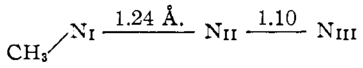
symmetrical in molecular crystals such as CH_3N_3 **(b)**.[13]

$$NH_4^+ [N_I \overset{1.15 Å.}{\text{———}} N_{II} \overset{1.15}{\text{———}} N_{III}]$$

a



$$CH_3{-}N_I \overset{1.24\ Å.}{\text{———}} N_{II} \overset{1.10}{\text{———}} N_{III}$$

b

Thus one expects that the asymmetrical N_3 stretching frequency is higher in covalent molecules than in ionic crystals, since the N_{II}–N_{III} distance of the former is shorter. As is shown in Table III, the observed results are in good accord with the above expectation.

The asymmetrical N_3 stretching frequencies of Cr^{3+} and Co^{3+} azido complexes are also given in Table III. The Cr^{3+} complexes always show higher frequencies than the corresponding Co^{3+} complexes. This fact suggests that the M–N bond of the latter is more ionic than that of the former and agrees with the observation that the aqueous solution of the Co^{3+} azido complex is more easily aquotized than that of the corresponding Cr^{3+} complex.

Acknowledgments.—The authors wish to express their sincere thanks to Prof. R. E. Rundle who kindly pointed out the importance of hydrogen bonding in our earlier short note.

NAKANOSHIMA, KITA, OSAKA, JAPAN

TABLE III

THE NN STRETCHING FREQUENCIES OF AZIDO COMPOUNDS ($CM.^{-1}$)

	Asym. str.
NH_4N_3[a]	2050(solid)
	2030(solid)
HN_3[b]	2140(gas)
	2169(solid)
CH_3N_3[c]	2143(gas)
$[Cr(NH_3)_5N_3]I_2$	2094
$[Co(NH_3)_5N_3]I_2$	2047
$[Cr(NH_3)_3(N_3)_3]$	2072
$[Co(NH_3)_3(N_3)_3]$	2017

[a] D. A. Dows, E. Whittle and C. C. Pimental, *J. Chem. Phys.*, **23**, 1475 (1955). [b] D. A. Dows and C. C. Pimental, *ibid.*, **23**, 1258 (1955). [c] E. H. Eyster and R. H. Gillet, *ibid.*, **8**, 369 (1940).

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[13] L. Pauling, "The Nature of the Chemical Bond," Cornell Univ. Press, Ithaca, N. Y., 1940, p. 200.

[CONTRIBUTION FROM THE JAMES FORRESTAL RESEARCH CENTER, PRINCETON UNIVERSITY]

High Temperature Reaction Kinetics of the System H_2–HI–I_2[1]

BY WENDELL M. GRAVEN[2]

RECEIVED DECEMBER 5, 1955

An investigation of the kinetics of the reactions which comprise the equilibrium $2HI = H_2 + I_2$ has been conducted within the temperature interval of 600–775°. With the use of a flow system both forward and reverse reactions have been examined under conditions such that the extent of reaction ranged from 3 to 95% of its equilibrium value. Five to 24-fold variations in the reactant and product concentrations have provided kinetic information in substantial agreement with extrapolations of data obtained at lower temperatures. The following second-order rate constants have been calculated for decomposition of hydrogen iodide and combination of hydrogen and iodine, respectively, $k_1 = 3.59 \times 10^{12} \exp(-49200/RT)$ and $k_2 = 1.23 \times 10^{12} \exp(-41000/RT)$ l. mole^{-1} sec.$^{-1}$.

Introduction

Bodenstein's investigation of the hydrogen iodide synthesis and decomposition[3a–d] was the first comprehensive study of the kinetics of gaseous processes. This system has remained the best example of bimolecular gas phase reactions, having withstood tests of the influence of moisture,[4,5] glass surface[6] and extended concentration range.[7] It has been re-examined in conjunction with studies of the analogous reactions of deuterium iodide.[8–12]

Lewis, in his introduction to the collision theory of reaction rates,[13] noted that at high temperature the normally bimolecular hydrogen iodide decomposition could be superseded by a unimolecular process. His choice of a unimolecular rate constant with an activation energy of 66 kcal. led him to predict that in the neighborhood of 1200°K. the observed reaction rate expression would be no longer exactly second order in hydrogen iodide.

