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Complex Formation due to Polarization. II. The System Propane and Hydrogen Chloride

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Molecules of saturated hydrocarbons are rare gas-like in structure and they may be supposed to behave in many respects like rare gases. They may then be expected to show complex formation with other molecules or atoms of dipole character, depending on their own polarizability (preceding article). An experimental study of the *P-V-T* relations of the gaseous mixtures of propane and hydrogen chloride shows that interaction does indeed take place between

these two types of molecules. The expression for the second virial coefficient as a function of composition of the gaseous mixtures, is shown to require an interaction term between unlike molecules in order to agree with experiment. This question of complex formation of saturated hydrocarbons is further discussed on the basis of Brönsted's theory of acids and bases.

INTRODUCTION

IN a former paper² the question was discussed as to whether or not rare gas atoms had any chemical properties in the sense that they could react with other atoms or molecules to form chemical compounds. It was shown that compounds of the usual valency type were energetically unstable if they involved a rare gas atom as one of the reaction partners. However, evidence was cited to show that the rare gases could form loosely-bound structures with other molecules and that such complexes could be more easily formed if the rare gas in question had a large polarizability and if the other reaction partner had a high dipole moment. It is, of course, well known that methane for example is very much like a rare gas.³ It may then be expected that rare gas-like molecules such as methane should show a similar behavior to the rare gases in the sense that methane should show no further chemical reactivity by *addition*. That is, primary valency compounds of methane which involve an electron pair either by sharing or transfer are probably energetically impossible, and they are not known. However, secondary

complexes of the hydrate type may be expected. More generally solvates may be formed or at least a further interaction between a hydrocarbon of large polarizability and a permanent dipole molecule or an excited atom may be possible.

HYDRATES OF HYDROCARBON MOLECULES

Hydrocarbon molecules may then form complex secondary structures with molecules such as water, especially if, they themselves have large polarizabilities. Hydrates of the hydrocarbons have been described by Frocrand⁴ (Table I) and

TABLE I.

	CH ₄	C ₂ H ₆	C ₃ H ₈	C ₂ H ₄	C ₂ H ₂
Polarizability $\alpha \times 10^{24}$	2.6	4.5	6.3	4.0	3.5
Hydrates	6H ₂ O	7H ₂ O	—	7H ₂ O	6H ₂ O

these complex secondary structures seem to be held together by forces due to the induced polarization of the hydrocarbon and the consequent interaction of the field of the induced dipole with that of the permanent dipole of the water molecule.

ISOELECTRONIC SYSTEMS

Just as the consideration of isoelectronic systems in the case of rare gases led to the view

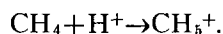
¹ This article is based upon a thesis presented to the faculty of the Graduate School of the University of Minnesota by Donald L. Fuller in partial fulfillment of the requirements for the degree of Doctor of Philosophy.

² See preceding article, *J. Chem. Phys.* **1**, 703 (1933).

³ Geo. Glockler, *J.A.C.S.* **48**, 2021 (1926).

⁴ M. deFrocrand, *Comptes Rendus* **135**, 959 (1902).

that they may have a small residual affinity for protons, so again it may be supposed that the rare gas-like hydrocarbons should have a similar property. For our purposes the important question suggested by the theory of pseudo-atoms is: Does the methonium ion exist? That is, is it conceivable that a proton may enter the complete octet of methane or a similar hydrocarbon in accordance with the equation:

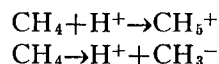
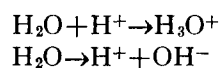
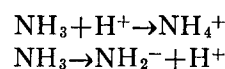


At once it is realized that high polarizability of the hydrocarbon molecule would be advantageous, for then the forces of interaction would be largest. The idea that a complete structure like a saturated hydrocarbon can react further with other molecules by addition arises then in two ways: (1) because of its polarizability other molecules or ions can further interact with it; and (2) it may have a proton affinity like an iso-electronic system of similar structure. These two points of view remind one strongly of the situation encountered in discussing so-called primary valency compounds on the basis of ordinary valency principles, and on the basis of Werner's theory of coordination compounds.

