I	126.932	The other isotopes of tin, xenon and mercury show the same differences from integral values
Sn^{120}	119.912	
Xe^{134}	133.929	
Hg^{200}	200.016	

The resolution of the lines of tin, xenon, mercury and lead points to the following composition of these elements (see also Aston, *Nature* **120,** 224 (1927)).

	Atomic number	Atomic weight	Mass numbers of isotopes in order of intensity
Sn	50	118.70	120, 118, 116, 124, 119, 117, 122, 121, 112, 114, 115
Xe	54	130.2	129, 132, 131, 134, 136, 128, 130, 126, 124
Hg	80	200.61	202, 200, 199, 198, 201, 204, 196
Pb	82	207.22	208, 207, 206, 209 (?), 203 (?), 204 (?)

Aston[27] was unable to distinguish between the mass spectra of ordinary mercury and that found in coal tar.

In the table of atomic weights on page 615, for which the author of this report solely is responsible, changes from the 1927 table are made in the cases of helium,[28] argon, dysprosium, neon and yttrium. The atomic weight of potassium seems to be in some doubt, but further evidence should be awaited before a change.

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THEORIES OF UNIMOLECULAR GAS REACTIONS AT LOW PRESSURES. II

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Certain gas reactions, termed by Hinshelwood quasi-unimolecular, are unimolecular at high pressures but fall off in rate below the unimolecular law at low pressures. In a recent paper[1] we have attempted, on the basis of collision hypotheses and classical statistical mechanics, to develop equations giving the relation between pressure and rate of reaction. We considered chiefly two theories which led to equations (5) and (19), respectively.

In the former article[1] we applied the theories to the decomposition of propionic aldehyde, which had been studied by Hinshelwood and Thomp-

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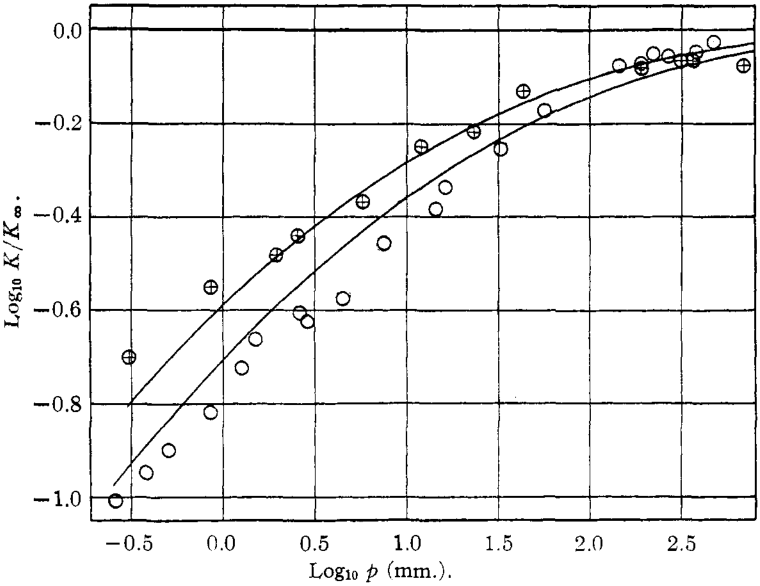
[27] Aston, *Nature*, **119,** 489 (1927).

[28] A recent unpublished determination of the compressibility of helium below one atmosphere by Mr. R. B. Ellestad and the author has yielded the value for $(PV)_0/(PV)_1$ of 0.9995. This value combined with the density found by Baxter and Starkweather, 0.17846, gives as the atomic weight of helium 4.002, a result identical with that found by Aston with the mass spectrograph.

[1] Rice and Ramsperger, This Journal, **49,** 1617 (1927).

son,[2] and found that we could not distinguish between the two theories. In this paper we shall apply our considerations to the decomposition of azomethane.[3]

In this case Theory I does not fit the data at all. If we make the curve fit the upper points it misses the lower ones by a factor of 10. The comparison of Theory II with the data is given in Fig. 1. In making the calculations we set[4] $n = 25$, which makes the rate fall off at about the right pressure, and $\epsilon_0 = 50{,}600$. s is given throughout the value of[5] 6×10^{-8}.



Upper curve, ⊕, 290°C.; lower curve, ○, 330°C.

Fig. 1.

It must be remembered that ϵ_0, as given, is not the heat of activation as calculated from the original Arrhenius equation, but is related to it, as shown in our former article by equation (20) for Theory II. We have used the temperature coefficient originally found by Ramsperger.[6] We would now make a second approximation by using the temperature coefficient taken from the K_∞ values from the curves at the two temperatures, but the correction is negligible. It may be well to remark that, although the values of many of the quantities involved are known to order of magnitude only, the temperature coefficients of all of them are known, and the relative positions of the curves at different temperatures, as well as their shapes, are fixed, in the plot used, once n is determined.

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[2] Hinshelwood and Thompson, *Proc. Roy. Soc.* (*London*), **113A**, 221 (1926).

[3] Ramsperger, This Journal, **49**, 1495 (1927).

[4] For the nomenclature and for the method of fitting curves to data see Rice and Ramsperger, ref. 1.

[5] Though strictly the theory holds only for initial rate constants, average rates during a run were taken for azomethane as they were practically the same.

[6] Ramsperger, This Journal, **49**, 912 (1927).