Recently, Benson[14] has revived the hypothesis that at high temperature the reactions are more complex. His calculations lead him to postulate that above 600°K. free radical processes contribute, and above 900°K. predominate in the over-all synthesis of hydrogen iodide.

In view of the above conclusions it becomes worthwhile to report the results of an examination of these reactions within the temperature interval of 600–775°.

The purpose of this investigation was to examine the kinetics of the decomposition and synthesis of hydrogen iodide at as high a temperature as possible

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[1] This research was supported in whole or in part by the United States Air Force under Contract No. AF33(038)-23976 monitored by the Office of Scientific Research.

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[3] (a) M. Bodenstein, *Ber.*, **26**, 2603 (1893); (b) *Z. physik. Chem.*, **13**, 56 (1894); (c) **22**, 1 (1897); (d) **29**, 295 (1899).

[4] B. Lewis and E. Rideal, THIS JOURNAL, **48**, 2553 (1926).

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[6] H. A. Taylor, *J. Phys. Chem.*, **28**, 984 (1924).

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[10] J. Blagg and G. Murphy, *J. Chem. Phys.*, **4**, 631 (1936).

[11] A. Taylor and R. Crist, THIS JOURNAL, **63**, 1377 (1941).

[12] N. Bright and R. Hagerty, *Trans. Faraday Soc.*, **43**, 697 (1947).

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[14] S. Benson and R. Srinivasan, *J. Chem. Phys.*, **23**, 200 (1955).

in search of evidence indicative of mechanistic deviations.

It was thought that the experimental technique which was used successfully in a previous investigation[15] offered a practicable approach to the problem.

Experimental

The cylindrical quartz reaction vessel, 43 ml. in volume, equipped with tangential entrance and exit tubes, capillary leads and thermocouple sheaths has been described previously.[15] A tubular electric furnace provided with power control maintained the temperature at the center of the vessel at 700.0 ± 0.5° as measured with a Bureau of Standards calibrated Pt thermocouple.

Commercial hydrogen and nitrogen were purified prior to metering with capillary flowmeters. Iodine vapor was generated from re-sublimed crystals in a vacuum-jacketed flask by means of a glass-enclosed immersion heater. Flow rates were controlled by adjusting the power input to the heater. The flask, stopcocks and connecting tubing were kept at sufficiently high temperature that an atmosphere of iodine vapor could be maintained.

Hydrogen iodide was prepared by passing an iodine-hydrogen mixture through the reaction vessel which was heated above 800°. The unreacted iodine sublimed upon the walls of a five-liter flask cooled below room temperature and the hydrogen iodide was frozen out at Dry Ice temperature. After evacuation of the system the hydrogen iodide was distilled into a stainless steel storage cylinder from which it was metered in the same manner as were the non-condensable gases.

A constant reaction time was permitted by the use of nitrogen as a diluent to maintain a flow rate of about 1.6 l. min.$^{-1}$. The total pressure was approximately 78 cm.

Rates of forward and reverse reactions were measured by gravimetric analysis of effluent mixtures for I_2 or HI. For determination of the rate of decomposition of HI iodine was sublimed in a packed U-tube which was cooled to 0°. The rate of combination of H_2 and I_2 was measured by absorption of HI in ascarite after the unreacted I_2 had been removed in a manner similar to that of the reverse reaction.

Although it was desirable to make measurements at as high a temperature as possible with the available apparatus a reaction time of less than 0.4 sec. was not feasible. For this reason all runs except those designed to determine the temperature coefficients of the rates were carried out at 700°.

Results and Discussion

Although the flow pattern within the vessel probably was not clearly defined, calculations of rate constants were based upon an assumed coincidence of the major axis of the vessel with the time axis of the reaction. No corrections were made for the dissociation of I_2 vapor, which amounted to 2–3% at the experimental temperatures.

