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Complex Formation due to Polarization. I. The System Krypton and Hydrogen Chloride

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Rare gases form compounds of a loose complex nature such as hydrates, solvates or mercury complexes. Such molecular aggregates contain a molecule of permanent dipole moment or an excited atom or molecule of dipole character as the other reaction partner besides the rare gas. The forces holding the complex molecule are the attraction between the permanent dipole and the dipole induced in the rare gas molecule due to its polarizability. Five lines of evidence are cited which indicate the formation of such complex molecules: (1) Band spectra of complex

HgA and HgKr are known. (2) Rare gas hydrates have been described. (3) Isoelectronic systems similar to the rare gases have proton affinity. (4) Rare gas hydride ions have been found in the mass-spectrograph. (5) The *P-V-T* relation of gaseous mixtures show that interaction between the unlike molecules exists. The second Virial coefficient is determined experimentally for Kr-HCl mixtures as a function of composition and it is shown that interaction exists between the rare gas atom Kr and the permanent dipole HCl.

INTRODUCTION

THE rare gases are usually considered to be chemically nonreactive although periodically the preparation of some chemical compounds involving rare gases is announced.² In this paper we wish to discuss this question and make clear the distinction between "primary valency compounds" and "complex molecules" involving the rare gases. Whenever the possibility exists for the formation of an electron pair,³ then the usual valency forces are acting. However, the further possibility exists that atoms which cannot react in the normal state with other atoms or molecules may still form complex structures on account of the van der Waals force field⁴ which surrounds them. It will be shown that hydrate formation and the behavior of rare gas molecules toward dipole structures in general give evidence of such loosely bound molecular complexes held together by polarization forces.

One of the latest attempts to produce chemical compounds involving a rare gas has been described by Antropoff⁵ who has studied the reaction between chlorine and krypton in electrical discharge. He believes that a compound "krypton chloride" is possible. That such a compound cannot be held together in the ordinary way by primary valency forces, may be shown quite definitely by the use of thermodynamic arguments involving a Born-Haber cycle. Grimm and Herzfeld⁶ show that hypothetical KrCl is endothermic to the extent of 95,000 calories. If it be supposed that the compound be salt-like with chlorine as the positive ion in the crystal-lattice, then it can be shown that the hypothetical "chlorine kryptide" would be endothermic to the extent of 165,000 calories, if the electron affinity of Kr is zero and the grating energy is that of RbCl. Either of the two structures considered seems then energetically impossible mainly because of the high ionization potentials. If the two elements krypton and chlorine really combine, then the resulting compound must have a different structure from the salt-like configurations assumed so far. The bond of the hypothetical molecule KrCl may be made between an excited state of krypton and

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

² Gmelin-Kraut, *Handbuch Inorg. Chem.* 8th Edition. Verlag Chemie, Leipzig-Berlin (1926). Mellor, *Inorg. Chem.* Vol. VII, Longmans, Green & Co., London (1927).

³ G. N. Lewis, *Valence and the Structure of Atoms and Molecules*. Chemical Catalog Co., N. Y. (1923). Heitler and London, *Zeits. f. Physik* **44**, 455 (1927).

⁴ F. London, *Zeits. f. Physik Chemie* **11B**, 222 (1931).

⁵ A. von Antropoff, *Naturwiss.* **20**, 688 (1932).

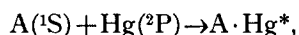
⁶ Grimm and Herzfeld, *Zeits. f. Physik* **19**, 141 (1923).

the normal state of chlorine, and the resulting energy rich molecule may at least have transient existence. Compounds of the rare gases of the ordinary valence type are then not to be expected and we shall next consider the evidence for more loosely bound structures or complex molecules of a van der Waals type.

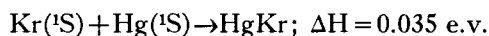
EVIDENCE FROM BANDSPECTRA

Complex molecules which have their origin in the combination of one excited and one unexcited atom are well known in band spectroscopy.

