

Our data for the vapour pressure of B_2O_3 and its heat of vaporisation are in good agreement with all published effusion measurements^{2,5,6} but differ considerably from data obtained by dynamic methods^{3,7} (Table 3). A flow method is hardly suitable because of substantial errors introduced by the formation of volatile compounds of boron oxide with water vapour if the stream of inert gas is inadequately dried; the sharp increase in the volatility of boron oxide in the presence of water vapour has been reported repeatedly¹⁰⁻¹².

SUMMARY

1. An effusion method was used to measure the vapour pressure of boron oxide at 1299°–1515°K. An equation relating $\log p$ to $1/T$ is given.
2. Dissociation of B_2O_3 at 1299°–1515°K has been shown to be negligible.
3. The heat of vaporisation of boron oxide was calculated from experimental and published data.

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THE COMBINED ACTION OF SULPHIDES AND ORGANIC COMPOUNDS ON THE ACID CORROSION AND BRITTLINESS OF IRON

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The action of inhibitors on the rate of corrosion of iron in acid solutions depends not only on the chemical nature and structure of the inhibitor molecules, but also, to a considerable extent, on the electrochemical state of the metal surface: the magnitude and sign of the surface charge, the simultaneous adsorption of inorganic ions, etc.

Certain classes of organic compound (nitrogen-containing organic bases, alkaloids, and some aldehydes) show a retarding action on the corrosion of iron in acid solution only in the presence of halide ions¹⁻³. Many systems contain sulphides or hydrogen sulphide, the latter being produced

when the metal contains sulphur or when sulphur is present in low oxidation states, in an aggressive medium. Hydrogen sulphide intensifies the corrosion of iron⁴⁻⁷ and leads to brittleness as a result of the inclusion of hydrogen by the metal. In the presence of certain organic compounds, however, the intensifying action of hydrogen sulphide disappears, and, in addition, small concentrations of the latter bring out, and in some cases intensify considerably, the protective action of a number of organic inhibitors².

The mechanism of the combined action of hydrogen sulphide and organic compounds of various types has not been exhaustively examined, in spite of the theoretical and practical importance of this question.

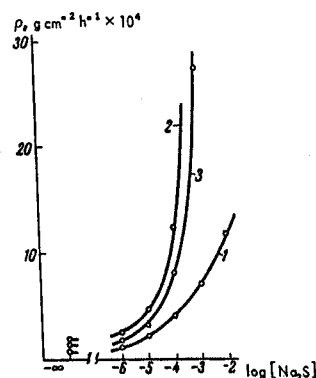


Fig. 1. Dependence of the rate of corrosion of iron on the logarithm of the Na_2S concentration: 1) NH_4SO_4 ; 2) + 0.01 M $C_6H_5OSO_3Na$; 3) + saturated $C_{18}H_{37}OSO_3Na$.

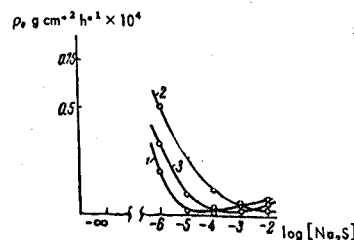


Fig. 2. Dependence of the rate of corrosion of iron on the logarithm of the Na_2S concentration in NH_4SO_4 : 1) + 0.001 M $(C_6H_5CH_2)_3N$; 2) + 0.001 N $N(C_4H_9)_4^+$; 3) + 0.0005 M narcotine.

EXPERIMENTAL

The rate of corrosion was determined at $18^\circ \pm 1^\circ$ from the volume of hydrogen liberated and from the loss in weight of the specimen (Armco iron and, in some confirmatory experiments, plates of Hilger chemically pure iron) in

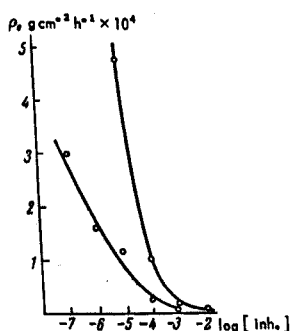


Fig. 3. Dependence of the rate of corrosion of iron in $N H_2SO_4 + 0.001 N Na_2S$ on the logarithm of the concentration of added organic base: 1) $(C_6H_5CH_2)_3N$; 2) $N(C_4H_9)_4^+$.