A preliminary examination of the data indicated approximately second-order reactions. Accordingly, the differential equation which represents the rate of approach to equilibrium of the system

$$2\mathrm{HI} \underset{k_2}{\overset{k_1}{\rightleftarrows}} \mathrm{H_2} + \mathrm{I_2} \qquad (1)$$

was integrated to obtain expressions for the rate constants. The equation, which may be written in the form

$$\mathrm{d}(x)/\mathrm{d}t = k_1\{(\mathrm{HI})_i - (x)\}^2 - k_2\{(\mathrm{H_2})_i + (x)/2\}\{(\mathrm{I_2})_i + (x)/2\} \qquad (2)$$

where the (i) subscripts indicate initial concentrations, was integrated for the three special cases of interest in this investigation.

If $(\mathrm{H_2})_i = (\mathrm{I_2})_i = 0$:

$$k_1 = \frac{2.30K^{1/2}}{(\mathrm{HI})_i t} \log \left[\frac{(\mathrm{HI})_i - (\mathrm{I_2})\{2 - K^{-1/2}\}}{(\mathrm{HI})_i - (\mathrm{I_2})\{2 + K^{-1/2}\}}\right] \qquad (3)$$

if $(\mathrm{I_2})_i = 0$:

$$k_1 = \frac{4.61K}{at} \log \left[\frac{2K(\mathrm{HI})_i^2 - (\mathrm{I_2})\{4K(\mathrm{HI})_i + (\mathrm{H_2})_i - a\}}{2K(\mathrm{HI})_i^2 - (\mathrm{I_2})\{4K(\mathrm{HI})_i + (\mathrm{H_2})_i + a\}}\right] \qquad (4)$$

where

$$a = [(\mathrm{H_2})_i^2 + 4K(\mathrm{HI})_i\{(\mathrm{HI})_i + 2(\mathrm{H_2})_i\}]^{1/2}$$

if $(\mathrm{HI})_i = 0$:

$$k_2 = \frac{4.61}{bt} \log \left[\frac{4(\mathrm{H_2})_i(\mathrm{I_2})_i - (\mathrm{HI})\{(\mathrm{H_2})_i + (\mathrm{I_2})_i - b\}}{4(\mathrm{H_2})_i(\mathrm{I_2})_i - (\mathrm{HI})\{(\mathrm{H_2})_i + (\mathrm{I_2})_i + b\}}\right] \qquad (5)$$

where

$$b = [\{(\mathrm{I_2})_i - (\mathrm{H_2})_i\}^2 + 16K(\mathrm{H_2})_i(\mathrm{I_2})_i]^{1/2}$$

In the above expressions K is the equilibrium constant for reaction (1). No reliable experimental determinations of K have been reported at temperatures above 500°. Tabulated values of the appropriate free energy functions are available[16]; however, the selected value of ΔH_0^0 is not in accord with all previous data. Bigeleisen, who has reviewed the available data,[17] quotes Wagman of the Bureau of Standards as giving a "best" value of ΔH_0^0 of 2014 ± 20 cal.

For evaluation of k_1 and k_2 in this investigation Murphy's temperature dependent expressions for K and ΔH[18] have been adjusted for the "better" value of ΔH_0^0 (1980.8 ± 8 cal.) of Taylor and Crist[11] to give the equations

$$\log K = -320.90/T + 1.5845 \log T - 3.5544 \times 10^{-4}\, T + 2.166 \times 10^{-8} T^2 - 5.5486 \qquad (6)$$

$$\Delta H = 1468.1 + 3.1482T - 1.6266 \times 10^{-3} T^2 + 1.982 \times 10^{-7} T^3 \qquad (7)$$

Hydrogen Iodide Decomposition.—The effect of HI concentration upon the rate of decomposition was studied over a sevenfold variation in the initial concentration with the results given in Table I.[19]

In addition to the constancy of the rate constants calculated from eq. 3, the dependence upon initial HI concentration of the fractional approach to equilibrium which is given by $(\mathrm{I_2})/(\mathrm{I_2})_e$, where the (e) subscript indicates equilibrium concentration, furnishes proof that the reaction is second order.