Oldenberg⁷ has studied band spectra excited by fluorescence with $\lambda 2537\text{\AA}$ in mixtures of rare gases and mercury vapor, and he explains these spectra by means of the assumption that molecule formation is possible not only between normal rare gas atoms and excited mercury atoms



but that normal atoms of the two species considered can also combine into loosely bound structures of the type HgKr and HgA :



The small value of the heat of dissociation is readily understood, for the forces acting between these atoms are due to their mutual polarization. Oldenberg favors the view that the normal state of these molecules has a definite system of vibrational levels and a definite heat of dissociation. Another interpretation due to Condon⁸ is to suppose that the normal state of the complex molecule $\text{A} \cdot \text{Hg}$ is essentially repulsive and that maxima of intensity in the true continuum are really not bands in the ordinary sense but are due to the oscillatory behavior of the wave functions describing the system and its transitions. The possibility of such interaction exists because the excited mercury atom possesses a high dipole moment, and it can therefore polarize the rare gas atom. The same type of interaction might then be expected between normal rare gas atoms and other normal atoms or

molecules possessing permanent dipole moments such as hydrogen chloride and water resulting in the formation of a structure of greater complexity.

RARE GAS HYDRATES

The formation of hydrates of gases was studied very early⁹ and the heavier rare gases form such hydrates. It is interesting to note that the stability of the rare gas hydrates increases with increasing atomic weight and polarizability of the rare gas.

ISOELECTRONIC SYSTEMS

However, an entirely different point of view gives rise to the same ideas. This point of view is based on octet theory of atomic structure and has been stated by Grimm.¹⁰ An atom and a molecule are said to be isoelectronic systems if they have the same outer electronic configuration. They are also called pseudo-atoms. For example hydroxyl ion (OH^-) is a pseudo atom of fluorine. Table I gives such related structures. The

TABLE I. *Isoelectronic systems.*

				Ne	Na^+
			F	HF	NeH^+
	O	OH	OH	H_2O	$\text{H}_2\text{F}(?)$
	NH	NH_2	NH_2	NH_3	H_3O^+
C	CH	CH_2	CH_3	CH_4	NH_4^+
					CH_5^+

formation of NH_4^+ and H_3O^+ follows very simply on the basis of these considerations. A study of the table immediately suggests that perhaps neon and methane may possess a slight proton affinity like water and ammonia. This entirely different view then leads also to an understanding of the existence of hydrates of the rare gases and it suggests possible complex structures between rare gas molecules and hydrogen chloride. This point of view would, however, lead one to consider these structures as "primary valency" compounds.

APPLICATION OF QUANTUM MECHANICS

Recently quantum mechanics has been applied to this problem with considerable success. The

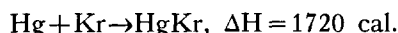
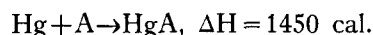
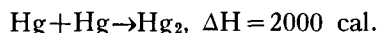
⁷ O. Oldenberg, *Zeits. f. Physik* **55**, 1 (1929).

⁸ E. U. Condon, *Phys. Rev.* **32**, 858 (1928).

⁹ M. de Frocrand, *Comptes Rendus* **135**, 959 (1902); M. P. Villard, Thesis, Paris, 1896.

¹⁰ H. Grimm, *Zeits. f. Electrochemie* **31**, 474 (1925).

simplest case of proton affinity has been studied by Unsöld¹¹ who has given a theoretical solution of the problem: $H+H^+\rightarrow H_2^+$. The problem of weak or van der Waals molecules has been considered by Eisenschütz and London¹² who give a perturbation method for the calculation of the mutual energy of two molecules at large separation. In this calculation the following forces are considered: (1) the mutual interaction from the electronic motions of the molecule; (2) the polarization of the electron shell of one atom by a permanent field of the other when the latter possesses electric asymmetry; and (3) the ordinary electrostatic forces between two asymmetric molecules. London⁴ was thus able to calculate the order of magnitude of van der Waals a and to find the heats of such reactions as



In all cases the results are in good agreement with the band spectra evidence mentioned above.⁷ Margenau¹³ has extended the problem by calculating interactions due to quadrupoles.

MASS-SPECTROSCOPY

Consideration of Table I shows that the rare gas atoms may have a tendency to combine with charged ions to form more complex gaseous ions of the type HeH^+ , NeH^+ , etc. It is interesting to note that workers in the field of mass-spectroscopy have found evidence of such structures. The following ions have been observed:¹⁴⁻¹⁷ $(HeH^+)^+(5)$, $(HeH^2)^+(6)$, $(HeH^1H^1)^+(6)$, $(NeH)^+(23)$ and $(ArH)^+(41)$. The experimental evidence favors the view that the proton is outside the nucleus because in the case of helium for example the mass found is 5.01 and not 5.00

¹¹ A. Unsöld, *Zeits. f. Physik* **43**, 563 (1927).

