[CONTRIBUTION FROM THE PITTSBURGH EXPERIMENT STATION, U. S. BUREAU OF MINES]

Kinetics of the Methane-Oxygen Reaction[1]

BY G. L. FREAR[2]

In connection with studies on the utilization of waste natural gas, more information than was available in the literature was desired concerning the kinetics of the oxidation of methane. This reaction is so complicated that complete interpretation of the data previously available appeared impossible. Curtailment of funds has necessitated interruption of the present investigation, but publication of the results to date seemed desirable.

Bone and Wheeler[3] studied the rates of reaction of various methane-oxygen mixtures in a static system; they also employed circulatory experiments to isolate transient intermediate products. Bone and Allum[4] have recently repeated some of this work in silica vessels, again having shown the high reactivity of 2:1 methane-oxygen mixtures, which they adduced in support of the hydroxylation theory of hydrocarbon combustion. Fort and Hinshelwood,[5] working at temperatures of 447 to 487° and at pressures less than atmospheric, have shown by static experiments the relatively greater dependence of the reaction rate upon the concentration of methane than upon that of oxygen. Induction periods complicated their results so as to preclude detailed analysis, but the order of the reaction appeared to lie between third and fourth, and the heat of activation was estimated to be 61,500. Increase in the silica surface was shown to decrease the rate, indicating breakage of the reaction chains at the walls. In the present work flow experiments were employed to study the yields of intermediate and final products as contact time, total pressure, and surface were systematically varied.

Experimental

Mixtures of methane and oxygen in constant proportions were passed under constant pressure head through drying tubes charged with magnesium perchlorate. The silica reaction tubes were heated in a horizontal, manually controlled electric furnace containing a heavy alloy steel tube to reduce temperature gradients. Exploration of the reaction chamber with a movable thermocouple showed that at 600° fully one-half of the chamber was within 1° of the temperature of the middle, and only about 10% of the volume was as much as 10° cooler. Reaction tube I consisted of an annulus formed by one silica tube of 0.5 cm. o. d. held concentrically within another of 0.67 cm. i. d. The effective length of the annulus was 20 cm., providing a 3.12-cc. reaction chamber with a surface-volume ratio of 23.5 cm.$^{-1}$. The inner tube served as protection for two calibrated platinum-platinum-10% rhodium thermocouples connected through an ice-bath cold junction with a Leeds and Northrup portable potentiometer. Rapid preheating of the inlet gas and quenching of the exit gas were accomplished by passage through constricted annuli at either end of the reaction tube. Tube II, of 31.1 cc. capacity, was constructed from a 23-cm. length of 1.37-cm. i. d. tube, into which projected 0.5-cm. o. d. thermocouple protection tubes, 2.5 cm. from the inlet end and 9 cm. from the exit end of the reaction chamber. The surface-volume ratio was 3.75 cm.$^{-1}$. Tube III was prepared by packing tube II with cracked sections of transparent silica tubing so as to give a free space of 22.4 cc. and a surface-volume ratio exceeding 20 cm.$^{-1}$.

Methane was prepared by fractionation of Pittsburgh natural gas. Fractionation analysis indicated the absence of higher hydrocarbons and neither carbon monoxide nor carbon dioxide was detectable by Orsat analysis. About 0.1% oxygen and 98% methane were present, the remainder being nitrogen. Commercial 99.5% oxygen was used without further purification.

The mixed gases were admitted to the reaction tubes through glass tubes attached by water-cooled wax joints. Manometers at the inlet and exit of the reaction tube indicated the pressure in the reaction chamber. In the experiments at atmospheric pressure the inlet gas passed through a trap immersed in solid carbon dioxide and acetone before entering the furnace, and a series of such traps at the exit of the reaction tube collected the formaldehyde and moisture formed in the reaction. A bead tower filled with water and immersed in an ice-bath scrubbed out any remaining formaldehyde. Formaldehyde was determined by the Romijn iodometric method. The remainder of the condensate in the carbon dioxide traps was reported as water. No methyl alcohol was detected and no test for peroxides was attempted. Beyond the bead tower, direct connection with an all-glass Orsat apparatus permitted collection of a composite sample of the off-gas during sampling of the condensate. The volume of the remainder of the off-gas was observed by collection at constant pressure in a calibrated receiver. Prior to sampling, a sufficient quantity of the reaction mixture was passed through the apparatus to assure establishment of steady conditions. In the experiments at reduced pressures determination of the condensable matter was neglected, the off-gas being collected in an ex-

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(2) Associate physical chemist, U. S. Bureau of Mines, Pittsburgh Experiment Station, Pittsburgh, Pa.

(3) Bone and Wheeler, *J. Chem. Soc.*, **81**, 535 (1902); **83**, 1074 (1903).

(4) Bone and Allum, *Proc. Roy. Soc.* (London), **A134**, 578 (1932).

(5) Fort and Hinshelwood, *ibid.*, **A129**, 284 (1930).

hausted receiver, from which it was transferred to the Orsat by a Toepler pump.

