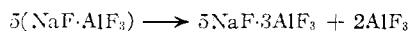


obtained in the collection flasks was a fine, fluffy powder of low apparent density. The particle size distribution was about 75% in the 0-10 μ range and 25% in the 10-20 μ range. The particle shape was rather evenly distributed between short rods and spheres. In still larger scale work with very high gas velocities, 10,000 liters/hour, the particle size distribution was 90% in the 0-2 μ range and 10% in the 2-4 μ range. Table II contains X-ray diffraction data for this new compound.

Properties of Sodium Tetrafluoroaluminate

Solid Phase Transformation.—When a slow gas stream was used in the experiments carried out in the small diameter tubes, crystalline deposits were obtained on the copper liner in the hot zone downstream from the charge and no deposit on the Seitz filter. Chemical analysis showed the weight ratio of NaF/AlF₃ to be about 0.50 or a 1:1 molar ratio. X-Ray powder diffraction analysis, however, showed the crystalline phases present to be largely chiolite mixed with small to medium amounts of aluminum fluoride. This suggested that the vapor phase above the charge consisted of molecules having a 1:1 molar ratio of NaF to AlF₃. If these vapors were rapidly swept from the hot zone, they could be condensed in a cold zone as sodium tetrafluoroaluminate. On the other hand, if the vapors were cooled slowly, a solid phase transformation occurred so that the hot zone deposits consisted of chiolite and aluminum fluoride. The reaction may be expressed by the equation



This theory was substantiated by an X-ray powder diffraction analysis of the deposits collected along the entire length of the tube from experiments using high gas velocities. A typical distribution of the crystalline deposits would be 50% chiolite and 50% aluminum fluoride in the hot zone, 10% chiolite plus 90% sodium tetrafluoroaluminate in the condenser and 100% sodium tetrafluoroaluminate on the Seitz filter. The amount of sodium tetrafluoroaluminate increased toward the cold zone, even though the chemically-determined ratio of NaF/AlF₃ was found to be approximately 0.5 in all cases.

Further substantiation was obtained by showing that sodium tetrafluoroaluminate exhibited a solid phase trans-

formation. The thermal analysis equipment was not sensitive enough to detect the transformation. Therefore, the transformation temperature was bracketed by heating samples of sodium tetrafluoroaluminate containing a trace of chiolite at various temperatures for different time intervals. Examination of the product by the X-ray powder diffraction method showed that the samples held at 470-480° for a very short period of time were almost completely transformed to chiolite and aluminum fluoride, while samples held below 470° showed no change in the crystalline composition over a period of several hours. These experiments showed a transformation temperature above 470°. There is a possibility that the small chiolite impurity may have nucleated the transformation.

To determine whether sodium tetrafluoroaluminate could be formed from the liquid phase, samples at about the 1:1 molar ratio of NaF/AlF₃ composition were fused and the melts quenched by pouring into a large quantity of cold water. X-Ray powder diffraction analyses showed that the quenched samples consisted of approximately 75% sodium tetrafluoroaluminate and 25% chiolite. Slowly cooled melts of the same composition were found to consist only of chiolite and aluminum fluoride.

Thermal Analysis.—Thermal analyses of some of the sodium tetrafluoroaluminate samples and of mixtures of NaF and AlF₃ at about this composition were made by determining heating and cooling curves. A specially-constructed furnace in which the rate of heating or cooling was controlled by differential temperature measurements was used. The charges were held in platinum crucibles and the temperature continuously recorded from a platinum, platinum-10% rhodium thermocouple encased in a platinum tube.

The liquidus temperatures of separate fusions starting with sodium tetrafluoroaluminate and with the 1:1 molar mixture of NaF and AlF₃ were found to be 690 ± 3°. A heat effect presumed to be the solidus was found in the system in both cases at 664 ± 3°. Because of the solid phase transformation previously described, the residue from the sample which was initially sodium tetrafluoroaluminate was chiolite and AlF₃ by X-ray powder diffraction analysis. The residue from the fusion of NaF and AlF₃ also consisted of chiolite and AlF₃.

