

The Use of a Shock Tube for Exploratory Studies of High Temperature Equilibrium and Reaction Rates: Hydrogen-Deuterium Exchange

MARTIN E. GLUCKSTEIN and STUART W. CHURCHILL

The University of Michigan, Ann Arbor, Michigan

A shock wave is a compression wave that moves through a fluid at a velocity greater than the velocity of sound in the undisturbed gas, producing an essentially discontinuous change from one thermodynamic state to another. The physical behavior of shock waves has been studied extensively since the mid-nineteenth century, but chemical applications have only recently received attention as indicated by the absence of indicial heading in *Chemical Abstracts* for *Shock Waves* or *Shock Tubes* prior to 1947. The modern theory of shock waves is treated in detail in books such as Courant and Friedrichs (1) and Rudinger (2), and the use of shock tubes in Wright (3) and Bradley (4).

Early investigators of chemical reactions behind shock waves include Davidson and co-workers (5, 6, 7, 8), Greene (9), and Glick, Squire, and Hertzberg (10). A number of studies have been reported since this work was initiated in 1954 (11, 12, 13, 14, 15, 16, 17, 18, 20, 21). These investigations have been concerned primarily with reaction mechanisms.

The purpose of this investigation was to study the possibilities of a simple shock tube as a tool for the chemical

engineer in the exploratory study of chemical reaction rates and equilibria at high temperatures. The hydrogen-deuterium exchange reaction was chosen for investigation because of its molecular simplicity.

THE SHOCK TUBE

This most common device used to produce and confine shock waves is called a *shock tube*. It consists of high and low pressure sections separated by a diaphragm. If the pressure ratio between the two sections is sufficient, a shock wave propagates through the low-pressure section when the diaphragm is suddenly ruptured.

The behavior of such a tube is illustrated in the several segments of Figure 1. Figure 1b shows the pressure and temperature profile along the tube before the high-pressure diaphragm is ruptured. Figures 1c and 1d show the pressure and temperature profiles at some arbitrary time t^* after the diaphragm is ruptured. The shock wave propagates to the right through the low-pressure section producing a discontinuous increase in pressure, and a rarefaction wave propagates to the left through the high-pressure section producing a continuous decrease in pressure. As indicated the compression produced by the shock wave is accompanied by an increase in temperature and the expansion produced by the rarefaction wave by a decrease in temperature. A wave diagram is shown in Figure 1e. The slopes of the time-distance lines are inversely proportional to velocity relative to the tube wall.

The eventual terminations of the high- and low-pressure sections produce reflected shock or rarefaction waves which retrace the tube and produce secondary changes in temperature, pressure, velocity, etc. Shock tubes differ in character and performance primarily owing to differences in the relative lengths of the high- and low-pressure section and in the types of termination. The shock tube used in this investigation was unique in that the low-pressure (test) section was terminated by a thin diaphragm opening into a large evacuated vessel. [Wetherford (22) and Jacobs and Giedt (23) have recently reported the use of similar methods of quenching.] When the shock wave reached and ruptured this second diaphragm, a rarefaction wave passed backward through the previously compressed and heated gas and the resulting expanded and cooled gas flowed on into the evacuated vessel. Conservation of energy requires that reheating occur when this expanded gas is brought to rest. However since the quench section also serves as a mixing chamber for the cold driver

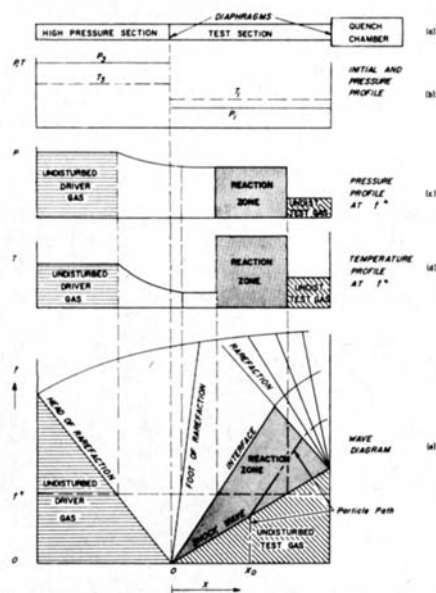


Fig. 1. Shock tube behavior.

gas and the reaction products, the reactants do not reheat significantly.

