

## The Para, OrthoHydrogen Conversion by Paramagnetic Substances in Solution

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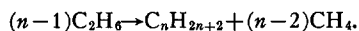
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*n*-paraffins since these predominate with cobalt catalysts. Methane and ethane were taken as the independent components and the other products were expressed in terms of these by means of equations of the form



H. A. Wilson investigated similar systems many years ago.<sup>6</sup> Unfortunately, his calculations were based upon the inaccurate hydrocarbon free energy data of the period and yielded erroneous equilibrium compositions.

Expressions for the equilibrium distribution were finally developed which involved three variables as required by the phase rule. For convenience, the parameters chosen for the calculations were the temperature, the methane-ethane ratio, and the over-all hydrogen-carbon ratio. It was soon apparent that the equilibrium distribution was of the same type as that obtained experimentally and the effect of varying the parameters was accordingly studied over a limited range. Typical calculated distribution curves are shown in Fig. 1 for  $T=473^\circ$ ,  $600^\circ\text{K}$ ;  $\text{CH}_4:\text{C}_2\text{H}_6=11.5$ ,  $7.0$ ;  $\text{H}:\text{C}=2.67$ ,  $2.59$ . Detailed results will be published elsewhere.

In confirmation with Craxford's general viewpoint it may be concluded that partial equilibration probably occurs among the *n*-paraffins in the cobalt-catalyzed synthesis reaction. It is interesting that equilibrium appears to be approached at a higher temperature level than corresponds to the measured operating temperature. This is evident from Fig. 1 where better agreement with the experimental data is secured at  $600^\circ\text{K}$  (curve with upper peak) than at  $473^\circ\text{K}$ . Also a more systematic variation of the temperature, keeping the other parameters constant, yields distribution curves at lower temperatures with the maxima shifted toward the  $\text{C}_8\text{--C}_{12}$  region in agreement with Craxford's hydrogenation-cracking results. These observations are in accord with the recognized fact that the true catalyst temperature in the Fischer-Tropsch synthesis is considerably higher than measured temperatures on account of the exothermic nature of the reaction.

<sup>1</sup> F. Fischer and H. Pichler, *Brennstoff Chem.* **20**, 221 (1939).

<sup>2</sup> H. H. Storch, p. 1827 in Lowry's *Chemistry of Coal Utilization* (John Wiley and Sons, Inc., New York, 1945).

<sup>3</sup> A. J. V. Underwood, *Ind. Eng. Chem.* **32**, 449 (1940).

<sup>4</sup> S. R. Craxford, *Fuel* **26**, No. 5, 119 (1947).

<sup>5</sup> S. R. Brinkley, *J. Chem. Phys.* **14**, 463 (1946); **15**, 107 (1947).

<sup>6</sup> H. A. Wilson, *Proc. Roy. Soc.* **140A**, 1 (1933).

### The Crystal Structure of $\text{U}_2\text{F}_9$ \*

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February 24, 1948

THIS unusual compound was discovered by R. Livingston.<sup>1</sup> The correct formula,  $\text{U}_2\text{F}_9$ , was established by Weller, Grenall, and Kunin<sup>2</sup> by direct chemical analysis. The compound is black in color and converts to green  $\text{UF}_4$  when exposed to air.

Using Dr. Livingston's original preparation, the writer determined the unit cell as well as the number and the

positions of the uranium atoms.<sup>3</sup> When the correct chemical composition was deduced it became possible to assign positions also to the fluorine atoms.<sup>4</sup>

$\text{U}_2\text{F}_9$  is cubic with four molecules in the unit cell which has an edge  $a=8.4545\pm0.0005\text{Å}$ . The calculated density is  $\rho=7.06$ . The space group is  $I\bar{4}3m(T_d^3)$ . In the notation of the *International Tables for the Determination of Crystal Structures* the atomic positions are:

8U in 8(c) with  $x=0.187\pm0.004$ ,  
12F<sub>I</sub> in 12(e) with  $x\approx0.225$ ,  
24F<sub>II</sub> in 12(g) with  $x\approx0.20$  and  $z\approx0.40$ .