Discussion of Results

The rate of reaction of 76:22 methane–oxygen mixtures in tube I proved too slow for convenient study; an average result from three runs is included in Table III, showing the influence of surface. The effect of contact time on the yields of carbon dioxide, carbon monoxide, and formaldehyde is shown by the data of Table I, obtained with the same mixtures at atmospheric pressure and 600° in tube II. Other conditions remaining fixed, yields of carbon dioxide increase with time of contact. Irregularities in this relationship probably are attributable to the sensitivity of chain reactions to small variations in experimental conditions; each experiment represents a single run. The yields of carbon monoxide and of formaldehyde are each approximately 0.2% for the shortest contact times, and decrease to at most a few hundredths of one per cent. at times longer than seventy seconds. The individual results are somewhat erratic, but become more regular when the percentage of carbon dioxide is taken as the independent variable. Oxidation of the carbon monoxide by steam formed in the reaction is no doubt responsible for the trend of the carbon monoxide concentrations. The experiments are not sufficiently reproducible for prediction of the yields at shorter times of contact, but there is no definite evidence of induction periods in these runs.

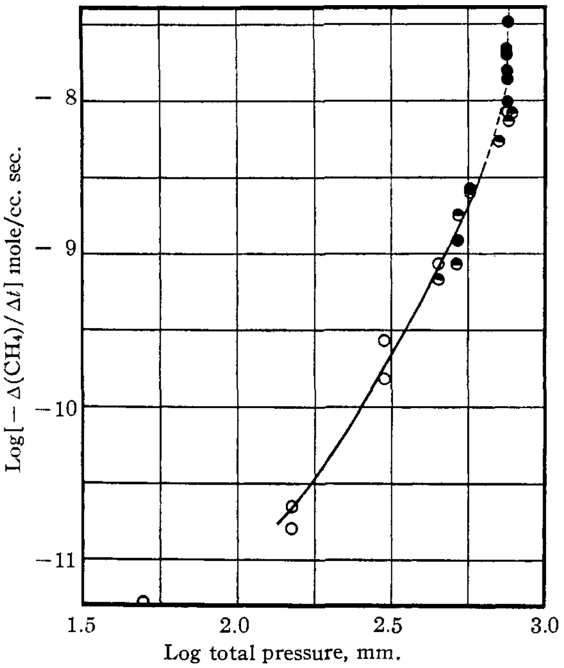

Fig. 1.—Influence of pressure on over-all rate of oxidation of methane: 77:21 CH_4–O_2 mixtures at 600° in 1.37 cm. silica tube. CH_4 oxidized: ○, < 1%; ◒, 1–4%; ●, > 4%.

Table I

Influence of Contact Time on Products of Methane Oxidation in 1.37-Cm. Silica Tube at 600° and Atmospheric Pressure

Expt.	Proportions of reactants, % CH_4	O_2	Temp., °C.	Pressure, mm.	Contact time, sec.	Percentage conversion of methane to CO_2	CO	H_2CO
8:09	77.6	20.8	602	760	11.0	0.47	0.22	0.17
8:10	77.4	21.0	606	750	12.7	.69	.17	.143
7:30	74.1	24.3	600	757	16.3	5.17	.05	.045
9:14	74.8	22.2	600	752	20.7	3.79	.18	.143
9:20	77.0	21.4	600	756	22.0	1.15	.19	.17
7:28	77.7	20.7	600	742	54.4	10.90	.14	.023
9:22	77.6	20.8	600	747	56.5	4.87	.00	.102
9:12	78.5	19.9	600	754	69.0	9.90	.00	.034
7:26	76.6	21.8	600	746	103.00	13.2	.41	.035

The variation in the over-all rate of oxidation of methane in the same mixture as a function of the total pressure is shown by the logarithmic plot of rate *vs.* total pressure in Fig. 1. The slope of this curve indicates the apparent order of the reaction.[6] Above 700 mm. the rate increases very rapidly with pressure, being more than doubled in a rise of 50 mm. Probably a chain mechanism is responsible for the high order of the reaction at atmospheric pressure. Fairly reproducible results obtained in the range from 450 to 575 mm. indicate an apparent order of reaction of 3.5. However, the slope continues to decrease as the pressure is lowered. Analytical errors probably are responsible for the irregularity of the results at the lowest pressures. The investigation was discontinued before the influence of the proportions of methane and oxygen on the reaction order could be studied.