NEW KENSINGTON, PENNSYLVANIA

[CONTRIBUTION FROM THE RESEARCH INSTITUTE OF TEMPLE UNIVERSITY]

The Fluorides of Permanganic¹ and Perrhenic Acids, MnO₃F and ReO₃F

BY ALFRED ENGELBRECHT AND ARISTID V. GROSSE

RECEIVED NOVEMBER 9, 1953

Pure permanganyl fluoride and perrhenyl fluoride were isolated, some of their physical constants determined, and their chemical behavior investigated. Permanganyl fluoride, MnO₃F, forms dark green crystals, melting at -38° to a dark green liquid and vaporizing to an intense green gas. The boiling point, extrapolated from its vapor pressure at low temperature, is near 60°. It is stable only below 0°. Above this temperature it decomposes, often explosively, to MnF₂, MnO₂ and O₂. It is extremely reactive with organic matter and hydrolyzes instantaneously on exposure to moist air to give deep purple vapors of HMnO₄. Perrhenyl fluoride, ReO₃F, forms a yellow glass or very fine crystalline powder, melting at 147° and boiling at 164° at 760 mm. It is very easily reduced to blue colored rhenium compounds of lower valence states and is immediately hydrolyzed by water to perrhenic and hydrofluoric acids.

Neither one of the acid fluorides of heptavalent manganese and rhenium, MnO₃F or ReO₃F, has been isolated in a pure state. The suitable names of these oxyfluorides as derivatives of the corresponding acids, HMnO₄ and HReO₄, are permanganyl fluoride and perrhenyl fluoride.

Many rather conflicting statements have been made about these compounds. More than a century ago, Wöhler² observed that the green vapors

turned purple violet in air while heating a mixture of potassium permanganate, calcium fluoride and concentrated sulfuric acid in a platinum retort. Since then several chemists³⁻⁶ have confirmed the formation of a green volatile manganese compound when permanganates reacted with anhydrous hydrogen fluoride or fluorosulfonic acid. None of them, however, was able to separate it from hydrogen fluoride and isolate this extremely reactive compound in a pure state. Ruff⁴ questioned even whether the gas contained fluorine and suggested

(1) Presented before the Chemistry Section of the American Association for the Advancement of Science at Philadelphia, Pa., on December 26, 1951; see General Program of the 118th Meeting of the American Association for the Advancement of Science, 1951, p. 140.

(2) F. Wöhler, *Ann. chim. phys.*, [2] **37**, 101 (1828), *Ann. Miner.*, [2] **3**, 163 (1828).

(3) J. Gore, *J. Chem. Soc.*, **22**, 368 (1869).

(4) O. Ruff, *Ber.*, **47**, 658 (1914); "Chemie des Fluors," 1920, p. 115.

(5) K. Fredenhagen, *Z. Elektrochem.*, **37**, 684 (1931).

(6) K. Fredenhagen, *Z. anorg. allgem. Chem.*, **242**, 23 (1939).

that it may be simply the well known manganese heptoxide.

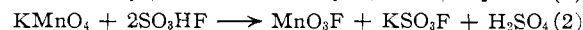
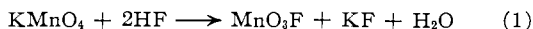
Recently Wiechert⁷ was at least partly successful; he, however, failed to separate hydrogen fluoride completely from his green concentrate.

A similar rather conflicting situation is found in regard to the oxyfluorides of rhenium, particularly ReO_3F , the fluoride of perrhenic acid. In 1934, Ruff and Kwasnik⁸ isolated, besides other oxyfluorides, a rhenium compound which they claimed to have a F:Re ratio of 1:1, and therefore concluded it to be ReO_3F . In a general and recent study of the oxycompounds of manganese and rhenium, Aynsley, Peacock and Robinson⁹ repeated the work by Ruff and Kwasnik, but they were not able to confirm the formation of ReO_3F , ReOF_4 , ReOF_2 and ReO_2F_2 , as reported by them. They succeeded in the preparation of two new oxyfluorides of rhenium, ReOF_5 and ReO_2F_3 , by the reaction of ReO_2 or KReO_4 with fluorine. The same authors question the existence of the green gaseous oxyfluoride of manganese because of their failure to obtain such a compound by the fluorination of Mn_3O_4 , MnO_2 or KMnO_4 with fluorine at temperatures from 100 to 150°. As will be shown in this paper, no formation of MnO_3F is to be expected at this temperature, since MnO_3F is not stable above room temperature.

Wiechert,⁷ in his general investigation of acid fluorides believed that he had obtained ReO_3F from KReO_4 and anhydrous HF, which he thought hydrolyzed to HReO_4 and HF by the water formed simultaneously. He based his conclusion on the 2:1 F:Re ratio found in the residue after evaporating the excess HF. He assumed the residue to be ReO_3F and KF, overlooking the fact that certainly KHF_2 rather than KF would be formed in his reaction. This explains the 2:1 ratio of F:Re, without leaving any fluorine for ReO_3F .