The second part of Table I shows the results of runs in which H_2 was present initially. While a constant initial HI concentration was maintained the H_2 concentration was varied 24-fold. Again the constancy of k_1, calculated from equation 4, is satisfactory. Addition of I_2 to the reaction mixture was not experimentally feasible.

Adjustment of the total flow rate permitted a sixfold variance in the reaction time. With the exception of the run in which the system nearly reached equilibrium the rate constant was unaf-

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(17) J. Bigeleisen, *J. Chem. Phys.*, **18**, 481 (1950).

(18) G. Murphy, *ibid.*, **4**, 344 (1936).

(19) All concentrations shown in the tables are given in units of millimoles liter.$^{-1}$ The unit of reaction time is the second. The rate constants are expressed in liters mole^{-1} sec.$^{-1}$. Each run was made at 700.0 ± 0.5° at which temperature the value of the equilibrium constant calculated from eq. 6 is 0.0339

TABLE I

EFFECTS OF HI AND H_2 CONCENTRATIONS ON RATE OF HI DECOMPOSITION

$(HI)_i$	$(H_2)_i$	t	(I_2)	$(I_2)/(I_2)_e$	k_1
0.811	...	0.486	0.00368	0.0338	23.1
1.62	...	.486	.0189	.0867	30.4
2.43	...	.486	.0435	.133	31.6
3.24	...	.486	.0710	.163	29.2
4.05	...	.486	.110	.202	29.5
4.86	...	.486	.154	.236	29.0
5.67	...	.486	.201	.264	28.0
3.21	0.200	.486	.0722	.196	31.1
3.21	0.401	.486	.0701	.222	31.0
3.21	0.802	.486	.0674	.283	31.4
3.21	1.60	.486	.0648	.410	33.4
3.21	2.40	.486	.0612	.519	34.6
3.19	3.99	.486	.0532	.657	33.0
3.19	4.79	.486	.0508	.731	34.5

fected. Because of the sensitivity of the calculated rate constant to the choice of equilibrium constant when the system is in close proximity to equilibrium, calculations were repeated with an arbitrarily chosen value of K of 0.0484. The improvement in the constancy of k_1 is shown by the parenthetical data in the last column of Table II.

TABLE II

EFFECT OF REACTION TIME ON RATE OF HI DECOMPOSITION

$(HI)_i$	t	(I_2)	$(I_2)/(I_2)_e$		k_1	
3.19	0.486	0.0906	0.211	(0.139)	39.3	(38.9)
4.26	0.864	.257	.448	(.395)	39.1	(38.6)
4.26	1.30	.345	.601	(.530)	38.8	(37.5)
4.26	2.59	.552	.962	(.848)	61.2	(42.8)

The temperature dependence of the rate of decomposition was ascertained from a series of runs carried out at 8 different temperatures between 597 and 774°.

In Fig. 1 the logarithms of the rate constants divided by the square roots of the corresponding temperatures have been plotted against the reciprocals of the temperatures. The slope of the straight line corresponds to an activation energy of 49.2 kcal. When this value is combined with the average of 32 measurements of k_1 at 700° (32.0 l. mole^{-1} sec.$^{-1}$) the expression results

$$k_1 = 3.59 \times 10^{12} \exp(-49200/RT) \text{ l. mole}^{-1} \text{ sec.}^{-1} \quad (8)$$

The equation with which Bodenstein represented his data within the temperature interval of 283–508°[3d] has been used to obtain an "extrapolated" rate constant at 700° of 35.0 l. mole^{-1} sec.$^{-1}$. An average activation energy of 45.8 kcal. has been found over the temperature range of 394–506°[11,12]; however, Kassel[20] has predicted that the activation energy obtained between 900 and 1000°K. would be 51 kcal.

Hydrogen–Iodine Combination.—The study of the H_2–I_2 combination proved to be more difficult, and this experimental difficulty is reflected in the wide fluctuations of the rate constants calculated from eq. 5. However, no trends which would indicate deviation from an over-all second-order rate law are evident.