Each uranium atom is bonded to nine fluorine atoms with an average distance  $\text{U--F}=2.31\text{Å}$ .

The most interesting feature of the structure is the equivalence of the uranium atoms. Accordingly, it must be concluded that tetravalent and penta- or hexavalent uranium atoms replace one another isomorphously, or that each uranium atom resonates between the tetravalent state and higher valence states.

A detailed account of the investigation will appear in the Manhattan Project Technical Series.

\* The results given below were obtained within the Manhattan Project during the war and have been declassified by authority of the Atomic Energy Commission.

<sup>1</sup> R. Livingston and W. Burns, Manhattan Project Report CN-982 October, 1943.

<sup>2</sup> S. Weller, A. Grenall, and R. Kunin, Report A-3326, March, 1945.

<sup>3</sup> W. H. Zachariasen, Report CP-961, October, 1943.

<sup>4</sup> W. H. Zachariasen, Report CC-2753, March, 1945.

### The *Para*-, *Ortho*-Hydrogen Conversion by Paramagnetic Substances in Solution

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February 16, 1948

SINCE the published work of Farkas and Sachsse,<sup>1</sup> little has appeared to further the investigation of the relationship between magnetic moment, ionic radius, and the rate of conversion of *para*-hydrogen to *ortho*-hydrogen by paramagnetic substances in solution. From theoretical considerations, Wigner has predicted that the rate is directly proportional to the sixth power of the distance of closest approach of the hydrogen molecule and the paramagnetic ion.<sup>2</sup>

We have undertaken to investigate this relationship by studying the *para*-hydrogen conversion by complex paramagnetic ions whose radii can be varied at will. The investigation is far from complete but present work indicates that the process is not so sensitive to variation of the radius as the Wigner theory predicts.

Current interest as to the state of the electron in liquid  $\text{NH}_3$  led us to undertake a study of the conversion by alkali and alkaline earth metals in liquid  $\text{NH}_3$ . Preliminary measurements indicate that the rate of conversion by a Na solution is not simply related to the magnetism of the solution. The process is very rapid, e.g.,  $0.033M$  solution of Na gave a measured half-life in solution of 37 sec. at

-53°C. The rate for this process is approximately 30 times as fast as that for the corresponding concentration of cupric ion in H<sub>2</sub>O at 25°C. Since the magnetism of the Na solutions is very much smaller than that for the cupric solutions, a further comparison upon the basis of magnetism (such as for equal values of the square of the magnetic moments) would be even more striking.

<sup>1</sup> Farkas and Sachsse, *Zeits. f. physik. Chemie* **B23**, 1 (1933); **B24** 429 (1933).

<sup>2</sup> Wigner, *Zeits. f. physik. Chemie* **B23**, 28 (1933).

## On the Probability Formulation of Chemical Reaction Kinetics

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February 16, 1948

CHEMICAL kinetics has been usually described by kinematic differential equations. Recently, Erofeyev<sup>1</sup> started a phenomenological formulation from the probability concept. The fact that a constant probability, independent of the time for a molecule to undergo reaction, will lead to a first-order kinetic equation is well known. However, it is interesting to see what form of the probability function will give a kinetic equation of zero or higher order.

Let  $\bar{p}(t)$  be the average probability per unit time in which a molecule undergoes reaction, then the average probability that a molecule would survive from reaction over a finite period of time  $t$  is<sup>2</sup>

$$Q(t) = \exp\left(-\int_0^t \bar{p}(t) dt\right). \quad (1)$$

For the transformation of molecules of a single chemical species the kinematic equation of kinetic order  $n$  is

$$-c(t) = k_n c(t)^n,$$

where  $c$  is the concentration of the molecules. Dividing through by  $c$  and integrating yields

$$Q(t) = c(t)/c(0) = \exp\left(-k_n \int_0^t c(t)^{n-1} dt\right). \quad (2)$$

Therefore,

$$\bar{p}(t) = k_n c(t)^{n-1} \quad (3)$$

by comparing (2) and (1).