BRÖNSTED THEORY OF ACIDS AND BASES

The question raised as to a possible proton affinity of saturated hydrocarbon molecules can be put into another language. It can be asked: Has the methane molecule any acidic or basic properties? On the principle of Brönsted,⁵ that any substance able to give up a proton is of acid character and any substance able to take on a proton is of basic character, the above question is quite proper. On these modern views such molecules as ammonia and water are basic in nature when it is considered that they will add protons to form ammonium and hydronium ions. But they also ionize to a slight extent into hydrogen ions and they therefore exhibit also acid properties. Ultimately it is found to be the surrounding medium which determines the predominant acidic or basic characteristics of the substance in question. In this way it may be expected to find that methane acts like a base if

it is brought into contact with a substance which gives protons readily, that is, an acid in the Brönsted sense. Of course the basic character of methane may be very weak and it may be difficult to discover evidence of it. However, the formation of hydrates noted above seems to indicate that even such a symmetrical molecule as methane shows the incipient stages of basic action. Substitution of other radicals for the hydrogen atoms of methane will no doubt have great influence upon the basic or acidic character of the resulting molecule. Such methano acids and bases have been considered by E. C. Franklin.⁶ The basic and acidic character of the highly symmetrical methane molecule would be expected to be very slight but, to deny the existence of these properties would be to remove a very reasonable method of accounting for these hydrates. While the possible basic character of saturated hydrocarbons is the main topic for consideration in this paper it is of interest to recall that the acid character of substituted methanes is very marked as pointed out by Franklin. For example the substitution of a "CH" radical for three of the hydrogen atoms of the molecule of methane will make the hydrogen atom in the resulting acetylene so "acidic" that it is easily replaceable by metals such as silver and copper, and the well-known acetylides result. Cyclopentadiene, indene and fluorene are hydrocarbons which behave in the same manner. They have hydrogen atoms in their structure which are replaceable by metals and Franklin considers these structures as substituted methano acids. It seems then possible to consider that methane is amphoteric in character like ammonia and water.



While such reactions of methane probably happen only to a very slight extent, the possibility of such behavior must be admitted.

⁵ J. N. Brönsted, *Chem. Rev.* **5**, 231 (1928).

⁶ E. C. Franklin, *J.A.C.S.* **46**, 2137 (1924).

BAND SPECTROSCOPY AND QUANTUM MECHANICS

While evidence of a very interesting nature was at hand for "rare gas mercury" molecules obtained by Oldenberg² who showed the existence of band spectra carried by complex molecules, and while further progress is being made in their interpretation⁷ no such experimental evidence has as yet been procured for rare gas-like molecules such as the saturated hydrocarbons.⁸ The quantum mechanical arguments of London⁹ on the other hand are entirely general, and they are therefore applicable to the case at hand, and on this basis one might again predict with confidence that saturated hydrocarbons can interact with permanently polar molecules or with excited atoms which have dipole moments due to their excitation.

MASS-SPECTROSCOPY

Lukanow and Schütze¹⁰ mention the possibility that ions of mass 17 could be hydroxyl ions (OH^+) or methonium ions (CH_5^+) and they find ions of mass 18 (H_2O^+ or CH_6^+) and mass 31 (C_2H_7^+). In themselves these experiments furnish no proof that these ions possess the proposed structures, but taking these suggestions together with similar ideas regarding complexes between rare gases and protons they stand in a better light than that of mere speculation. Such charged ions should as a matter of fact be really more stable than the neutral complexes studied in this research, because the forces acting between an ion and a polarizable molecule will be stronger at a given distance of separation than in the neutral case. It is also interesting to remember in this connection that the existence of the ion H_3^+ is fully established by the methods of mass-spectroscopy¹¹ while the evidence for the existence of H_3 molecules is mostly negative. The interaction between $\text{H}_2 + \text{H}^+ \rightarrow \text{H}_3^+$ would be greater than the interaction between $\text{H}_2 + \text{H} \rightarrow \text{H}_3$. If a neutral H_3 should be formed in accordance with Heitler-London spin-theory or ordinary

valency consideration, then the Pauli principle would have to be considered, and the resulting odd molecule would have one of its electrons in some excited state.