Our use of a vacuum apparatus constructed of copper and Kel-F tubing for the preparation and investigation of chromyl fluoride¹⁰ seemed to make possible the isolation of the rather reactive acid fluoride of permanganic acid.

Pernanganyl fluoride can be prepared by two methods



The second reaction has the advantage of a much easier separation of the MnO_3F from an excess of fluorinating agent. It can easily be separated from the less volatile SO_3HF (b.p. at 760 mm. 163°) by distilling *in vacuo*. However, the problem of separating MnO_3F from HF arises here also, since small amounts of HF are always formed



This impurity of HF can be removed in a second step with excess KMnO_4 , or KF with which HF again forms MnO_3F or KHF_2 , respectively.

The MnO_3F is always accompanied by a small quantity (1–2%) of a brown manganese-containing

(7) K. Wiechert, *Z. anorg. allgem. Chem.*, **261**, 310 (1950).

(8) O. Ruff and W. Kwasnik, *ibid.*, **219**, 65 (1934).

(9) E. E. Aynsley, R. D. Peacock and P. L. Robinson, *J. Chem. Soc.*, 1622 (1950).

(10) A. Engelbrecht and A. V. Grosse, *THIS JOURNAL*, **74**, 5262 (1952).

solid possessing a vapor pressure definitely below that of MnO_3F . No attempts were made to isolate or identify it at this time.

Pure MnO_3F forms very dark green crystals which melt at -38° to a dark green liquid. Even at 0° its vapor pressure is enough to fill the apparatus with its very intense green vapors. The vapor pressure of the liquid was measured in the range of -15° to $+10^\circ$. Values obtained above 0° were not as reliable as those below, because decomposition occurs. These values follow an approximately straight line logarithmic plot and can be expressed by the equation

$$\log_{10} p_{\text{mm}} = 8.2 - 1770/T$$

The extrapolated boiling point at 760 mm. is about 60° . The heat of vaporization of liquid MnO_3F from the above equation is 8100 cal./mole.

TABLE I
VAPOR PRESSURE OF LIQUID MnO_3F

°C.	-15.0	-10.0	0.0	+10.0
mm.	22.5	30	52	90

The microradiowave spectrum of MnO_3F was measured^{11,12} and various molecular constants of the symmetric spinning top molecule were obtained. The quadrupole hyperfine structure confirmed the nuclear spin of $5/2$ for Mn^{55} and gave a quadrupole coupling constant of $+16.8$ Mc.

The oxyfluoride is perfectly stable at Dry Ice temperature and can be kept in the storage vessel for many months without any increase in pressure. Highly pure samples of the fluoride may be handled at room temperature for a short time. On standing longer it decomposes, sometimes rather violently. This explosive decomposition is accompanied by a flame and MnF_2 , MnO_2 and O_2 are formed. It is therefore recommended that samples be kept below 0° and below a pressure of 100 mm. if handled as a gas. If MnO_3F is brought into contact with moist air, the intense violet vapors of Mn_2O_7 or HMnO_4 appear and the sample usually decomposes more or less violently, often accompanied by a flame and a loud report. With excess water the MnO_3F hydrolyses to HMnO_4 and HF.

MnO_3F is a particularly strong oxidizing agent. The liquid and gaseous fluoride reacts violently with organic compounds. It is rather soluble in anhydrous HF, forming a deep green solution, slowly decolorizing and decomposing to MnF_2 and O_2 at temperatures above 0° .

Copper is not attacked at room temperature, thus copper apparatus is recommended for handling the compound. Mercury is immediately attacked by MnO_3F and therefore cannot be used as a manometric fluid, unless protected with a layer of Kel-F oil.

Perrhenyl fluoride was anticipated to be rather similar to MoO_2F_2 ¹³ and much less volatile than MnO_3F ; hence it is unlikely that it can be prepared from KReO_4 and HF,⁷ since H_2O would be formed simultaneously.

(11) A. Javan and A. V. Grosse, *Phys. Rev.*, **87**, 227 (1952).

(12) A. Javan, G. Silvey, C. H. Townes and A. V. Grosse, *ibid.*, **91**, 222 (1953).

(13) O. Ruff and F. Eisner, *Ber.*, **40**, 2931 (1907).