Similar considerations for a bimolecular reaction between two different molecules  $A$  and  $B$ , i.e.,

$$-c_A(t) = -c_B(t) = k_2 c_A c_B,$$

give the following result:

$$\left. \begin{aligned} Q_A(t) &= \exp\left(-\int_0^t \bar{p}_A(t) dt\right), \\ Q_B(t) &= \exp\left(-\int_0^t \bar{p}_B(t) dt\right), \end{aligned} \right\} \quad (4)$$

with

$$\bar{p}_A(t) = k_2 c_B(t) \quad \text{and} \quad \bar{p}_B(t) = k_2 c_A(t). \quad (5)$$

It can be shown that the functions (3) and (5) are the unique solution for the probability functions defined in

(1) and (4) which satisfy the corresponding kinematic equations. The form of these probability functions for reactions of second and higher orders are in accord with the collision mechanism of chemical reactions.

Furthermore, if the probability functions for the molecules of different energies be put in the form

$$p_i(E_i, t) = f(E_i) p(t),$$

then

$$\bar{p}(t) = 2\pi^{-1} (kT)^{-1} p(t) \int_0^\infty f(E_i) E_i^{\frac{1}{2}} \exp(-E_i/kT) dE_i.$$

Further, the assumption that

$$f(E_i) = \begin{cases} 0 & \text{for } E_i < E_0, \\ 1 & \text{for } E_i \geq E_0, \end{cases}$$

leads to the following temperature dependence of the probability function,

$$kT^2 \frac{\partial \ln \bar{p}}{\partial T} = \frac{\int_{E_0}^\infty E_i^{\frac{1}{2}} \exp\left(-\frac{E_i}{kT}\right) dE_i}{\int_{E_0}^\infty E_i^{\frac{1}{2}} \exp\left(-\frac{E_i}{kT}\right) dE_i} - \frac{3}{2} kT. \quad (6)$$

For a first-order reaction,  $\bar{p}$  is identical to the rate constant  $k_1$ , and such a temperature dependence of  $k_1$  has been first derived by Tolman.<sup>2</sup>

It is hereby shown that the generalized kinetic equation (1) is a partially integrated form of the usual kinematic equation and it is therefore equivalent to the latter. For cases where the reaction probability function can be formulated *a priori*, the present formulation will give the reaction kinetics directly without solving the differential equations.

<sup>1</sup> B. V. Erofeyev, *Comptes Rendus U.R.S.S.* **52**, 511 (1946).

<sup>2</sup> R. C. Tolman, *J. Am. Chem. Soc.* **42**, 2506 (1920).

## Erratum: Absorption Spectrum of Carbon Dioxide from 14 to 16 Microns

[*J. Chem. Phys.* **15**, 809 (1947)]

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DR. FRANK MATOSSO kindly pointed out to the author an error on page 812 of the above paper. The half-width in wave numbers should be equal to the collision frequency divided by  $2\pi$  times the velocity of light.<sup>1</sup> Since the value of  $0.17 \text{ cm}^{-1}$  obtained appears to be close to the correct value at atmospheric pressure,<sup>2</sup> the kinetic theory diameter seems to be too small by a factor of about  $\sqrt{2\pi}$ , which would account for the compensating error. Born<sup>3</sup> estimates the ratio of the optical diameter to the kinetic theory diameter to be 3.0 for carbon dioxide, 2.2 for nitrogen, and 2.3 for oxygen, resulting in an effective optical diameter of 2.6 times the kinetic theory value.

<sup>1</sup> M. Born, *Optik* (Verlag Julius Springer, Berlin, 1933), p. 437; H. Margenau and W. W. Watson, *Rev. Mod. Phys.* **8**, 37 (1936).

<sup>2</sup> Dr. Arthur Adel, in a communication to the author, has given a probable value of  $0.15$  to  $0.18 \text{ cm}^{-1}$ , based on the procedure described in *Rev. Mod. Phys.* **16**, 236 (1944).

<sup>3</sup> Reference 1, p. 441.