The mean length of time which the gas originally at any point x_0 is maintained at high temperature and pressure is thus determined by the length of the low-pressure section as indicated in the wave diagram. In a reacting system the time-distance lines of the rarefaction wave starting from the quench chamber would be curved owing to variation in pressure, temperature, and composition in the reaction zone.

The high-pressure section was terminated by a solid wall resulting in reflection of the primary rarefaction wave. However, as indicated, the tube lengths were designed so that interactions between the several waves and between the waves and the interface occurred only after the test gas had been expanded and cooled.

Previous workers have utilized different methods of quenching and controlling reflections and in some cases have permitted reflection of the shock wave resulting in a second compression and increase in temperature. Greater control and precision is possible at the expense of instrumentation and automatic control as in the apparatus described by Glick, Squire, and Hertzberg (11).

QUANTITATIVE DESCRIPTION OF SHOCK WAVES

Experimental work has demonstrated that for most practical purposes a shock wave can be considered a one-dimensional discontinuity with negligible mass, momentum, and energy transfer by molecular and eddy motions. The equations of motion become algebraic for this simple model. If chemical equilibrium is assumed behind the shock wave, the equations of equilibrium and of conservation of atoms must be solved and the heat of reaction included in the energy balance. The case when equilibrium is not attained will be considered later. The complex dependency of the equilibrium constants and other physical properties on temperature and composition usually requires that this system of equations be solved on a computer. The equations governing this model are derived in references 1, 2, 3, 4, and 24.

For the hydrogen-deuterium exchange reaction the heat of reaction is very small, and the other physical properties change very little with composition. In this case the equations of motion are essentially independent of the reaction. This simplification can be attained for stronger reactions by diluting the reactants with an inert gas.

If the rarefaction wave generated by the rupture of the diaphragm is assumed to be an isentropic expansion, a relationship can be derived between the shock strength (pressure ratio across the shock wave) and the original pressure ratio across the diaphragm. The shock strength increases as the ratio of the molecular weight of the driver gas to the shocked gas decreases and the temperature of the driver gas increases, suggesting the use of hydrogen or helium as a driver gas, the use of a high molecular weight gas as a diluent for the reactants, and the use of a preheated driver gas. The shock strength approaches a maximum as the diaphragm pressure ratio increases, but shock strengths of 100 or more are readily attainable. The relationships governing the shock strength are plotted in generalized form in reference 24.

A shock compression of 100 in air produces a temperature in excess of 4,000°K. as compared with approximately 1,000°K. for an isentropic compression. The almost instantaneous production of such a high temperature is responsible for the considerable current interest in the use of shock waves in the laboratory.

CHEMICAL KINETICS BEHIND A SHOCK WAVE

The situation is more complicated if chemical equilibrium is not attained immediately behind the shock wave.

The reaction zone extends from the shock wave to the interface. The extent of this zone increases with time until the shock wave reaches the quench chamber. The rarefaction wave propagated backward from the quench chamber cools the reactants and is presumed to stop the reaction. The reaction time for any element of gas is the interval between the time the element is reached by the shock wave and the time it is reached by the rarefaction wave; this time varies from zero adjacent to the quench chamber to a maximum for particles adjacent to the interface. In general the velocity of the rarefaction wave from the quench chamber will vary owing to the variation in temperature and composition across the reaction zone. However for the hydrogen-deuterium system or for any sufficiently dilute system this variation is negligible. The t - x lines for the particles and for this rarefaction wave are seen in Figure 1 to be, respectively

$$x - x_0 = u_2 \left(t - \frac{x_0}{u_s} \right) \text{ for } t > \frac{x_0}{u_s} \quad (1)$$

and

$$x - L = -u_r \left(t - \frac{L}{u_s} \right) \text{ for } t > \frac{L}{u_s} \quad (2)$$

where all of the velocities are absolute values, measured relative to the tube wall. The rarefaction wave travels at sonic velocity relative to the gas ahead; that is

$$u_r = a_2 - u_2 \quad (3)$$

Solution of these three equations gives the reaction time for any element of gas initially at x_0

$$t' = t - \frac{x_0}{u_s} = \left(1 - \frac{x_0}{L} \right) t'_{\max} \quad (4)$$