¹² Eisenschütz and London, *Zeits. f. Physik* **60**, 491 (1930).

¹³ H. Margenau, *Phys. Rev.* **38**, 747 (1931).

¹⁴ T. R. Hogness and E. C. Lunn, *Phys. Rev.* **26**, 44 (1925).

¹⁵ H. Lukanow and W. Schütze, *Zeits. f. Physik* **82**, 610 (1933).

¹⁶ K. T. Bainbridge, *Phys. Rev.* **43**, 103; **44**, 57 (1933).

¹⁷ H. Kallmann and W. Lasareff, *Naturwiss.* **20**, 206 (1932).

which latter value would be expected if the ion considered were an isotope of helium.

INTERMOLECULAR FORCES

It was expected that some evidence of molecule formation could be obtained at high pressures by studying the pressure-volume-temperature relations of gaseous mixtures of krypton and hydrogen chloride. By such experimental studies we hope to contribute evidence for the existence of loose complex molecules involving the rare gases. A good summary of the theory of imperfect gases has been given by Fowler.¹⁸ According to this treatment the theory of molecular interaction in a binary gas mixture leads to the following equation

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

where

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

and

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

and P =pressure, T =abs. temperature, R =gas constant, B =second virial coefficient, x =mole fraction of gas No. 1.

$E_{\alpha\beta}$ =interaction energy between molecule α and β , where α and β may refer to the same or to different species. From these equations it is seen that $b_{\alpha\beta}$ will be zero if $E_{\alpha\beta}$ is zero. In other words *the existence of interaction between molecules of type α and type β can be determined by studying the second virial coefficient B and noting whether or not the interaction term b_{12} is necessary for the description of B as a function of composition.* This study is made by investigating the pressure-volume-temperature relations of a gaseous mixture such as krypton and hydrogen chloride. Krypton was chosen because it has a high polarizability and no chemical reactivity in the ordinary sense; hydrogen chloride was chosen because it has a large permanent dipole moment.

APPARATUS

An apparatus has been designed for studying the pressure-volume-temperature relations of

¹⁸ R. H. Fowler, *Statistical Mechanics*, Ch. VIII, page 171, Eq. (487). Cambridge University Press, 1929.

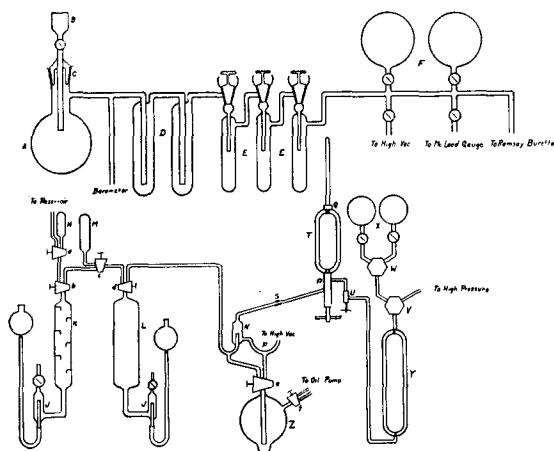


FIG. 1. General plan of experimental system.

systems between -40°C and $+250^{\circ}\text{C}$ and at pressures from 1 to 200 atmospheres. A general outline is given in Fig. 1. An improvement over the usual Cailletet apparatus¹⁹ was made by connecting permanently the high pressure parts of the system to the supply and vacuum sections so that it was unnecessary to dismantle the capillary for each refilling. The hydrogen chloride is generated in flask *A* from H_2SO_4 and NaCl , dried with P_2O_5 , purified by sublimation and stored in flask *F*. The krypton was obtained from a commercial source and was not further purified. The pure or mixed gases were measured in the Ramsay burette *K* and run into the Toepler pump *L*. The needle valve *U* was closed and the large valve *R* was opened and the entire system to stopcocks *d* and *e* evacuated to 10^{-4} mm Hg. Now the gas in *L* was led into the cylinder *T* (1000 cc) and capillary *Q*. After *R* was closed *U* was opened and the gas compressed with mercury as a confining liquid. The upper part of *Y*, which was connected directly to the gauge tester by means of the joint at *V*, was filled with glycerine; the lower end of *Y* was filled with mercury. This arrangement was necessary in order to prevent mercury from making contact with the gauge tester. The gauges which were calibrated with the piston tester are shown at *X*.