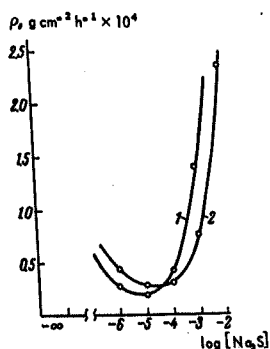


Fig. 4. Dependence of the rate of corrosion of iron in $8 N H_2SO_4$ on the logarithm of the Na_2S concentration: 1) $1.2 \times 10^{-4} M (C_6H_5CH_2)_3N$; 2) $0.001 N N(C_4H_9)_4^+$.

a solution of redistilled sulphuric acid containing the appropriate organic substances.

Fig. 1 shows the dependence of the rate of corrosion ρ ($g\ cm^{-2}\ h^{-1}$) of iron in $N H_2SO_4$ containing aliphatic sulphonic acids on the logarithm of the Na_2S concentration in the solution. The sulphonic acids* intensify the corrosive action of the hydrogen sulphide, although by themselves, in the pure state, they have no effect on the corrosion. Aromatic sulphonic acids also intensify the corrosive action of hydrogen sulphide.

Organic bases show different behaviour. Unlike organic anions, organic cations are able to prevent completely the intensifying action of hydrogen sulphide on the corrosion process, while the hydrogen sulphide brings out, or intensifies considerably the inhibiting action of the organic bases (Fig. 2). Thus the cations of tetrabutylammonium sulphate,

* The authors do not seem to distinguish between sulphonic acids (RSO_3H) and sulphonic-acid monoesters ($ROSO_3H$). The compounds referred to in Fig. 1 belong to the latter class (Ed. of Translation).

TABLE 1.

H_2SO_4	Inhibitor	H_2S, N	$\rho, g\ cm^{-2}\ h^{-1}$
1 N	0	0	$1.5 \cdot 10^{-4}$
	α -Thiophenecarboxylic acid	0	$1.6 \cdot 10^{-4}$
	"	0.001	$2.3 \cdot 10^{-5}$
	Thiourea 0.1 M	0	$2.1 \cdot 10^{-4}$
	" 0.1 M	0.001	$4.5 \cdot 10^{-4}$
	" 0.01 M	0	$2.6 \cdot 10^{-5}$
	" 0.01 M	0.001	$5.5 \cdot 10^{-5}$
	Diphenylthiourea, saturated	0	$1.4 \cdot 10^{-5}$
	"	0.001	$1.9 \cdot 10^{-5}$
	Allylphenylthiourea, $4 \times 10^{-4} M$	0	no dissolution
8 N	" $4 \times 10^{-4} M$	0.001	"
	Allylphenylthiourea	0	$1.1 \cdot 10^{-4}$
	"	10^{-5}	$0.6 \cdot 10^{-4}$
	"	10^{-3}	$10 \cdot 10^{-4}$

tribenzylamine, and narcotine retard the corrosion of iron, and a similar effect is shown by other nitrogen-containing organic bases and alkaloids. Tribenzylamine, even in the presence of extremely low concentrations of Na_2S ($\sim 10^{-8} M$) decreases the rate of dissolution of iron by a factor of 8; in the absence of hydrogen sulphide, however, tribenzylamine has almost no effect on the corrosion of iron.

Increase in the concentration of organic base at constant hydrogen sulphide concentration increases the inhibiting effect (Fig. 3). The addition of $10^{-7} M$ tribenzylamine to $N H_2SO_4$ solution $10^{-3} N$ with respect to Na_2S prevents completely the corrosive action of the hydrogen sulphide.

The rate of corrosion in these systems in some cases increased with time, and in others decreased. The curves and the data in Table 1 were obtained from the average values of the rate of corrosion, measured at definite intervals after the start of the corrosion.

In concentrated acid solutions ($8 N H_2SO_4$) the promoting action of hydrogen sulphide on the inhibitor decreases with increase in the hydrogen sulphide concentration, and the corrosion starts to increase (Fig. 4): a minimum appears on the curve at approximately $10^{-4} N Na_2S$ (see also Fig. 2).

Organic compounds which exist in solution as neutral molecules, for example aliphatic acids and alcohols, are weakly adsorbed in pure sulphuric-acid solution at the steady-state potential of the spontaneous dissolution of iron^{2,8} so that they have no inhibiting action, but their presence in the acid solution in a number of cases intensifies the corrosive action of hydrogen sulphide (Fig. 5).

TABLE 2.

Organic compound	H_2S, N	Time required for rupture
No additive	0	$> 6\ h$
"	0.001	2-3 min
0.001 M tribenzylamine	0	$> 5\ h$
"	0.001	5 h
$C_6H_{13}OSO_3Na$	0	8 h
$C_6H_{13}OSO_3Na$	0.001	1.5-2 min
Hexyl alcohol	0	3 h
"	0.001	2 min
"	0.001	12 min.