where

$$t'_{\max} = \frac{L}{u_s} \left(1 + \frac{u_2}{a_2} \right) \quad (5)$$

If the net rate of reaction can be represented by a single expression of the type $k F_I \{C_A\}$, the change of composition with time can be expressed as

$$\frac{dC_A}{dt} = k F_I \{C_A\} \quad (6)$$

If the variation in temperature across the reaction zone is slight, so that k can be assumed constant, Equation (6) can be integrated formally to give a relationship between residence time and composition:

$$k t' = \int_{C_{Ao}}^{C_A} \frac{dC_A}{F_I \{C_A\}} = F_{II} \{C_A\} \quad (7)$$

or formally,

$$C_A = F_{III} \{k t'\} \quad (8)$$

The elements of gas with differing residence times are all mixed in the quench chamber. The mixed concentration (based on the reactor volume only) is obtained from the space mean average over the test section as follows:

$$\bar{C}_A = \int_0^1 C_A d \left(\frac{x_0}{L} \right) = \int_0^1 F_{III} \left\{ k \left(1 - \frac{x_0}{L} \right) t'_{\max} \right\} d \left(\frac{x_0}{L} \right) = F_{IV} \{k t'_{\max}\} \quad (9)$$

or formally,

$$k = \frac{F_V \{\bar{C}_A\}}{t'_{\max}} \quad (9a)$$

Equations (5), (7), and (9a) and the equations for the shock wave then define k for a given rate expression in