It is now necessary to use equation (24) of our previous article in order to test our assumption that deactivation, or at least sufficient loss of energy, occurs at every collision of an activated molecule. The curves used in the graphical integration of equation (19) for azomethane (which are similar to those of Fig. 1 of our previous paper) show that at the lowest pressure used at 330° approximately only 11.5% of the reaction was due to molecules having a greater energy than 62,600 calories per mole. The energy of an average molecule at this temperature, from our value of n, is about 15,000. Let us then take $\epsilon' = 77{,}600$ in equation (24); and let us take $\epsilon'' = 57{,}600$, since molecules of this energy lack equilibrium numbers by only 5%. (The number of molecules actually present is to the number present at equilibrium as the integrand in equation (19) is to the integrand at infinite pressure.) The value of (24) evaluated by a more accurate method than formerly used is less than 0.013, which is so small that Theory II needs no modification.

Correction to Previous Article.—The sentence below Fig. 1 should read: "At $\epsilon - \epsilon_0$ equal to 5000 the concentration lacks about 8% of the equilibrium value."

Note on Diethyl Ether

Hinshelwood has recently studied the decomposition of diethyl ether.[7] This fits Theory II a little better than Theory I. On Theory II it requires a value of n of 6.

Discussion

One of the most striking features of the results is the difference in the number of degrees of freedom[8] in the various cases. The number of degrees of freedom of azomethane fits well with the specific heats of similar compounds, C_p for acetone being about 24 calories per mole per degree in the range from 129 to 233°.[9] But the numbers of degrees of freedom of the propionic aldehyde and diethyl ether are surprisingly low; the specific heat of ether is about 44.5 calories per mole per degree at 350°. This might be due to some impedance to the transfer of energy in the molecule, only a few degrees of freedom being in communication in the proper place in the molecule, so the molecule acts like one with a smaller number of degrees of freedom.

One objection that might be brought against our interpretation of the results is the possible presence of some sort of a chain reaction, as the decomposition of azomethane is undoubtedly exothermic.[10] If this is

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[7] Hinshelwood, *Proc. Roy. Soc. (London)*, **114A,** 84 (1927).

[8] By the number of degrees of freedom we mean, as explained in our previous paper, the number of quadratic terms in the energy expression. C_v in calories is then approximately equal to the number of degrees of freedom.

[9] Landolt-Börnstein, "Tabellen," **1923,** p. 1275.

[10] Azomethane explodes, presumably of course, with evolution of heat, when an electric discharge passes through it. The products are different from the products of thermal decomposition and contain a little over 20,000 calories more energy per mole of azomethane decomposed (estimated by us from heats of combustion). The heat of reaction must, therefore, be more than 20,000 calories per mole of azomethane [see Thiele, *Ber.*, **42,** 2575 (1909)].

the chief means of activation at low pressure, and unless the mechanism of transfer of energy is very specific, we would expect the reaction rate to fall off during the course of a run as the products of reaction accumulate but practically this is not the case, though the run falls off in most cases to a very small extent. What the effects of simple local heating might be, and whether such an effect could be combined with our theory to give satisfactory results, we cannot at present decide.

Summary

Two theories based on collision hypotheses of quasi-unimolecular reactions, which we have previously developed, are applied to the decomposition of azomethane. It is possible to explain the falling off of the rate with pressure and to decide between the two theories. The efficiency of activation and deactivation at collision is considered, and the following are discussed: (1) the number of degrees of freedom involved in the various cases; (2) the effect of heat of reaction in the case of azomethane. The decomposition of diethyl ether is also considered briefly.

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[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE JOHNS HOPKINS UNIVERSITY]

AN ATTEMPT TO PREPARE TRIATOMIC HYDROGEN[1]

BY HUGH M. SMALLWOOD[2] AND H. C. UREY

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Introduction

The preparation and properties of an active modification of hydrogen, supposed to be triatomic, have been described by a number of investigators.[3] According to their papers, whenever hydrogen is ionized or dissociated a small amount of active product is formed. The activating agents that have been used with success include α-particles, the Siemens ozonizer, the vacuum discharge and the corona discharge. It has also been stated that if oxygen is burned in an atmosphere of hydrogen, or if hydrogen-oxygen mixtures containing deficiency of oxygen are detonated, part of the hydrogen remaining after the combustion is activated. It has furthermore been reported that hydrogen is activated by passage over

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[1] Extract from Dissertation submitted by Hugh M. Smallwood in partial fulfilment of the requirements for the degree of Doctor of Philosophy.

[2] Du Pont Fellow in Chemistry.

[3] (a) Duane and Wendt, *Phys. Rev.*, [2] **10,** 116 (1927); (b) Wendt and Landauer, THIS JOURNAL, **42,** 930 (1920); (c) **44,** 510 (1922); (d) Newman, *Phil. Mag.*, **43,** 455 (1922); (e) Venkataramaiah, *Nature,* **106,** 46 (1920); (f) **112,** 57 (1923); (g) *Chem. News,* **124,** 323 (1922); (h) THIS JOURNAL, **45,** 261 (1923); (i) Venkataramaiah and Swamy, *Proc. Sci. Ass. Mah. Coll. Viz.*, p. 23, Dec., 1922; (j) Grubb, *Nature,* **111,** 600, 671 (1922); (k) Paneth, *Z. Elektrochem.*, **30,** 504 (1924); (l) Anderegg, THIS JOURNAL, **47,** 2429, (1925).