The action of aliphatic aldehydes depends on the sulphuric-acid concentration. In N H_2SO_4 , freshly-distilled propionaldehyde, like alcohols and acids, intensifies the corrosive action of hydrogen sulphide, but in $8N$ H_2SO_4 , propionaldehyde, like amines, retards the corrosion process in the presence of hydrogen sulphide (Fig. 6). Butyraldehyde is a weak inhibitor in pure sulphuric-acid solution, but is a strong inhibitor in the presence of hydrogen sulphide. n-Heptaldehyde $[CH_3(CH_2)_5CHO]$ prevents the corrosion of iron completely in pure H_2SO_4 and also in the presence of hydrogen sulphide. Thus in N H_2SO_4 (and $8N$ H_2SO_4) + $10^{-3}N$ Na_2S + saturated n-heptaldehyde, an iron plate showed no loss in weight and no hydrogen was evolved over a period of 30 days. When removed from the solution and placed in pure acid containing no inhibitor, the plates did not dissolve, even after one month. In the case of amines, the inhibiting action is not retained when the plate is transferred to pure acid.

We have also studied the effect on the corrosion of iron of the sulphur-containing organic compounds: α -thiophenecarboxylic acid, dibenzyl sulphoxide, thiourea, diphenylthiourea, and allylphenylthiourea. In the presence of iron dissolving in acid, all these compounds decompose to form hydrogen sulphide, which can be detected from its odour or with suitable reagents. The action of each compound depends on the stability and structure of its molecule, on its solubility, and on the concentration of acid in which the iron is corroding⁹⁻¹³. Allylphenylthiourea, diphenylthiourea, and dibenzyl sulphoxide strongly retard the acid corrosion of iron¹⁴. In the presence of diphenylthiourea there is a prolonged induction period (approximately 40 h) in which the iron does not corrode. At comparatively high concentrations (0.1 M) thiourea intensifies the corrosion and does not prevent the accelerating action of hydrogen sulphide added to the solution; at small concentrations (0.01 M), however, thiourea prevents the intensifying action of hydrogen sulphide at concentrations of the latter equal to $10^{-3}N$ (Table 1).

α -Thiophenecarboxylic acid does not influence the rate of corrosion of iron in pure N H_2SO_4 , but increases the intensifying action of hydrogen sulphide. The addition of $10^{-3}N$ sulphide to a solution of diphenyl- or allylphenylthiourea in N H_2SO_4 does not reduce the inhibiting effect of these organic compounds, but in $8N$ H_2SO_4 the inhibiting effect is greatly reduced.

Brittleness Resulting from the Inclusion of Hydrogen

The rate of inclusion of hydrogen and the production of brittleness in iron in acid solutions containing various additives was studied by determining the time required for the rupture of a 0.2 mm diameter steel wire with a load of 1 kg and under cathodic polarisation ($i = 0.01$ A/cm²)¹⁵. N H_2SO_4 was used; the wire contained 0.05% of carbon and less than 0.05% of other impurities. The average results of the experiments are given in Table 2.

The organic nitrogen-containing bases which are inhibitors in the presence of hydrogen sulphide also prevent the production of brittleness in iron and steel when these are corroded in acid containing hydrogen sulphide. A similar action is shown by n-heptaldehyde and by some thiourea derivatives. Additives which do not decrease the corrosive action of hydrogen sulphide, such as sulphonic acids, alcohols, and organic acids, do not prevent the inclusion of hydrogen by iron. Similar results were obtained when the

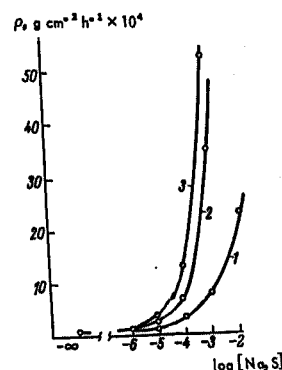


Fig. 5. Dependence of the rate of corrosion of iron in N H_2SO_4 on the logarithm of the Na_2S concentration (1); 2) + saturated caproic acid; 3) + saturated hexyl alcohol.