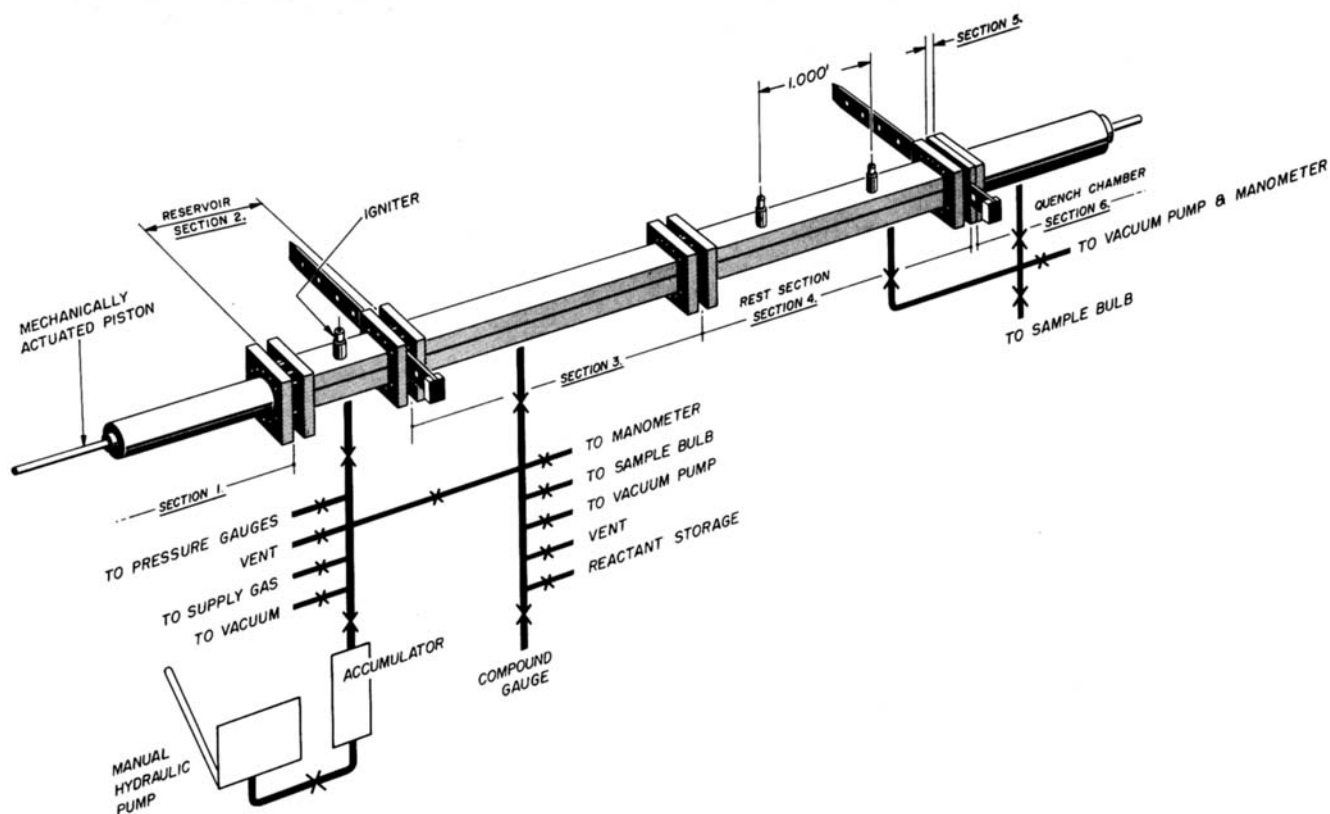


Fig. 2. Diagrammatic sketch of shock tube.

terms of the wave velocity and final mixed composition only.

The assumption of an infinite rate of quenching by the rarefaction has been examined by Kervorkian, Heath, and Boudart (18) and the effect of the boundary layer on the shock wave by Roshko (25). The corrections to the idealized model appear to negligible for the conditions utilized herein but may not be for all conditions. The assumption of no mixing of the driver and test gas in the reaction zone was tested and apparently substantiated in later work in the apparatus (21).

EXPERIMENTAL EQUIPMENT AND PROCEDURE

A schematic diagram of the shock tube is shown in Figure 2. The shock tube had a $\frac{1}{2}$ -in. sq. cross section with a 4 ft. long test section and a 2 ft. long high-pressure reservoir. The tube was fabricated from mild carbon steel and was designed for 100,000 lb./sq.in.abs. The quench section was 3 in. in diameter and its length was varied by the movement of a piston. The gas in the high-pressure reservoir could be compressed to greater than 20,000 lb./sq.in.abs. by a mechanically driven ram. An igniter was included to permit pressurization of the reservoir by combustion. Stainless steel, brass, and aluminum shim stock 0.042 in. or less in thickness were used for the diaphragm separating the reservoir from the test section, and mechanically weakened 0.001-in. steel and 0.006-in. photographic film were used for the diaphragm separating the test section and quench chamber.

The principal instrumentation consisted of two ionization probes 1 ft. apart in the test section. These probes, operating through thyratron circuits, started and stopped an interval timer as the shock wave passed. The timer was accurate to $\pm 0.1 \mu\text{sec}$.

The operating procedure consisted of evacuating the reservoir, test, and quench section; charging the test section; charging and precompressing the reservoir gas; further compressing or igniting the reservoir gas to burst the diaphragm; reading the indicated time interval; and sampling and analyzing the mixture of the product and driver gas. As indicated previously the initial composition, pressure, and temperature of the test gas, the final gas composition, and the wave velocity determine

all the characteristics of the wave. The gas samples were analyzed on a mass spectrograph. Owing to the methods used to rupture the high pressure diaphragm the diaphragm pressure ratio was not always known precisely. Values of the wave velocity, calculated from the diaphragm pressure ratio with the well-known shock tube equations for ideal gases, were from 15 to 25% higher than the corresponding measured values. This agreement is indicative and typical of the efficiency of a shock tube and diaphragm. The measured velocities were of course used to calculate the pressure, temperature, and particle velocity behind the wave.

Details of the equipment and operating procedure are given in reference 24.

EXPERIMENTAL CONDITIONS AND RESULTS

Experimental data were obtained for the hydrogen-deuterium exchange reaction:



For this reaction, $\Delta H^\circ_{298} = +0.074 \text{ k.cal./g. mole}$, and the equilibrium constant varies only from 3.7 at 20°C . to a theoretical maximum of 4.0 at high temperature (26). Farkas and Farkas (27), Farkas (28), Farkas and Wigner (29), Van Meersche (30), and Roginsky (31) have studied the mechanism of the reaction at low temperatures. However Miller and Churchill (21), and Snow, Peck, and von Fredersdorff (32) have shown that extrapolation of rate constants may be unreliable.

Thirteen to 36% oxygen was added to the hydrogen-deuterium mixture in some tests to partially burn the hydrogen and deuterium and hence raise the temperature behind the wave. 67.4% argon was added in some tests to dilute the reacting mass and hence produce more nearly isothermal conditions behind the wave, and also to increase the molecular weight of the test gas and hence increase the shock strength. Helium or nitrogen were used as the driver gas in most tests. Carbon monoxide and oxygen were ignited to provide a greater shock strength in a few runs.