In making the P - V - T measurements the pressure was noted when the mercury meniscus just reached one of the eight finely etched

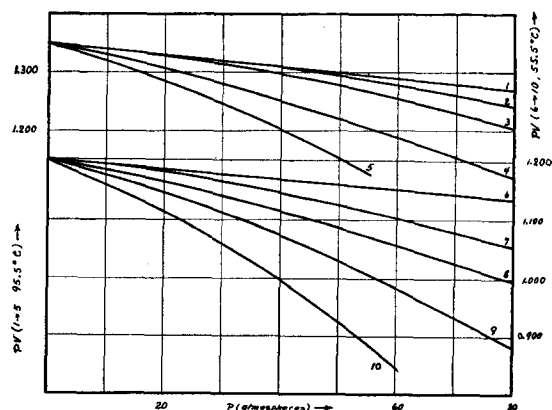
calibrating marks on the capillary which was 40 cm long and 0.2 cm internal diameter. The temperature was easily controlled by the vapors of ether, acetone, ethyl alcohol, and propyl alcohol at their boiling points. The capillary was surrounded by a long unsilvered Dewar flask ($20 \times 3''$), and was calibrated by weighing the amounts of mercury between the marks. This was done by sealing the end of the capillary and filling to the desired mark with mercury from a still finer capillary. A correction was made for the inverted meniscus.

DATA AND RESULTS

We shall only give a summary of a large amount of data on krypton and hydrogen chloride and their mixtures. The PV - P relations are shown for two temperatures in Fig. 2 and the needed data are collected in Table II.

TABLE II. PV - P measurements for krypton-hydrogen chloride mixtures. X = mole fraction HCl .

X T	P	0	0.263	0.492	0.729	1.000
95.5°C	0	1.350	1.350	1.350	1.350	1.350
	20	1.328	1.328	1.325	1.301	1.286
	40	1.305	1.310	1.295	1.249	1.207
	60	1.283	1.277	1.248	1.189	1.112
	80	1.261	1.243	1.203	1.123	1.006
	100	1.239	1.217	1.167	1.066	0.902
55.5°C	0	1.203	1.203	1.203	1.203	1.203
	20	1.170	1.184	1.164	1.144	1.112
	40	1.137	1.144	1.115	1.073	0.997
	60	1.104	1.097	1.052	0.980	0.845
	80	1.072	1.054	0.995	0.881	0.626
	100	1.038	1.018	0.935	0.780	—

FIG. 2. PV - P isothermals for HCl -krypton mixtures. ($PV=1$ when $P=0$ and $T=0^{\circ}\text{C}$.) Data for curves 1-10 from Table III.

¹⁹ K. Jellinek, Lehrbuch d. Phys. Chemie, Vol. I, pp. 310-936. F. Enke, Stuttgart (1928).

TABLE III. *Experimental values of B. Kr-HCl.*

$-B = 0.00114(1-X)^2 + 0.00102(1-X)X + 0.00309X^2$						
10 atm.	X	0	0.263	0.492	0.729	1.000
95.5°C	-B	0.00111	0.00112	0.00123	0.00192	0.00310
$-B = 0.00168(1-X)^2 + 0.00194(1-X)X + 0.00445X^2$						
10 atm.	X	0	0.263	0.492	0.729	1.000
55.5°C	-B	0.00165	0.00169	0.00196	0.00283	0.00447

The data were calculated from the original observations taking $PV = 1$ at $P = 0$ and $T = 0^\circ\text{C}$. The $PV-P$ curves are given at two temperatures: 55.5° and 95.5°C . Each family of these curves represents mixtures of different compositions for one temperature. It is seen that the second virial coefficient is a function of the pressure at the temperature considered, with exception of pure krypton where curves 1 and 6, Fig. 2, are straight lines over the pressure range studied.

