of such high values of the frequency factor, we suggest here an approach which, we hope, will provide a basis for further elaboration.

In order to illustrate our suggestion we shall make use of a purely hypothetical scheme for the thermal decomposition of propylene as follows:

$$CH_2=CH-CH_3\rightarrow CH_2=CH-CH_2\cdot+H, \quad (1)$$

$$CH_2=CH-CH_2\cdot\rightarrow CH_2=C=CH_2+H, \quad (2)$$

$$CH_2=CH-CH_3+H\rightarrow CH_2=CH-CH_2\cdot+H_2. \quad (3)$$

The investigation of the pyrolysis of propylene[4] seems in fact to indicate that the reactions (1), (2), and (3) represent the first steps in the thermal decomposition of that compound. Let us now assume that reaction (3) is much faster than reaction (2), while the latter is much faster than reaction (1), and that reaction (2) is *the only* one which consumes allyl radicals. Such assumptions lead to a decomposition mechanism in which the allyl radicals *do not attain* the stationary concentration. Their concentration increases as a consequence of reaction (1), whereas the net result of the reactions (2) and (3) does not affect the concentration of allyl radicals.

To find the rate of the over-all reaction we shall discuss first a special case, in which the percentage of decomposition is kept so low that we can consider the concentration c of propylene as a constant throughout the whole time of the reaction (this can be achieved by using a very short time of contact). The rate of formation of allyl radicals is given by $2k_1\cdot c$,** and the concentration of allyl radicals after time t is, therefore, $2k_1\cdot c\cdot t$. The rate of the over-all reaction (which on our assumptions is equal to the rate of formation of allene or H_2) is, therefore:

$$\text{rate of the over-all reaction}=k^{**}=2k_1\cdot k_2\cdot c\cdot t.$$

Let us examine this result more closely. The rate of the reaction is proportional to the first power of the concentration of propylene, and the reaction is, therefore, of the first order for a constant time of contact. On the other hand, the constants k_1 and k_2 represent the constants of the "true" unimolecular reactions (1) and (2), and thus they will have frequency factors of the order of 10^{12}–10^{13} sec.$^{-1}$, and energies of activation E_1 and E_2, respectively. As a result, k^{**} will have a frequency factor of the order of 10^{24}–10^{26} sec.$^{-1}$, and an energy of activation E_1+E_2.

We suggest that this type of reaction is responsible for the very high frequency factors found for some "unimolecular" decompositions. This type of reaction is further characterized by the increase of the rate with the time, which is a principal feature of the decomposition of explosives, and can be expressed in another way by the statement: the quantity of material decomposed is proportional to the square of time.

The generalization of this example is quite simple. The conditions which must be fulfilled in order to obtain the required kinetics are:

1. The molecule A decomposes into B and C; B decomposes easily into the molecule D and a reactive species C_1, while both C and C_1 react rapidly with A, regenerating B.
2. The decomposition of B should be much more probable than any other reaction in which B can participate. This demands a very low reactivity of B and a very low energy of activation for its decomposition, and leads in consequence to the *non-stationary state* for the species B.

In the case discussed the reactivity of the allyl radical is very low (the radical is stabilized by its high resonance energy), and it is probable that at a high enough temperature and a very short time of contact the required conditions would be fulfilled.

The discussion of these kinetics for the case not restricted to a very low percentage of decomposition reveals some interesting features. Returning to our example, let us denote the initial concentration of propylene by C_0 and the concentration of allyl radicals and allene after time t as x and y, respectively. The previously suggested mechanism leads to the following system of differential equations:

$$dx/dt=2k_1\cdot(C_0-x-y) \quad (a)$$

$$dy/dt=k_2\cdot x. \quad (b)$$

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