The influence of pressure on the reaction of 75:22 methane–oxygen mixtures in tube III may be seen from the five experiments reported in Table II. Evidently the rate in the packed tube is relatively unaffected by pressure, the reaction being approximately first order. Table III presents a comparison of the rates of reaction of

(6) Clearly, the above rates are mere averages, for no account is taken of the decrease in concentration of the reactants as the change proceeds. However, the maximum decrease in methane content amounted to roughly 14%; while the concentration of oxygen in a few instances was reduced by more than one-half, the results of Bone and Allum[4] and of Fort and Hinshelwood[5] show plainly the lesser influence of oxygen on the rate. The conformity to the equation $CH_4 + 2O_2 = CO_2 + 2H_2O$ indicates that the influence of volume change is negligible. In fact, the three designations used in Fig. 1 to denote the extent of oxidation of methane in the individual experiments reveal no definite trend of over-all rate with methane consumption.

like mixtures at equal pressures with and without packing. As observed by Gibson and Hinshelwood[7] in their study of the hydrogen–oxygen reaction, packing retards the oxidation at the higher pressures and accelerates it at the lower pressures.

TABLE II

OVER-ALL REACTION RATE OF 75:22 CH_4–O_2 MIXTURES AT VARIED PRESSURES IN PACKED SILICA TUBE AT 600°

Expt.	Press., mm.	Initial compn., % CH_4	Initial compn., % O_2	Contact time, sec.	Compn. of off-gas, % CO_2	Compn. of off-gas, % CO	$-\Delta(CH_4)/\Delta t$ moles/cc. sec.
6:29	150	74.8	21.9	56.1	0.24	0.43	3.44×10^{-10}
6:26	300	75	22.0	118	.74	.18	4.21×10^{-10}
3:20	450	73.7	22.1	222	1.31	.20	5.44×10^{-10}
3:21	522	73.7	22.1	293	2.78	.21	9.22×10^{-10}
3:23	575	75.1	22.3	355	5.10	.13	13.72×10^{-10}

TABLE III

COMPARISON OF OXIDATION RATES OF 76:22 METHANE–OXYGEN MIXTURES IN UNPACKED AND PACKED TUBES

Press., mm.	Reaction tube surface/volume ratio, cm.$^{-1}$	$-\Delta(CH_4)/\Delta t$, moles/cc. sec.			Ratio of rates: packed to unpacked
		1.37 cm. unpacked (interpolated) 3.5	1.37 cm. packed (20)	Tube I annulus (average) 23.5	
740		12.0×10^{-9}		1.5×10^{-9}	0.12
575		2.2×10^{-9}	1.37×10^{-9}		.61
522		1.4×10^{-9}	0.92×10^{-9}		.65
450		0.81×10^{-9}	$.54 \times 10^{-9}$		.67
300		$.18 \times 10^{-9}$	$.42 \times 10^{-9}$		2.3
150		$.022 \times 10^{-9}$	$.34 \times 10^{-9}$		15

Apparently the homogeneous reaction predominating in the absence of packing is propagated in chains of some length, as may be inferred from the sensitivity of the rate to pressure. The retardation at atmospheric pressure produced by packing indicates breakage of the reaction chains at the walls. That a distinct heterogeneous mechanism prevails in the packed tube is evidenced by the relatively slight influence of pressure on the rate.

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Summary

1. The influence of contact time, pressure, and of packing upon the oxidation of 76:22 methane–oxygen mixtures in silica tubes at 600° has been studied by a flow method.

2. In the absence of packing, a chain mechanism predominates, the apparent reaction order being 3.5 at 450 to 575 mm. pressure, and increasing rapidly with pressure.

3. In the packed tube the reaction is approximately first order; its rate exceeds that of the reaction in the unpacked tube when the pressure is 300 mm. or lower.

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[7] Gibson and Hinshelwood, *Proc. Roy. Soc.* (London), **A118**, 170 (1928); **A119**, 591 (1928).

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF THE CARNEGIE INSTITUTE OF TECHNOLOGY]

Thermodynamics of Solid Solutions. I. Perfect Solutions

BY HARRY SELTZ

Binary systems which solidify with the formation of solid solutions can be classified as follows. 1. Complete miscibility in the solid state: (a) all points on the liquidus and solidus curves lie between the melting points of the two components. (b) The liquidus and solidus curves pass through a maximum. (c) The liquidus and solidus curves pass through a minimum. 2. Partial miscibility in the solid state: (a) the two series of solid solutions form an eutectic. (b) The two series of solid solutions show a transition.

Roozeboom,[1] following the thermodynamic treatment of Gibbs, showed the forms of the free energy curves, for liquid and solid states, which would give rise to the above types of solid solution formations. This treatment is entirely qualitative and is difficult to apply quantitatively owing to the fact that the partial molal free energy of a constituent of a solution approaches minus infinity as its concentration approaches zero. The purpose of this paper is to attempt to apply the concept of fugacity or activity to this problem, following the methods which G. N. Lewis[2] and his collaborators have developed so successfully in the treatment of liquid solutions.

Theoretical

If a binary solution contains n_A moles of a component "A" and n_B moles of a component "B" and the total free energy of the solution is F, the partial molal free energies of the components,

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[1] Roozeboom, *Z. physik. Chem.*, **30**, 385 (1899).

[2] Lewis and Randall, "Thermodynamics," The McGraw-Hill Book Co., Inc., New York.