The reaction of KReO_4 with SO_3HF , corresponding to the second possible preparation of MnO_3F , did not yield any volatile rhenium compounds up to the boiling point of SO_3HF . Only HF could be distilled from the Pt tube serving as the reaction vessel. After heating the KReO_4 solution in SO_3HF for some time near the boiling point, the formation of blue colored substances indicated partial reduction of the rhenium compound.

We succeeded in preparing the ReO_3F by the reaction of $\text{ReO}_2\text{Cl}^{14}$ with anhydrous HF and vacuum sublimation of the reaction product after the excess HF had been eliminated by heating.

Pure ReO_3F is a yellow solid, melting at 147° to a very viscous yellow liquid, and boiling at 164° with slight decomposition.¹⁵ It is very reactive, especially with reducing compounds. It is readily hydrolyzed with water and gives fumes on exposure to moist air. It does not react with glass even at its boiling point. It usually forms a glass, but can be obtained crystalline by very slow sublimation in high vacuum. Table II gives a comparison with other oxyfluorides of heptavalent rhenium. The boiling point of ReO_2F_3 , unfortunately, seems not to have been determined exactly⁹ ("it can be distilled without decomposition in a luminous bunsen flame at 200° ") despite the fact that it was reported to be the main product of the fluorination.

TABLE II
OXYFLUORIDES OF HEPTAVALENT RHENIUM

	M.p., °C.	B.p., °C.	Color
ReOF_5^9	34.5	55	Cream
ReO_2F_3^9	90-95	200 ?	Pale yellow
ReO_3F	147	164	Yellow

Somewhat surprising is the thermal instability of the ReO_3F in view of its very stable heptoxide. It slowly turns blue above the melting point, definitely decomposing at the boiling point, giving a dark residue. No thermal decomposition was mentioned with ReOF_5 and ReO_2F_3 .

Experimental

(a) MnO_3F . **Apparatus.**—The apparatus consisted of copper tubing with Kel-F traps and standard refrigeration flare fittings, and the techniques employed were essentially as described previously.¹⁰

Preparation of Crude Permanganyl Fluoride.—A 100-g. (0.63 mole) sample of fine crystals of J. T. Baker analyzed grade potassium permanganate was added very slowly, in small portions, to 250 g. (2.50 moles) of fluorosulfonic acid (General Chemical Co., 98.5% pure), *i.e.*, in a molar ratio of 1:4, placed in a copper flask and cooled in Dry Ice. The flask was then attached to the main train of the apparatus and was allowed to warm up to room temperature very slowly in a vacuum. Green gaseous MnO_3F was condensed in Kel-F traps and cooled in Dry Ice. The crude fluoride was free of fluorosulfonic acid, but contained very small amounts (of the order of 1-2%) of another sublimable manganese compound and variable amounts of HF. These amounts varied depending on conditions prevailing in the reaction flask, *i.e.*, temperature, pressure, ratio of reactants and reaction time, but never amounted to more than a small fraction of the MnO_3F produced. Most of the HF was separated readily by fractional condensation, since it is substantially more volatile (v.p. 184 mm. at -15°) than MnO_3F (see Table I). Quantities of up to 40 g. of MnO_3F

have been prepared in one batch, taking the usual precautions in handling readily decomposable or explosive substances.

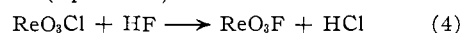
Purification of MnO_3F .—For complete separation of MnO_3F from HF, use was made of the fact that it does not react with KF, while HF forms KHF_2 . A Kel-F trap was filled with small pellets of pure *anhydrous* KF. The crude MnO_3F was distilled into this trap and kept there for a few hours at temperatures below 0° . For final purification this product was redistilled several times. During this purification process traces of the less volatile manganese compound were left behind. Another very simple way to eliminate the HF in MnO_3F is to treat it with excess KMnO_4 , with which HF again forms MnO_3F .

Vapor Pressure and Gas Density.—The vapor pressure of MnO_3F was determined by the static method. Mercury covered with Kel-F oil was used as a manometric fluid. Above 0° slow decomposition occurred, as evidenced by the formation of small amounts of a non-condensable gas (O_2). Results are presented in Table I.

Attempts have been made to determine the vapor density according to the method of Regnault. Partial decomposition of the sample could not be avoided even though all measurements were carried out in a cold room at 5° and the inner surface of the whole apparatus was coated with a protective layer of Kel-F polymer. Since oxygen was formed the values obtained for the molecular weight were substantially too low, *i.e.*, 98-105 (theory 121.9). The micro-radiowave spectrum of MnO_3F proved unequivocally that the molecule was monomeric.