INTERMOLECULAR FORCES

The various lines of evidence presented so far make it very plausible that a saturated hydrocarbon like "propane" and a dipole like "hydrogen chloride" should form complex structures by interaction. Propane was chosen for experimental investigation because the influence of the two methyl-groups was thought to have a tendency to make the remaining hydrogens on the central carbon atom more "basic" than in the case of methane. It was then expected that interaction could be demonstrated by studying the pressure-volume-temperature relations of mixtures of propane and hydrogen chloride. These experimental data will permit the determination of the "second-virial coefficient" for the various gas mixtures. The variation of this coefficient with composition should then indicate interaction between the unlike molecules of the mixture.² The pressure-volume relations should be given by

$$PV = RT + BP \quad (\text{for one mole of gas}) \quad (1)$$

where the second virial coefficient is

$$B = b_{11}(1-x)^2 + 2b_{12}(1-x)x + b_{22}x^2. \quad (2)$$

The quantities b_{11} , b_{12} and b_{22} are integrals showing the interaction of like and unlike molecules

$$b_{\alpha\beta} = \int_{V_{\alpha\beta}} (e^{-E_{\alpha\beta}/RT} - 1) dW_{\beta}. \quad (3)$$

The other symbols have the following meanings: P = pressure, T = abs. temperature, R = gas constant, x = mole fraction of gas No. 1.

$E_{\alpha\beta}$ = interaction energy between molecules of type α and β where α and β may refer to the same or different species. The parabola expressed by Eq. (2) is to be determined experimentally for the propane-hydrogen chloride system, and it is to be decided whether or not the term in b_{12} is needed in order to make experiment fit the curve of Eq. (2). It is important to note that the interaction integral b_{12} need not be evaluated in order to find out whether or not interaction between unlike

⁷ W. Finkelburg, *Zeits. f. Physik* **81**, 781 (1933).

⁸ Such work is being undertaken in this laboratory.

⁹ F. London, *Zeits. f. physik. Chemie* **11B**, 222 (1931).

¹⁰ H. Lukanow and W. Schütze, *Zeits. f. Physik* **82**, 610 (1933).

¹¹ T. R. Hogness and E. C. Lunn, *Phys. Rev.* **26**, 44 (1925).

molecules exist. It is seen that the integrand is "zero" if the interaction energy $E_{\alpha\beta}$ is zero. This situation applies even if the interaction energy is a function of the angle coordinates as well as of the distance r from the molecule. In the case of interaction involving a dipole like hydrogen chloride the interaction energy is evidently a function of the angles as well as of distance, but still it is possible to use the Eq. (2) to deduce the existence of interaction between propane and hydrogen chloride.

APPARATUS, DATA AND RESULTS

The apparatus used in this study of the pressure-volume-temperature relations of propane-hydrogen chloride mixtures has already been described² and we need only show the results of these experiments. The $PV-P$ relations for propane, hydrogen chloride and their mixtures are shown in Fig. 1 and the data are given in Table II. The numbers given were

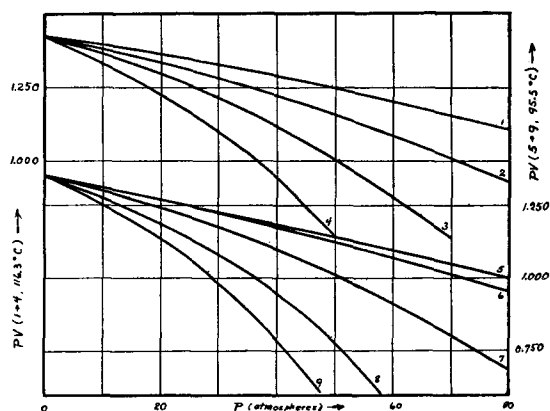


FIG. 1. $PV-P$ isothermals for HCl-propane mixtures. ($PV=1$, when $P=0$ and $T=0^\circ\text{C}$). Data of curves 1-9 from Table III.

