saturated aliphatic alcohols,[10] which has been shown to be 7.7 E. U. In the case of the alcohol series the free energy of formation changed by about 500 cal. per CH_2 group added. No similar definite statement can be made in the present case partly because the heats of combustion utilized in spite of their high percentage accuracy may be in error by a few hundred calories due to their magnitude.

Summary

1. Specific heat measurements on toluene covering the temperature range from 14 to 298°K. have been made.

2. The heat of fusion and temperature of fusion were measured.

3. The entropy and free energy of toluene at 298°K. have been calculated. Preliminary values on *m*-xylene are also included.

BERKELEY, CALIFORNIA

[CONTRIBUTION No. 16 FROM THE EXPERIMENTAL STATION, E. I. DU PONT DE NEMOURS AND COMPANY]

THE MOVEMENT OF GASES AROUND ELECTRICALLY HEATED WIRES

BY SAM LENHER AND GUY B. TAYLOR

RECEIVED MAY 11, 1929 PUBLISHED SEPTEMBER 5, 1929

In conducting some experiments on the kinetics of the catalytic oxidation of sulfur dioxide by the hot wire method in which the pressure change was being followed on a mercury manometer, it was observed that the mercury meniscus oscillated slightly, indicating a periodic pressure change. Further investigation showed that this periodic effect was not a catalytic phenomenon since it occurred in air and other gases where no chemical reaction was possible.

Platinum wires, 0.25 mm. in diameter and 10 cm. or more in length, were sealed in glass cylinders 3 to 6 cm. in diameter. When the wire was heated electrically to any temperature from about 300° to a white heat, a small periodic pressure change could be detected on a sensitive manometer. The fluctuations occurred from 50 to 100 times per minute and were synchronized with a minute change in the heating current. The current fluctuation was detected by putting the secondary of a small transformer in series with the storage battery used for heating the wire and connecting the primary with a high sensitivity galvanometer. The same effects were observed with wires sealed in spherical glass vessels.

The magnitude of the pressure change at a pressure of one atmosphere when the wire was either nearly vertical or horizontal was a fraction of a centimeter of water. As the tilt of the vessel was increased the periodic

---

[10] Kelley, THIS JOURNAL, 51, 779 (1929).

fluctuation became more pronounced, until at a tilt angle of 45° the change became several centimeters of water.

The periodic pressure change was observed with a nearly horizontal wire in air, nitrogen, argon and carbon dioxide but not in hydrogen or helium. The effect, with air, decreased with decrease of pressure from two atmospheres to one-quarter atmosphere, where in this particular experiment the periodic phenomenon stopped.

It appeared probable that the periodic phenomena were connected with convection currents in the gas; this was confirmed by experiment. A platinum wire was sealed vertically in a cylindrical glass vessel with a tungsten weight on the lower end dipping into mercury. The vessel was immersed in a large water thermostat and a gas along with a thin mist of sulfuric acid or titanium hydroxide was introduced. The white mist made the movements in the gas due to convection actually visible. The vessel was illuminated from the side by light from a Pointolite lamp. When the wire was heated electrically a zone was observed around the wire which was free from mist in sharp contrast to the body of gas. This zone appears to be the conduction zone postulated by Langmuir[1] and others.[2]

Langmuir, in studying the energy losses from hot wires, assumed that the transfer of heat from a hot body to a gas in contact with it took place across a thin film of gas next to the heated body through which heat was transferred principally by conduction and radiation. The mist-free zone

TABLE I

DIAMETER OF MIST-FREE ZONE AROUND A HOT PLATINUM WIRE (WIRE DIAMETER, 0.25 MM.)

E/I	Zone diam., mm.	Press., mm.	*E/I*	Zone diam., mm.	Press., mm.	Gas	*E/I*	Zone diam., mm.	Press., mm.
Air—Sulfuric Acid Mist			Helium—Titanium Hydroxide Mist			Titanium Hydroxide Mist			
1.8	5	760	1.1	4	760	Air	1.9	5	760
2.0	6	760	1.2	4	760	Air	2.0	6	350
2.3	6	760	1.3	5	760	Air	2.0	7–9	300
2.4	[a]	760	1.4	6	760	Air	2.0	[b]	200
2.0	6	340	1.5	7	760	H_2	2.0	10	760
2.0	10+	290	1.6	8	760	H_2	1.1	4	760
2.0	[b]	170	1.8	9	760	Air	1.3	3	760
			1.9	10	760	Air	1.8–2.0	5	760
			2.0	10	760	Air	2.3	6	760
						Air	2.5	[a]	760

[a] Zone broken up by convection currents. [b] Zone too wide to be measured.

---

[1] Langmuir, *Phys. Rev.*, **34**, 401 (1912); *Trans. Am. Inst. Elec. Eng.*, 31, 1011 (1912); *Trans. Am. Electrochem. Soc.*, **23**, 299 (1913).

