Reaction of Iron with Moist Chlorine

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The reaction of iron with moist chlorine has been studied at the temperature 20°C, a pressure of chlorine of 1 atm, and a water vapour pressure varying between 0.0003 and 17.54 mm Hg. The amount of iron which had reacted was measured gravimetrically and colourimetrically. The rate was found to be independent of the vapour pressure of water when this was below 0.05 mm Hg. At higher pressures a linear dependence was observed.

While numerous investigations have been reported dealing with the reactions of oxygen with metals, very few have dealt with the corrosive action of chlorine on metals. Heinemann[1] has investigated the corrosion of iron in commercial dry chlorine in the temperature range 77—251°C and at exposure times between 12 and 480 min. He found, that at 77°C the corrosion was proportional to time, while at higher temperatures, the dependence was parabolic. Brown[2] has examined the chlorine corrosion of several metals, including iron. For many metals, though not for iron, he found the rate of reaction to be proportional to the vapour pressures of the metal chlorides formed. Tsejtlin[3] examined the corrosion of iron in dry chlorine at temperatures between 240 and 310°C and by moist chlorine (1.5 and 30 % water by weight) between 130 and 310°C.

Apparently no work has been published dealing with the corrosion of iron in moist chlorine at about room temperature although this is of considerable importance in industry.

EXPERIMENTAL

The rate of reaction was measured in each case by weighing the sample before and after a known time of exposure to chlorine and by determining colourimetrically the amount of ferric chloride formed. The samples were kept under a constant pressure of chlorine, which was maintained by means of a gasometer. The experimental arrangement is shown in Fig. 1. The humidity of the chlorine was controlled by equilibration with saturated aqueous salt solutions and aqueous solutions of sulfuric acid all with known water vapour pressures. Details of these solutions are given in Table 1. Significant divergence is observed between values reported for the water vapour pressure of sulfuric acid solutions, but those of Shankman and Gordon,[4] Hornung and Giauque,[5] Daudt,[6] and
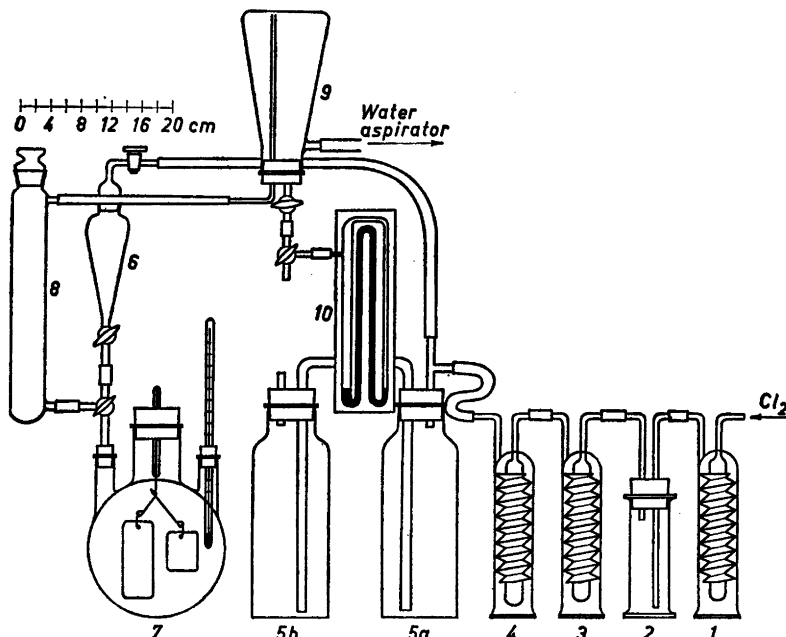
Fig. 1. The experimental arrangement for measurement of reaction rates: 1, Bubbling flask filled with concentrated sulfuric acid; 2, Safety trap, empty, 3 and 4, Bubbling flasks filled with humidity-controller; 5, Chlorine reservoir, consisting of two 3-litre flasks, partially filled with humidity-controller and connected by a tube; 6, Trap with glass-wool used for removing droplets from the gas; 7, Reaction vessel, a 2-litre, 3-necked distilling flask; 8, Calcium chloride drier; 9, Suction flask (1 litre); 10, Mercury manometer.