calculated from the original observations taking $PV=1$ at $P=0$ and $T=0^\circ\text{C}$. Two temperatures have been employed: 95.5°C and 116.3°C . From these data the second virial coefficient B has been obtained at 40 atmospheres pressure at the two temperatures for the various mixtures. The best parabolas which will fit the $B-X$ experimental relations have been calculated by the method of least squares. These experimental parabolas are then compared with the expression (2).

TABLE II. $PV-P$ measurements for propane hydrogen chloride mixtures. $X = \text{mol-fraction of HCl}$.

$\frac{X}{T}$	P	0	0.236	0.499	0.850	1.00
116.3°C	0	1.423	1.423	1.423	1.423	1.423
	20	1.227	1.290	1.330	1.360	
	40	0.956	1.115	1.220	1.290	
	60		0.880	1.084	1.202	
	80			0.929	1.108	
	100				1.007	
95.5°C	0	1.350	1.350	1.350	1.350	1.350
	20	1.133	1.179	1.242	1.268	1.270
	40	0.786	0.950	1.102	1.174	1.184
	60			0.913	1.070	1.093
	80			0.688	0.955	.994
	100				0.825	.886

TABLE III. Experimental values of B . Propane-hydrogen chloride.

$-B = 0.017(1-X)^2 + 0.00398(1-X)X + 0.00388X^2$						
40 atm.	X	0	0.236	0.499	0.850	1.000
116.3°C	$-B$	0.01710	0.01075	0.00618	0.00398	0.00370
$-B = 0.022(1-X)^2 + 0.00484(1-X)X + 0.00472X^2$						
40 atm.	X	0	0.236	0.499	0.850	1.000
95.5°C	$-B$	0.0220	0.0138	0.0095	0.00485	0.00445

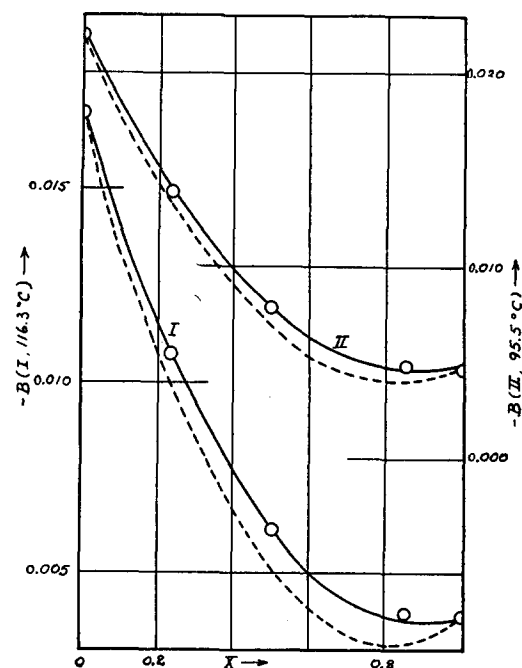


FIG. 2. $B-X$ curves for HCl-propane mixtures. Unbroken curves, $B = b_{11}(1-X)^2 + b_{12}X(1-X) + b_{22}X^2$. Broken curves, $B = b_{11}(1-X)^2 + b_{22}X^2$.

DISCUSSION OF RESULTS

The comparison of the experimental B - X relation with the terms of Eq. (2) is shown in Fig. 2. It is at once seen that the interaction term b_{12} is needed to make experiment fit the theoretical parabola and that it is of the same sign and lies between the values of b_{11} and b_{22} . Therefore these

experiments indicate that *propane molecules interact with hydrogen-chloride molecules, and on the basis of the various points discussed in the introduction it is believed that these results may be taken as further proof for the existence of complex polarization molecules of propane and hydrogen chloride.*