DISCUSSION OF RESULTS

Lennard-Jones²⁰ has shown that for mixtures of molecules with *spherically symmetrical* fields of force, the coefficients b_{11} , b_{12} and b_{22} are given by

$$b_{\alpha\beta} = 2\pi \int_0^\infty r^2 (e^{-E_{\alpha\beta}/RT} - 1) dr$$

where $E_{\alpha\beta}$ is the interaction energy between molecules α and β and from experimental data he was able to find the constants λ , μ , m and n in the force equation

$$\partial E_{\alpha\beta} / \partial r = f(r) = \lambda/r^n - \mu/r^m.$$

In the system HCl-Kr however *the interaction energy is not dependent on r alone but also depends on the angles θ and φ because hydrogen chloride is an asymmetric molecule of dipole character*. The simplified treatment given above is therefore not possible in the case studied. However, it is still possible to show interaction between hydrogen chloride and krypton despite the fact that the force constants cannot be evaluated. Although the second virial coefficient is a function of the pressure at any temperature, it is found that at a given pressure (10 atmospheres for example) B is still a quadratic function of the composition.

²⁰ Lennard-Jones, Proc. Roy. Soc. **A106**, 463 (1924).

Since it is of primary interest to show that b_{12} does not vanish for the case of the system in question, the analytical evaluation of the above integral becomes unnecessary. For B , the second virial coefficient for the mixture, can be experimentally determined as a function of composition. When the data obtained from the pressure volume measurements were used to determine the best parabola that could be fitted to the experimental points, it was definitely found that b_{12} was different from zero in the equation of this parabola. It should be noted, that even if $b_{12} = 0$, the resulting form of B is still a parabola, that is,

$$B = b_{11}(1-x)^2 + b_{22}x^2,$$

and this parabola can be obtained directly from the pressure volume data for the two pure gases. It is immediately found however, that this is in marked disagreement with the experimental facts. The situation is clearly pictured in Fig. 3, where the experimental points are shown by the circles, the best parabola that can be passed through them by the solid line, and the simplified parabola, that is with b_{12} set equal to zero, by the broken line. This last procedure amounts to the omission of interaction between the unlike mole-

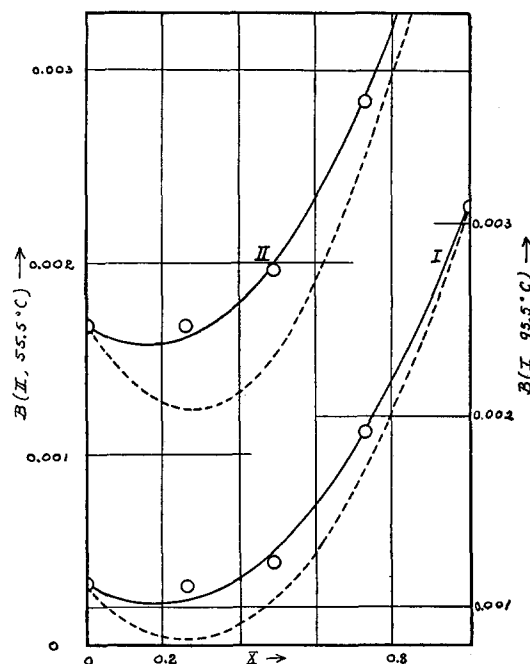


FIG. 3. $B-X$ curves for HCl-krypton mixtures. Unbroken curve, $B = b_{11}(1-x)^2 + b_{12}(1-x)x + b_{22}x^2$. Broken curve, $B = b_{11}(1-x)^2 + b_{22}x^2$.

cules Kr and HCl, while the interaction between like molecules is still considered. It is seen that the resulting dotted curves *do not fit the experimental curves nearly as well as do the parabolas including interaction between unlike molecules.*

The $P-V-T$ relations studied here give then evidence of interaction between a rare gas atom and a permanent dipole molecule. The interaction term b_{12} is seen to be of the same order of

magnitude and of the same sign as the terms b_{11} and b_{22} thus indicating attractive forces (Table III). This result is in keeping with the other lines of evidence obtained from band spectroscopy, hydrate formation, the general behavior of isoelectronic systems (pseudo-atoms) and their proton affinity. This behavior can best be understood on the basis of modern wave mechanics as studied by London.⁴