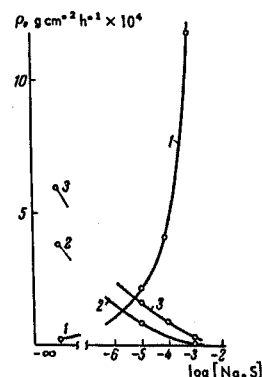


Fig. 6. Dependence of the rate of corrosion of iron on the logarithm of the Na_2S concentration: 1) N H_2SO_4 + CH_3CH_2CHO ; 2) $8N$ H_2SO_4 + 0.1 M CH_3CH_2CHO ; 3) N H_2SO_4 + 0.1 M $CH_3(CH_2)_2CHO$ (the ordinate should be decreased by a factor of ten for curve 3).

brittleness was studied by measuring the number of inflections required to fracture iron plates which had been polarised ($i = 0.01$ A/cm²) in corresponding solutions for 15 min.

DISCUSSION

The intensifying action of hydrogen sulphide on corrosion has been studied by many workers: Karnitskii and Golubev⁶ attribute the effect to the formation of FeS particles which create local galvanic cells; Hoar and Evans^{10,7} to the adsorption of sulphides on anodic regions; Makrides and Hackerman⁹ to a catalytic action involving the formation of FeS and its decomposition by acid to H_2S and Fe^{2+} ; and Kuznetsov and Iofa¹⁶ to the adsorption of HS^- ions and the production of a negative ψ_1 -potential which accelerates the cathodic and anodic reactions.

Fil'ko¹⁷ attributes the combined action of hydrogen sulphide and amines to the increase in the adsorption of amine in the presence of HS^- ions, and an increase in the strength of the bond between the latter and the iron atoms. These views, however, cannot be regarded as satisfactory.

The intensifying action of hydrogen sulphide on the rate of dissolution of iron must be due to the catalytic acceleration of the ionisation of the iron by adsorbed HS^- ions, which is similar to the acceleration of this process by adsorbed OH^- ions when the pH of the solution is increased¹⁸. When the sulphide ions are adsorbed from acid solutions, an irreversibly chemisorbed layer, firmly attached to the iron, is formed¹⁹. This bond between the iron and sulphur atoms may decrease the strength of the bonds between the iron atoms, and this will facilitate their dissolution.

The polarisation curves (Fig. 7) show that hydrogen sulphide accelerates the anodic process of iron ionisation to a much greater extent than the cathodic process. Thus at $\varphi = -0.2\text{ V}$, the anodic process is accelerated by a factor of 32, and the cathodic process at $\varphi = -0.3\text{ V}$ by a factor of 2. The acceleration of the cathodic process may arise because a negative ψ_1 -potential is set up¹⁶.

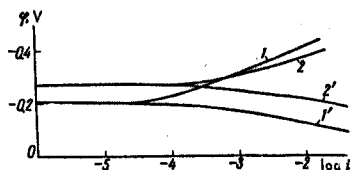


Fig. 7. Polarisation curves for iron electrode: 1) $\text{N H}_2\text{SO}_4$; 2) $+0.001\text{ N Na}_2\text{S}$.

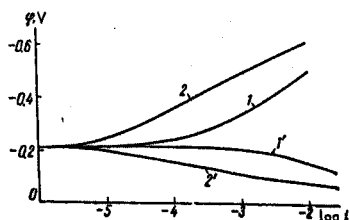


Fig. 8. Polarisation curves for iron electrode in $\text{N H}_2\text{SO}_4$: 1) $+0.001\text{ N (C}_6\text{H}_5\text{CH}_2)_3\text{N}$; 2) $+0.001\text{ N (C}_6\text{H}_5\text{CH}_2)_3\text{N} + 0.001\text{ N Na}_2\text{S}$.

Measurement of the HS^- ion adsorption indicates that the chemisorbed sulphur, like adsorbed halide ions², reacts on the iron surface to form iron-sulphur dipoles whose negative ends are directed towards the solution. This should cause displacement of the electrocapillary zero of iron to more positive potentials, so that in the presence of hydrogen sulphide at the steady-state potential, the iron surface acquires a less positive, or negative charge. The displacement of the steady-state potential in the presence of

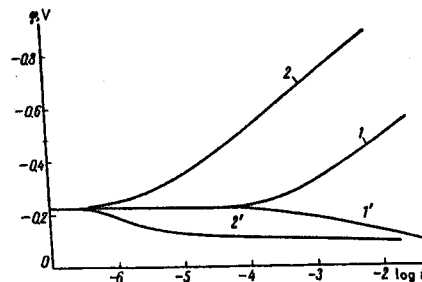


Fig. 9. Polarisation curves for iron electrode in $\text{N H}_2\text{SO}_4$: 1) $+0.1\text{ M CH}_3(\text{CH}_2)_2\text{CHO}$; 2) $+0.1\text{ M CH}_3(\text{CH}_2)_2\text{CHO} + 0.001\text{ N Na}_2\text{S}$.

hydrogen sulphide towards more negative values intensifies this effect.