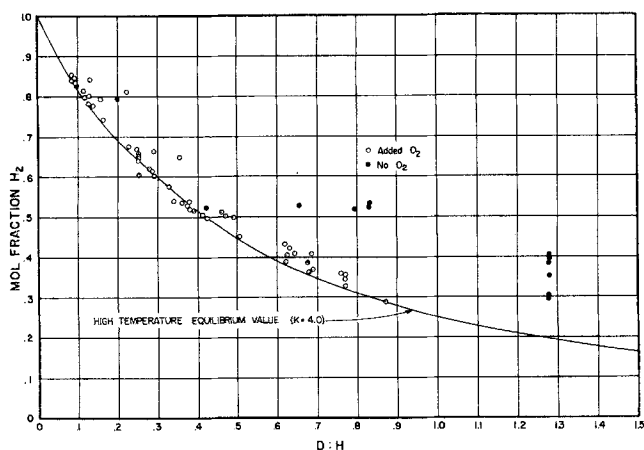


Fig. 3. Residual hydrogen as a function of hydrogen-deuterium ratio in product (basis hydrogen, deuterium, deuterium-hydride only).

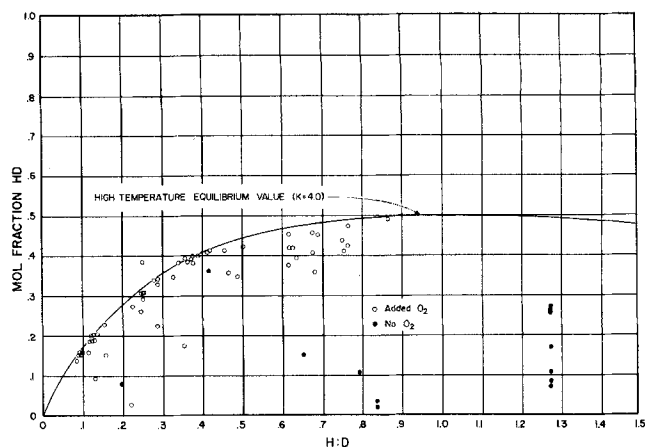


Fig. 4. Hydrogen-deuterium formation as a function of hydrogen-deuterium ratio in product (basis hydrogen, deuterium, deuterium-hydride only.)

Electrolytic hydrogen analyzing greater than 99.8 mole % hydrogen with water the principal impurity and deuterium analyzing greater than 99.5 mole % deuterium with a trace of deuterium-hydride were used.

The experimental compositions are plotted in Figures 3 and 4 as the mole fractions of deuterium-hydride and hydrogen vs. the ratio of deuterium to hydrogen atoms, all on the basis of hydrogen, deuterium, and deuterium-hydride only, that is, excluding argon and all compounds containing oxygen. The curves represent the computed equilibrium compositions for high temperature ($K = 4.0$). The open circles represent runs with added oxygen and the solid circles runs without added oxygen. Failure of one or the other of the ionization probes to actuate the timer necessitated repeated tests at some experimental conditions. All of the runs for which analyses were obtained are plotted in Figures 3 and 4, including those for which the wave velocity measurement was not successful.

It is observed that most of the open circles lie essentially on the equilibrium curve, and that in Figure 4 only one point is significantly above this curve. The maximum reaction time for any particle is computed to be of the order of 800 μ sec. This must be many times the minimum time to approach equilibrium, since the measured composition represents a linear average of reaction times from zero to the maximum. The added oxygen may have acted as a catalyst as well as raising the reaction temperature. The agreement of the data with the theoretical equilibrium

3 and 4 also indicate the potential accuracy with which equilibrium compositions can be determined at very high temperatures in a shock tube.

Some kinetic information can be deduced from the runs in which the deviation of the final composition from equilibrium is significant. The set of oxygen-free runs at $D/H = 1.28$ is most suitable for analysis. Of the seven runs shown in Figures 3 and 4 for this feed composition, wave velocity measurements were obtained for four, representing three distinct operating conditions as indicated in Table 1. The conditions behind the wave were computed with uniform temperature across the reaction zone assumed. Reiterative computations substantiated this assumption. The failure to attain equilibrium in these oxygen-free runs is further evidence that significant reheating did not occur in the quench chamber.