Greenewalt[7] are supposed to be of the highest accuracy and as these values do not differ significantly among themselves they have been selected for use here. It should be noted, that the values given by Regnault,[8] which are apparently those referred to in the *Hand-book of Chemistry and Physics*[9] are in very poor agreement with the data cited in Table 1.

The temperature 20°C could be maintained within ± 0.01°C by immersion of the reaction flask in a water thermostat. The time of exposure was varied between 15 min and 100 h. The samples were made of SM-fluss steel, containing 99.9 % Fe. To correct for special edge effects 2 sizes of plates were used, the one 4 × 10 cm and the other 4 × 5 cm with surface areas of 82.65 and 40.85 cm², respectively. The plates were polished with 3/0 sand paper, rinsed with alcohol and ether, air-dried and until use stored in desiccators over silica gel. The samples were weighed with an accuracy of 0.1 mg. After reaction the samples were freed from the reaction layer by rinsing with alcohol and ether, dried in air and weighed again. The alcohol and ether used were then evaporated and the residue dissolved in hydrochloric acid, diluted in standard flasks and the iron content determined colourimetrically by formation of the 1,10-phenanthroline complex.

RESULTS

At water vapour pressures below 0.05 mm Hg the reaction rates showed such large variations that it was not possible to deduce, whether the reaction followed a rate law

$$w^n = k \times t \quad \text{with } n = 1 \text{ or } 2 \tag{1}$$

Table 1. Solutions used to control the water vapour pressure.

Solute	Concentration % by weight	Density g/ml	Water vap. press. mm Hg	Relative humidity %
None			17.54	100.00
$FeCl_3.6 H_2O$	satd.		6.85	39.0
$CaCl_2.6 H_2O$	satd.		5.61	32.0
H_2SO_4	56.5	1.461	3.80	22.8
»	65.8	1.562	1.45	11.4
»	71.9	1.633	0.53	5.70
»	74.4	1.662	0.33	4.03
»	76.6	1.687	0.180	2.85
»	82.7	1.756	0.047	1.14
»	96	1.835	0.00032	0.02

w is here the amount of iron reacted per unit area measured in g/m^2 and the exposure time t is measured in hours. The most likely possibility is $n = 2$, and the reaction rate is in that case given by the parabolic equation with $k = 0.005$ g^2/m^4 h.

At water vapour pressures above 0.05 but below 2 mm Hg the reaction was found to be linearly dependent on the water vapour pressure as shown at Fig. 2. The time dependence was found to be either nearly or truly parabolic
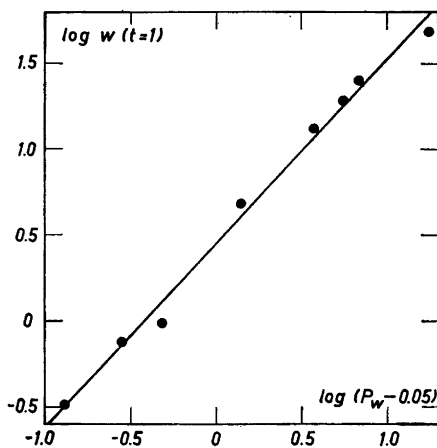

Fig. 2. The best values of the amount of iron reacted (g/m^2) after one hour's exposure (obtained from plots similar to that of Fig. 3) plotted logarithmically against the water vapour pressure, corrected by subtraction of 0.05 mm Hg. The slope of the line obtained by the method of least squares is 1.07, which is not significantly different from unity.
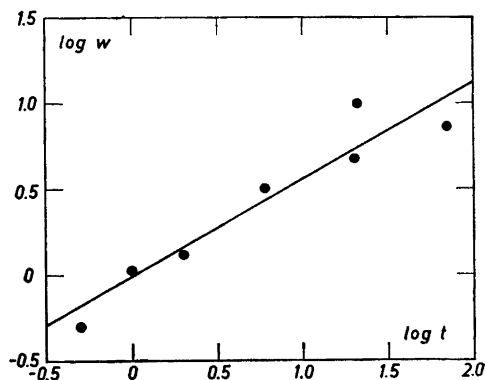
Fig. 3. The amount of iron reacted (g/m^2) at 0.53 mm Hg water vapour pressure plotted logarithmically *versus* time (h).