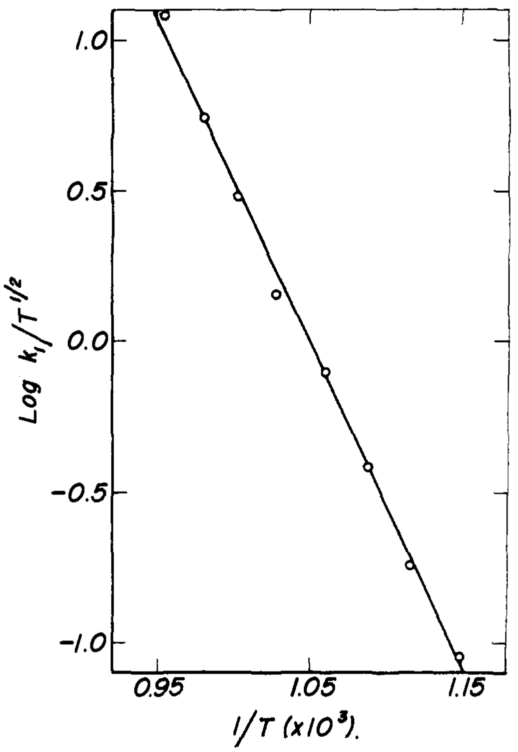

Fig. 1.—Effect of temperature on rate of HI decomposition.

In the first part of Table III the results of runs at constant initial I_2 concentration with an 11-fold variation in H_2 concentration show by the approximate constancy of k_2 and the fractional approach to equilibrium that the rate is proportional to the H_2 concentration.

TABLE III

EFFECTS OF H_2 AND I_2 CONCENTRATIONS ON RATE OF H_2-I_2 COMBINATION

$(I_2)_i$	$(H_2)_i$	t	(HI)	$(HI)/(HI)_e$	k_2
4.88	0.407	0.486	0.410	0.516	605
4.88	0.814	.486	0.872	.552	695
4.88	1.63	.486	1.66	.541	675
4.82	2.41	.486	2.46	.568	729
4.82	3.21	.486	3.22	.589	761
4.82	4.02	.486	4.00	.628	812
4.54	4.54	.457	4.00	.602	752
1.10	4.41	.444	1.16	.547	835
2.14	4.28	.432	1.93	.500	754
3.02	4.54	.457	2.94	.572	813
3.78	4.54	.457	3.61	.602	843
5.29	4.54	.457	4.48	.629	781
5.71	4.28	.432	4.26	.606	743

Runs were made at constant initial H_2 concentration covering a fivefold change in I_2 concentration as shown in the second part of Table III. The results require that the rate also is proportional to the I_2 concentration. It was not feasible to study the effect of HI upon the reaction rate.

More definite information is contained in Table IV. A sixfold variation in the reaction time affects the rate constant only slightly. As with the reverse reaction, a substitution of the arbitrary value of 0.0484 for K improves the constancy of k_2 and yields more reasonable values for the fractional

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(20) L. Kassel, "Kinetics of Homogeneous Gas Reactions," Chemical Catalog Co., New York, N. Y., 1932, p. 148.

approach to equilibrium, as shown by the parenthetical data in the table.

TABLE IV

EFFECT OF REACTION TIME ON RATE OF H_2–I_2 COMBINATION

$(I_2)_i$	$(H_2)_i$	t	(HI)	(HI)/$(HI)_e$		k_2	
4.54	4.54	0.457	4.00	0.602	(0.634)	752	(792)
4.79	4.11	0.818	4.95	.767	(.807)	753	(789)
5.01	4.01	1.20	5.72	.887	(.932)	733	(815)
4.34	4.34	2.59	5.93	.931	(.984)	512	(728)

The results of runs at 8 temperatures between 598 and 774° have been put in the form of a plot of log $k_2/T^{1/2}$ against $1/T$, as shown in Fig. 2. The slope of the straight line yields an activation energy of 41.0 kcal. which, together with the average of 16 measurements of k_2 at 700° (760 l. mole^{-1} sec.$^{-1}$), results in the expression

$$k_2 = 1.23 \times 10^{12} \exp(-41000/RT) \text{ l. mole}^{-1} \text{ sec.}^{-1} \quad (9)$$