These data obtained for a single-feed ratio do not provide a basis for selecting or testing a rate mechanism. However for illustrative purposes the rate constant for a simple second-order reversible reaction

$$\frac{dC_{HD}}{dt} = k \left(C_{D_2} C_{H_2} - \frac{C_{HD}^2}{K} \right) \quad (11)$$

was calculated. Integration for constant temperature and $K = 4.0$ then yields the following expression for the mixed concentration (based on the reactor volume):

$$\bar{C}_{HD} = \left(\frac{2C_{H_2} C_{D_2}}{C_{H_2} + C_{D_2}} \right)_o \left[1 - \frac{2}{k t'_{max} (C_{H_2} + C_{D_2})_o} \left(1 - e^{-\frac{k t'_{max}}{2} (C_{H_2} + C_{D_2})_o} \right) \right] \quad (12)$$

compositions for high temperature indicates that the quenching rate was sufficiently high and that significant reheating did not occur in the quench chamber. Figures

The values of the overall second-order rate constant calculated from this expression are included in Table 1. These values should be considered indicative only, until

TABLE 1. REACTION RATE DATA

Feed composition—14.3% H_2 , 18.3% D_2 , 67.4% A; $T_o = 293^\circ K$; $L = 4.0$ ft.

Product composition

H_2	HD	D_2	P_1	P_2	$T_2, ^\circ K$	u_2	a_2	t'_{max}	r	k
(mole fraction)	(mole fraction)	(mole fraction)	atm.	atm.		ft./sec.		sec. $\times 10^6$	$\frac{g. \text{ moles}}{(\text{sec.})(\text{liter})}$	$\frac{\text{liter}}{(\text{g.-mole})(\text{sec.})} \times 10^{-6}$
0.131	0.024	0.171	0.334	3.69	997	3,600	1,062	2,237	1,638	0.078
0.125	0.036	0.165	0.201	5.70	2,137	5,800	1,463	3,273	996	0.116
0.099	0.088	0.139	0.201	9.00	3,217	7,300	1,768	4,016	788	0.365
0.098	0.086	0.139	0.201	9.00	3,217	7,300	1,768	4,016	788	0.371
										0.48
										2.0
										8.6
										8.9

the mechanism at high temperature is established and the observed rates are confirmed.

The average rate defined as

$$\bar{r} = \frac{2\bar{C}_{HD}}{t'_{\max}} \quad (13)$$

is also included in Table 1.

DISCUSSION

From the preceding description and the experimental data for the hydrogen-deuterium exchange reaction several conclusions can be drawn regarding shock tube reactors:

1. Extremely high temperatures and moderate pressures can be obtained with relatively simple and inexpensive equipment. The absence of equipment for heating and cooling the reactor is a particular advantage.

2. Almost any combination of temperature, pressure, and residence time can be established by variation of the driver gas composition, pressure, and temperature; the test gas pressure and composition; and the reactor length. The use of reactants to change the temperature behind the wave was illustrated with oxygen and argon in this study. Combustion of the driver gas to produce a higher shock strength was also illustrated.

3. The reactants are compressed and elevated in temperature almost instantaneously (in the order of a few microseconds) and are expanded and cooled almost as fast. This rapid heating and cooling are difficult to obtain in conventional reactors. The rapid quenching is a particular advantage in reacting systems where relatively unstable compounds are to be produced.

4. Relatively uniform temperature and pressure can be maintained in the reaction zone by dilution with inert gases.

5. The conditions in the reaction zone can be estimated from measurement of the wave velocity and analysis of the product gas only. If the temperature, pressure, and composition in the reaction zone are relatively uniform, these computations are very simple and straightforward. If conditions vary significantly across the reaction zone, a reaction rate expression or expressions must be postulated and the computations carried out step-by-step and/or reiteratively. Measurement of the transient temperature and pressure in the reaction zone is possible and desirable if precise results are to be obtained. Expensive instruments with rapid response and high resolution are necessary for such measurements.

6. Each longitudinal element of gas in the reactor is subjected to elevated temperature and pressure for a different period of time and the reacted gas is all mixed before sampling and analysis of the reaction process. The rate constant must be evaluated from a twice-integrated form of the rate expression. These two integrations of course reduce the sensitivity of the determination of the best rate expression and the evaluation of the rate constant as compared with a differential reactor. If the temperature varies significantly across the reaction zone or if more than one reaction occurs, the determination of the form of the best rate expressions and the evaluation of a rate constant may be virtually impossible.