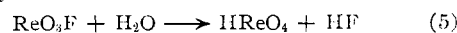
Analysis of MnO_3F .—Pure samples were hydrolyzed with excess ice-water in a polyethylene flask to HMnO_4 and HF. The HMnO_4 was titrated with standard sodium oxalate solution. The same values for Mn were obtained when the HMnO_4 was reduced to Mn^{2+} and precipitated as $\text{Mn-NH}_4\text{PO}_4$. Fluorine was determined as CaF_2 or PbClF . *Anal.* Calcd. for MnO_3F : Mn, 45.05; F, 15.58; Found: Mn, 44.5, 44.6, 44.5; F, 15.6, 15.3; atomic ratio of Mn: F, 1.00.

(b) ReO_3F . **Preparation.**—The ReO_2Cl used was prepared according to the procedure given by Bruckl and Ziegler.¹⁴ Fifteen grams of Re metal was converted to the pure oxychloride which was then distilled into a liquid-nitrogen cooled Kel-F trap containing a threefold excess of anhydrous HF (equation 4).



The Kel-F trap was then connected to a reflux condenser in which the material was exposed to Kel-F and Teflon parts exclusively. On slowly warming to above the melting point of HF, evolution of HCl is noted at the interface of the two compounds (as was first observed by E. A. Nodiff of this Laboratory). The reaction became rather violent if not properly cooled. At first a yellow solid is observed in the form of a fine powder suspended in the HF which gradually replaces the still solid, unreacted ReO_2Cl (m.p. 4.5°). This yellow powder, probably ReO_3F , slowly dissolved to a slightly pink solution when refluxed for about one hour, perhaps forming a soluble HF addition compound. After several hours refluxing, the excess HF was evaporated by heating *in vacuo* to about 80° . At this temperature the impure ReO_3F , now a fine bluish powder, began to sublime to the upper parts of the Kel-F tube, forming a yellow crust. The crude ReO_3F was transferred in a dry-box to a Pt tube connected to Kel-F tubing by means of a Teflon fitting (again excluding contact with any other metal). From this Pt tube, 14 g. of very pure ReO_3F (> 70% yield) was sublimed, forming a yellow glass in the Kel-F tubing.

Analysis of ReO_3F .—The total acidity of the aqueous solution was determined after a known amount of the oxyfluoride was hydrolyzed in water



It should be observed that one molecule of perhenyl fluoride should form two equivalents of acid, *i.e.*, one mole of perhenic acid and one mole of hydrofluoric acid. It was found that 0.492 mmole of perhenyl fluoride corresponded to a total of 0.986 mmole equivalent of acid, in accordance with theory.

The Re content was determined as nitron perhenate, after precipitation as Re_2S_7 and dissolving in NaOH and H_2O_2 . The fluorine was determined as PbClF , and titration of the Cl with AgNO_3 . *Anal.* Calcd. for ReO_3F :

(14) A. Bruckl and K. Ziegler, *Ber.*, **65**, 916 (1932).

(15) For its microradiowave spectrum see: J. F. Lotspeich, A. Javan and A. Engelbrecht, *Bull. Am. Phys. Soc.*, **29**, 52 (1954).

Re, 73.4; F, 7.51. Found: Re, 74.2, 74.0; F, 7.61, 7.60; atomic ratio Re:F, 1.00.

Boiling and Melting Points.— ReO_3F , sublimed a second time was refluxed in a glass tube, heated in a paraffin bath open to the atmosphere through a $\text{Mg}(\text{ClO}_4)_2$ drying tube. It boiled at 164° at 760 mm. Slow decomposition occurred

during the measurement, as indicated by the formation of a dark residue.

The melting point determined in sealed capillary tubes was 147° .

PHILADELPHIA 40, PENNA.

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, NORTHWESTERN UNIVERSITY]

The Possible Existence of a Reduced Potential Energy Function for Diatomic Molecules¹

BY ARTHUR A. FROST AND BORIS MUSULIN

RECEIVED AUGUST 14, 1953

A reduced potential energy is defined as V/D_e , where V is the potential energy, taking the zero for infinite separation of the nuclei. A reduced internuclear distance is defined as $(R - R_{ij})/(R_e - R_{ij})$ where R is the actual internuclear distance, R_e the equilibrium distance, and R_{ij} a constant for a given molecule formed from atoms i and j . It is shown that there exists an approximate universal relation, in the neighborhood of the minimum, between these variables for the ground states of a set of 23 diatomic molecules, chosen only for the accuracy of their experimental data. R_{ij} is interpreted as a measure of inner shell radii and is closely correlated with Badger's d_{ij} .