[2] For the early literature on the conduction zone theory of convection see Dalby, *Proc. Inst. Mech. Eng.* (*London*), 921 October (1909).

observed in the present experiments followed the behavior of the conduction zone postulated by Langmuir in all respects except one important one. As Langmuir observed, the diameter of the zone was greater in hydrogen and helium than for air at the same wire temperature. Its diameter increased with decrease in pressure as observed with the conduction zone by Kennelly.[1,3]

However, the zone observed here was not independent of the wire temperature. This is shown clearly by the data in Table I giving the relation of the diameter of the zone to the wire temperature and the gas pressure for several gases. Resistance of the wire measured as E/I was used as a criterion of equal temperature in the gases. At the high resistances the wire was white hot and at the lower resistances it was not visibly red. The dependence of the zone diameter on the wire temperature was also demonstrated under conditions where the body of the gas was not appreciably heated by the hot wire. A platinum wire was placed vertically in a large glass vessel containing a dilute titanium hydroxide mist in air. The air 1 cm. away from the glowing wire was only 10° above room temperature, but the increase in the diameter of the mist-free zone with increase of wire temperature was the same as that given in the experiments summarized in Table I.

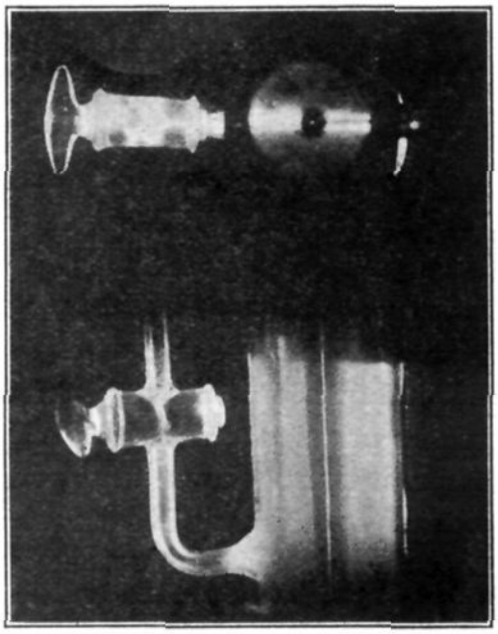

Fig. 1.

In hydrogen and helium the convection currents in the body of the gas outside the zone around the wire were streamline in character while in the other gases the currents tended to become turbulent, periodic and to break into the zone. The periodic pressure change synchronized with a clearly marked visible periodic turbulence in the convection currents.

Figure 1 shows the mist-free zone around a hot wire viewed from the side and from above through a plane window.

Summary

1. A periodic pressure change has been observed in vessels containing an axially placed electrically heated wire. The periodic pressure change has been found to be synchronized with a corresponding fluctuation in the heating current.

2. A mist-free zone around a hot wire in a gas containing a dilute mist

---

[3] Kennelly, *Trans. Am. Inst. Elec. Eng.*, **28**, 363 (1909).

has been noted. It has been shown that this zone behaves like the conduction film assumed to exist around a heated body.

3. It has been shown that the diameter of the mist-free zone is dependent on the wire temperature.

WILMINGTON, DELAWARE

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, OREGON STATE COLLEGE]

STUDIES ON HYDRAZINE. THE AUTO-OXIDATION

BY E. C. GILBERT

RECEIVED MAY 11, 1929 PUBLISHED SEPTEMBER 5, 1929

The strength of dilute solutions of hydrazine hydrate decreases rapidly in the presence of air. It has been shown[1] that this is due to oxidation by atmospheric oxygen. The reaction between oxygen and hydrazine has been studied also by Browne and Shetterly[2] who passed oxygen and ozone through hot hydrazine solutions, acid, neutral and alkaline. They found no products except nitrogen and in one case a trace of hydronitric acid. The oxidation of hydrazine in the presence of platinum black has been studied quite extensively[3] but this procedure as will be shown removes one of the principal products of the reaction. It is possible, though the evidence is conflicting, that platinum black also effects a catalytic decomposition of hydrazine. None was able to find a mathematical expression for the rate at which the hydrazine is oxidized.

The present work represents a study of the rate of oxidation of hydrazine hydrate in dilute solution by pure oxygen and by air. One of the most interesting developments was the discovery that considerable quantities of hydrogen peroxide are formed in the reaction. This is, of course, a concomitant of many auto-oxidations but hydrazine is a very powerful reducing agent and under some conditions at least reacts readily with peroxide. The presence of peroxide is of particular interest because it interferes seriously with many methods of determining hydrazine. In addition to this the velocity of oxidation under the conditions adopted has been found to follow a simple mathematical expression over a wide range of concentration, temperature and alkalinity.

Experimental Part

(1) **Procedure.**—The apparatus consists of an inverted Erlenmeyer flask into the mouth of which is fitted, by a ground joint, a Jena Gooch crucible containing a medium porous fritted glass disk through which oxygen may be passed into the solution. A hole made in what was formerly the bottom of the flask serves for the introduction of the

---

[1] Bray and Cuy, THIS JOURNAL, **46**, 1786 (1924).

[2] Browne and Shetterly, *ibid.*, 31, 790 (1909).

[3] Tanatar, *Z. physik. Chem.*, **40**, 475 (1902); **41,** 37 (1902); Purgotti and Zanichelli, *Gazz. chim. ital.*, **34,** I, 57 (1904); Gutbier and Neundlinger, *Z. physik. Chem.*, **84,** 203 (1913).