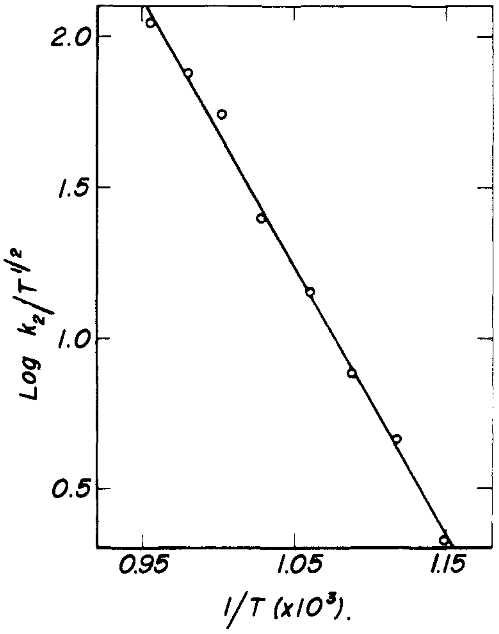

Fig. 2.—Effect of temperature on rate of H_2–I_2 combination.

Bodenstein's data,[3d] represented by an equation analogous to that of the reverse reaction, predict a value of k_2 at 700° of 690 l. mole^{-1} sec.$^{-1}$. Rate measurements between 394 and 479° have yielded activation energies of 42.5[11] and 43.3[9] kcal. for the combination reaction.

The difference between the observed activation energies for the two opposing reactions is 8.2 kcal. and the observed ratio, k_1/k_2, is 0.0421 at 700°. Equations 6 and 7, respectively, yield a value of K of 0.0339 and a heat of reaction of 3.17 kcal. at the same temperature. The range of applicability of the equation with which Bodenstein represented the temperature dependence of his equilibrium data may be extended to obtain a heat of reaction of 7.2 kcal. and a value of K of 0.0508 at 700°.

Figure 3 shows composite plots of all available kinetic data with the exception of those given in ref. 6, which are not in agreement with the remainder. Agreement among the results of seven independent investigations is indicated by the rather close fitting of the data to smooth curves. The plots span a temperature interval of 500°, within which a 10^8-fold variation of the rate constants is observed. The definite curvature of each plot points out the futility of assigning activation energies applicable throughout the entire temperature range.

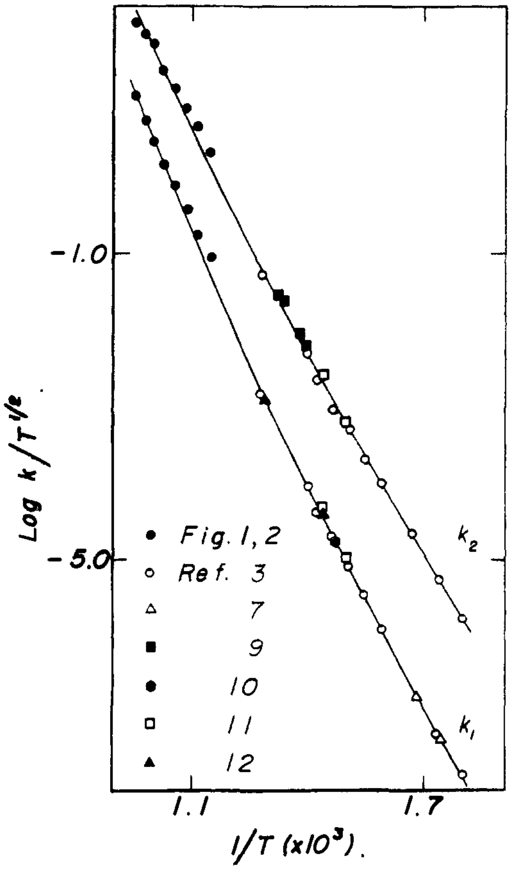

Fig. 3.—Comparison of kinetic data for the system H_2–HI–I_2.

This investigation has demonstrated that at 700° a bimolecular mechanism is paramount for each of the reactions studied. These data are in adequate agreement with extrapolations of the results of previous investigations. They do not constitute a refutation of the hypothesis of mechanistic deviations from bimolecularity at still higher temperatures.

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