7. In the simple apparatus described herein the product gas is also diluted by the much greater mass of driver gas before sampling. This reduces the potential accuracy of the analysis of the product gas. The addition of an inert component to the test gas to minimize the variation in temperature across the reaction zone further dilutes the product. Dilution by the driver gas prior to sampling is minimized in the more complicated apparatus described by Glick and co-workers (10, 13).

8. Equilibrium compositions at high temperature can readily be obtained and quenched in a simple shock tube as illustrated for a wide range of mixtures of hydrogen and deuterium.

9. Overall reaction rates can be measured by the simple technique described herein, but a more complex and better instrumented apparatus is required to determine the mechanism of a reaction.

SUMMARY

A simple shock tube of the type described herein is an inexpensive and flexible device for exploratory measurements of chemical equilibrium and reaction rates at high temperatures. The variable reaction time, mixing of the product, dilution of the product with the driver gas, and the complex dependence of the process on temperature reduce the sensitivity of this device for precise determination of the reaction rate.

A shock tube can be designed and instrumented to alleviate some of these limitations and hence provide more precise kinetic data. However the required instrumentation is very expensive.

The theoretical equilibrium compositions of hydrogen-deuterium mixtures at high temperature were confirmed experimentally.

Limited overall rate data were determined for the hydrogen-deuterium exchange reaction in the temperature range from 1,000° to 3,200°K.

NOTATION

a_2	= velocity of sound in reacting gas behind shock wave
C	= concentration, moles/volume, prior to expansion
$\bar{C}$	= mixed mean concentration, prior to expansion
$F\{z\}$	= function of z
k	= reaction rate constant
K	= equilibrium constant
L	= length of test section
P	= pressure
$\bar{r}$	= mean reaction rate = $2\bar{C}_{DH}/t'_{\max}$
t	= time after initiation of shock wave
t'	= reaction time of element of test gas
$t'_{\max}$	= reaction time of the element of test gas adjacent to the high pressure diaphragm
T	= absolute temperature
u_2	= velocity of reacting gas relative to the tube wall
u_r	= velocity of rarefaction wave from quench chamber relative to the tube wall
u_s	= velocity of shock wave relative to tube wall
x	= distance along test section from high pressure diaphragm

Subscripts

0	= initial
1	= undisturbed test gas ahead of shock wave
2	= reacting gas behind shock wave
I, II, III, IV, V	= particular functions
D ₂	= deuterium
H ₂	= hydrogen
HD	= deuterium hydride

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A Mathematical Solution for the Condensation of Vapors from Noncondensing Gases in Laminar Flow inside Vertical Cylinders

WILLIAM D. BAASEL and JULIAN C. SMITH

Cornell University, Ithaca, New York

Previous efforts (2, 3, 8, 9, 11) to predict the rate of condensation from noncondensing gases in a cylindrical tube have been successful with a turbulent main flow. However, with laminar main flow the predicted rates often differ widely from the measured rates. These efforts are based on the macroscopic approach, frequently called *film theory*.

This paper presents a fundamental approach to the problem. The method used may be compared with the Graetz solution for heat transfer and becomes the Graetz solution when there is no condensation. Graetz made certain simplifying assumptions and used the microscopic approach to predict the rate of heat transfer. The solution presented herein applies the microscopic approach to mass transfer. It permits the determination of the rate of condensation if the physical constants and the dimensions of the system are known and the main flow is laminar.

William D. Baasel is with Ohio University, Athens, Ohio.

The basic method of solution, although presented for condensation, also is applicable to other mass transfer systems such as wetted-wall columns, dissolution from pipes of soluble material, and gas absorption. Because it may be used for such widely diverse systems and because it estimates the concentration and velocity profiles as well as the amount of mass transferred, this solution probably may be used to check the validity of the following assumptions used in the mathematical solution:

1. Operation was at steady state conditions.
2. The fluids were Newtonian and isotropic.
3. The flow pattern inside the vertical cylinder had rotational symmetry.
4. The molar density and diffusivity of the gases were constant throughout the tube. (The former is true at constant temperature and pressure for an ideal gas.)
5. No supersaturation occurred in the condensing section.