

Complex Formation Due to Polarization

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In Fig. 1 of this paper, there is an error in the ordinate scale. The correct figure is published here.

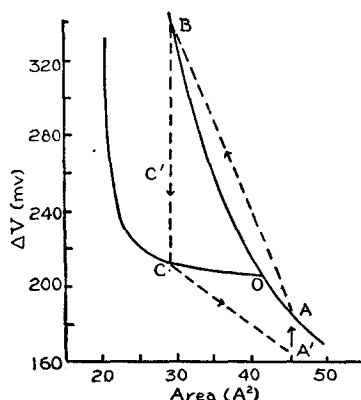


FIG. 1.

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LETTERS TO THE EDITOR

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Complex Formation Due to Polarization

Glockler, Roe and Fuller,¹ in a recent paper under the above title, have investigated the behavior of gaseous mixtures of Kr and HCl, to determine whether the polarization of the former by the polar molecules of the latter is sufficient to yield evidence for the formation of complex molecules. They obtain for B in the familiar equation $PV=RT+BP$, the expression $B = -0.00168N_1^2 - 0.00097N_1N_2 - 0.00445N_2^2$ at $T=328.7^\circ\text{K}$. N_1 and N_2 are the mole fractions of Kr and HCl, respectively. They conclude from the fact that the coefficient of N_1N_2 is not zero that there is interaction between the unlike molecules which is equivalent to complex formation. We wish to point out, however, that any pair of molecules, like or unlike, should show a van der Waals attraction, and to express the opinion that only an attraction in excess of this should be interpreted as the effect in question.

Such an excess does not appear to be present between the unlike molecules in the mixture investigated.

We have calculated the force coefficients for pure Kr and pure HCl by the aid of equations derived by Lennard-Jones,² assuming the attraction exponent to be 7 and the repulsion exponent to be 11. The use of any other probable exponent would not alter our conclusion. If the usual assumption is made that $\lambda_{12} = (\lambda_{11}\lambda_{22})^{\frac{1}{2}}$ where the λ_{12} represents the force constant for unlike molecules, and λ_{11} and λ_{22} those for like molecules, we get for the coefficient of N_1N_2 the value -0.0164 , much larger than the experimental value of -0.00194 . The evidence is therefore against the existence of action between Kr and HCl beyond the normal van der Waals attraction.

The reason for the excess of the calculated over the measured coefficient of N_1N_2 is doubtless to be sought in the fact that λ_{22} is enhanced by the polarity of the HCl

molecules leading to $\lambda_{12} < (\lambda_{11}\lambda_{22})^{\frac{1}{2}}$, as well as in the partial inapplicability of the equations of Lennard-Jones. The mixture in question doubtless belongs to the type frequently encountered in the liquid state (where the molecular crowding brings out clearly the effects of molecular fields) which deviates positively from the ideal solution laws, often to the extent of forming two liquid phases.

We admit that the difference between our point of view and that of Glocker and co-workers is largely one of definition. The division of intermolecular forces into distinct types is doubtless rather arbitrary but we believe that if one is to admit one type, such as polarization forces, one can hardly avoid considering the van der Waals forces which arise from electron interaction regardless of the presence of dipole forces.

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Department of Chemistry,
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Berkeley, California,
September 21, 1934.

¹George Glocker, C. P. Roe and D. L. Fuller, J. Chem. Phys. 1, 703 (1933).

²Lennard-Jones, Proc. Roy. Soc. London A106, 463 (1924); 115, 334 (1927).

Complex Formation Due to Polarization Definition of a Molecule

In the foregoing note Hildebrand and Wood express that the system Kr-HCl contains no complex structures but that the interaction between the unlike molecules is due to van der Waals forces only. I am indebted to Professor Hildebrand for his kindness in letting me see their remarks before publication.

I would like to reply as follows: To the view that the interaction between a krypton atom and an HCl molecule is no more due to complex formation than is the interaction between two krypton atoms I would readily subscribe. The difference of our points of view is one of definition only as Hildebrand and Wood state. I would like to take this opportunity to express my view regarding the matter of molecule formation and the definition of a molecule.

The complete picture of the interaction by two hydrogen atoms as described by Eisenschütz and London¹ shows that the two atoms at large distances react towards one another by attractive forces (interpreted as the van der Waals forces) and as they approach they disturb one another more and more, exchange-forces between the electrons come into play and the forces of valency will finally hold the two atoms together into a molecule. Even though the approach be in the antisymmetric state, still, at large distances, the two atoms will have a potential minimum (very small, only 0.001 e.v. at about 2Å). Two helium atoms approaching one another will also show a potential minimum. They will not form a molecule of great stability to be sure; but there is possible a situation (potential minimum) where no forces are acting between the two helium atoms (neither repulsion or attraction, $dV/dr=0$).

Now the question arises: What structure shall we call a molecule? I am tempted to define a molecule as "*any configuration of two or more atoms, simple molecules or radicals which show a potential minimum.*" This will include all coordination compounds and simple molecules of the non-polar and polar type. I do not think that this definition is too broad. It leads me to suppose that there exist molecules of varying stability. I am thinking of a whole series of structures to be called molecules. On one end of the series I would place the structure (He-He) made up of two helium atoms held together by van der Waals forces only and on the other end of the series I would place such a perfect molecule (in the ordinary sense) as H₂. However in between these two extremes I can think of a whole gradation of interactions and I believe no sharp break exists in the series mentioned. One cannot tell, in a given case somewhere in the middle of the series, whether valency forces or van der Waals forces are the predominant character of the force holding the structure together.

For when one considers the analysis of Eisenhütz and London concerning the approach of two hydrogen atoms then one sees that the reason the energy comes out as a sum of terms

$$E = E_1 + E_2 + \dots$$

is because we have made it so. It is because we had to solve the problem by perturbation methods that the result has been produced in the form of a series. And then we interpret the first approximation as valency-forces (Heitler-London) and the second term as polarization interaction² and so forth. How would the story read had we been able to solve the mathematical problem of the wave equation for two atoms completely without recourse to perturbation theory and without approximation? I believe the solution would be such that the various forces (at large and small distances) would merge into one another in a way that we could *not distinguish them and separate them into classes* depending on distance such as valency forces and van der Waals forces.

Many ideas come to my mind but I would like to mention two more points of argument. In the case of adsorption for example one finds oxygen adsorbed on tungsten with an enormous heat of adsorption (valency forces according to Langmuir) and for example argon adsorbed on KCl (held by London forces as per F. V. Lenel³). Some heavy organic molecules decompose on heating and do not evaporate, because the interaction between molecules is greater than the bonding between the parts or greater than the activation energy needed to cause them to decompose. In this connection I am reminded of a paper by Briegleb⁴ where similar views are put forth.

When one then considers the above view one gets the idea that any interaction between two atoms is a sign of incipient molecule formation. So two krypton atoms interact to be sure very feebly but nevertheless krypton is an imperfect gas and the second virial coefficient $B_{11} \neq 0$. And so if B_{12} for HCl-Kr mixtures is greater than zero then the two unlike atoms show a beginning tendency to interact.

The main idea I wish to present is the view that the separation of the forces acting between atoms into valency