It is of interest to consider the possibility of a reduced potential energy function of diatomic molecules, *i.e.*, a relation between a "reduced" potential energy and a "reduced" internuclear distance, analogous to a reduced equation of state.

Let V be the potential energy of a diatomic molecule in the ground state or in any attractive excited state taking the zero of energy at infinite separation of the nuclei. Let R be the internuclear distance, R_e being the equilibrium value. At the potential energy minimum $V = -D_e$ where D_e is the dissociation energy (including the half quantum of vibration). Now the simplest kind of reduced potential energy and distance would be defined as

$$V' = V/D_e \quad R' = R/R_e \quad (1)$$

in terms of which variables the P.E. minimum would be at $V' = -1$ and $R' = 1$ for every molecule. A reduced P.E. in this form V/D_e has been used by Puppi^{2a} while Davies^{2b} has used the reduced distance R/R_e . Puppi actually derived a reduced functional relation—his reduced distance variable being

$$y = \frac{R - R_e}{R_e \sqrt{D}}$$

This was obtained by assuming a Morse P.E. function and introducing an empirical relation equivalent to $kR_e^2 = \text{a constant}$, where k is the force constant. Puppi's reduced equation is not universal as kR_e^2 remains constant only within small groups of molecules. Furthermore his variable y is complicated in that it mixes distance and energy.

The value of reduced variables as defined in (1) is shown in Figs. 1 and 2 where in Fig. 1, V is plotted *versus* R and in Fig. 2, V' *versus* R' for the ground states of H_2 and H_2^+ . Atomic units are used for Fig. 1. The variables of Fig. 2 are by definition dimensionless. The H_2 curves are plotted according to the modified Morse function of Hulburt and Hirschfelder³ while the H_2^+ results are

the theoretical calculations of Burrau⁴ and of Teller.⁵

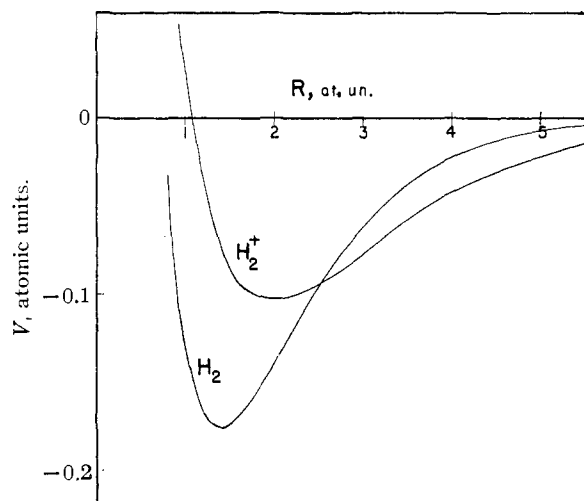


Fig. 1.—Potential energy curves for the ground states of H_2 and H_2^+ ; 1 atomic unit of energy = 27.2 e.v., 1 atomic unit of length = 0.529 Å.

A More General Reduced Internuclear Distance.—If P.E. functions for other than hydrogen molecules are plotted in Fig. 2 there is no general coincidence of curves. In particular, the curvature at the minimum, which is related to the force constant, may vary considerably from molecule to molecule. This is not surprising inasmuch as an inner shell repulsion for all atoms other than hydrogen should influence the internuclear distance at the minimum. To take this into account the definitions of equation 1 will be replaced by

$$V' = V/D_e \quad R' = (R - R_{ij})/(R_e - R_{ij}) \quad (2)$$

where R_{ij} is a constant for a given molecule and is a measure of inner shell radii of atoms i and j . Here, as before, the minimum is given by $V' = -1$ and $R' = 1$. R' of (2) is identical with R' of (1) when $R_{ij} = 0$ as it presumably is for H_2 and H_2^+ , there-

(1) A portion of this paper was presented at the Los Angeles Meeting of the American Chemical Society, March, 1953.

(2) (a) G. Puppi, *Nuovo Cimento*, **3**, 338 (1946); (b) M. Davies, *J. Chem. Phys.*, **17**, 374 (1949).

(3) H. M. Hulburt and J. O. Hirschfelder, *ibid.*, **9**, 61 (1941).

(4) O. Burrau, *Kgl. Danske Videnskab. Selskab.*, **7**, 1 (1927).

(5) E. Teller, *Z. Physik*, **61**, 458 (1930).