as exemplified by Fig. 3. On plotting the logarithm of w against the logarithm of the water vapour pressure, P_w (Fig. 2), it was observed that the fitting of the experimental points to a straight line was improved markedly by subtracting a small constant from the original value of P_w. By means of the method of least squares the value of this constant was found to be 0.05 mm Hg. Within the experimental uncertainty all the results obtained could be described by equation (2)

$$w^2/t = 5._8(P_w - 0.05)^2 \qquad (2)$$

measured in g^2/m^4 h, when P_w is measured in mm Hg and w and t as defined above.

At water vapour pressures above 2 mm Hg the reaction layer flowed off as a solution of ferric chloride. Although the correlation between reaction rate and water vapour pressure was the same as mentioned above, the time dependence of the reaction had undergone a transformation from parabolic to linear, the latter being true at the highest water vapour pressure. Hence, the correlation between reaction rate and water vapour pressure given by eqn. (2) could only be obeyed strictly for one given time of exposure, in this case about one hour. This is the reason, why the amount w (per unit area) after an exposure time of one hour has been selected in the plotting of w against P_w shown in Fig. 2. The plotting gives eqn. (3): w (1) $= 2._8 (P_w - 0.05)$, while inserting t equal to unity in eqn. (2) gives (4) w (1) $= 2._4 (P_w - 0.05)$ (g/m²), which is in reasonable accordance with (3). At the highest water vapour pressure, where the reaction was linearly dependent on time, the reaction followed (5) $w = 2.8$ $(P_w - 0.05)$ t (g/m²h). However, eqns. (3)—(5) are restricted in value by the very pronounced pitting observed. By microscopic examinations of the exposed specimens the deepest holes at the reacted surfaces were found to be 10 times as deep as the uniform corrosion given by the above equations. The pitting was of course not found at water vapour pressures below 2 mm Hg, where the reaction layers adhered to the metal.

DISCUSSION

As the hydrates of ferric chloride were very hygroscopic, the technique used here did not allow an examination of the reaction layers. For this purpose operation in a dry box would be required. Therefore no definite conclusion could be given. However, it is believed that the very strong humidity dependence of the reaction may be due to formation of ferric chloride hydrates. In favour of this hypothesis may be cited the humidity independence at the lowest water vapour pressures, at which only anhydrous ferric chloride is stable. Hence it may have meaning to compare the water vapour pressure critical for the humidity dependence of the reaction (0.05 mm Hg) with the equilibrium water vapour pressures of the ferric chloride hydrates, for which reason these are under investigation. Although the final values cannot yet be published, it has been found that the lowest water vapour pressures at which $FeCl_3 \cdot 2.5 \ H_2O$ and $FeCl_3 \cdot 2 \ H_2O$ are stable, must lie at about 0.18 and 0.03 mm Hg, respectively. From these values the equilibrium water vapour pressure

for the transition of $FeCl_3 \cdot 2.5\ H_2O$ to $FeCl_3$ is calculated to 0.04 mm Hg. Obviously the latter value seems to be that, which corresponds to the critical corrosion water vapour pressure. Further the rate of formation of $FeCl_3 \cdot 2\ H_2O$ is very slow in contrast to that of $FeCl_3 \cdot 2.5\ H_2O$. As the reaction layer flowed off at water vapour pressures above 2 mm Hg, neither solid $FeCl_3 \cdot 3.5\ H_2O$ or $FeCl_3 \cdot 6\ H_2O$ can be formed. Hence, the solid reaction layer is believed to be composed of $FeCl_3$ and $FeCl_3 \cdot 2.5\ H_2O$ (and perhaps $FeCl_3 \cdot 2\ H_2O$).

Future investigations would be concerned with measurements at other temperatures and chlorine pressures in order to obtain the activation energy and elucidate, what role the diffusion plays in the reaction.

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