The formation of Fe-S dipoles arranged with their negative ends towards the solution, together with the reduced positive charge on the surface, should facilitate the adsorption of organic cations, and experiments have shown that corrosion is retarded when hydrogen sulphide is added to an acidified solution of an organic base. The adsorption of the organic cations produces a positive ψ_1 -potential, which retards the cathodic and anodic processes. When the surface is filled with adsorbed molecules of the organic compound, the effect associated with the production of the positive ψ_1 -potential is accompanied by a retardation of the electrochemical reaction as a result of a change in the structure of the electrical double layer.

The formation of the dipoles on the surface hinders the adsorption of sulphonic acids, so that the latter do not reduce the intensifying action of hydrogen sulphide on the corrosion. The adsorption of organic acids and alcohols is hindered similarly, and the effect of other organic compounds can be explained in like fashion.

Molecules of aldehydes in acid solution are apparently able to combine with a proton to form positive ions which are adsorbed on the negatively charged iron surface, so that their inhibiting action, like that of nitrogen-containing bases, increases sharply when hydrogen sulphide is added to the solution. The polarisation curves (Figs. 7-9) show that a greater increase in the hydrogen overvoltage takes place in the presence of H_2S . The reason for the absence of inhibiting action in the case of propionaldehyde in sulphuric acid solution with concentration less than 1 N in the presence of Na_2S is not clear.

Derivatives of thiourea and other sulphur-containing organic compounds may intensify or inhibit the corrosion of iron, depending on the H_2S concentration produced at the surface by the decomposition of these compounds⁹. Concentrated thiourea solutions (0.1 N and above) decompose to yield H_2S in high concentrations, and have an intensifying effect. In dilute solutions (0.01 N), the H_2S concentration is low and the thiourea behaves as an inhibitor. The hydrogen sulphide formed by the decomposition of sulphur-containing compounds facilitates the adsorption of the undecomposed molecules and their decomposition products. It might be suggested that the thiourea derivatives and other sulphur-containing compounds are adsorbed on the iron surface independently of the adsorption of hydrogen sulphide, but we

have as yet been unable to find a sulphur-containing organic compound which is not decomposed to form sulphides at the potential of the spontaneous dissolution of iron.

These and earlier results indicate that organic compounds can act as inhibitors in acid solutions only when the metal surface is able to adsorb them. This ability results chiefly from the chemisorption of inorganic ions, such as halides, HS^- , and CNS^- , which must be added to the solution or produced by dissociation or decomposition of the organic compound.

Halide ions, whose effect on corrosion in the presence of organic bases resembles that of HS^- ions, do not by themselves intensify the corrosion of iron, but retard it (this is particularly true of I^- ions)¹⁻³. The reason for this difference is not yet clear.

SUMMARY

1. The combined action of hydrogen sulphide and organic compounds of various types on the rate of dissolution of iron in sulphuric-acid solutions has been studied.
2. Organic nitrogen-containing bases and certain aldehydes (butyraldehyde, n-heptaldehyde, etc.), which do not retard the rate of dissolution of iron in pure sulphuric-acid solutions, or which have a weak inhibiting action, become powerful inhibitors in the presence of hydrogen sulphide, and eliminate completely the intensifying action of the latter on the corrosion of iron.
3. Organic sulphonic acids and aliphatic alcohols and acids do not exhibit this property, and may even increase slightly the intensifying action of hydrogen sulphide.
4. Sulphur-containing compounds such as derivatives of thiourea and dibenzyl sulfoxide, which decompose to liberate hydrogen sulphide in the presence of iron dissolving in acid, have a powerful inhibiting action on the acid corrosion of iron.
5. Organic compounds which have an inhibiting action in the presence of hydrogen sulphide prevent the inclusion of hydrogen and the production of brittleness in iron by hydrogen sulphide.
6. These results, together with the polarisation curves for the systems and measurement of the adsorption of sulphur on iron, make it possible to reach certain conclusions regarding the mechanism of the combined action of organic compounds and hydrogen sulphide on the corrosion of iron in acid solutions.

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AEROSOLS FORMED IN RADIOCHEMICAL REACTIONS

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In experiments on the transformation of gaseous organic compounds¹ and also their oxidation² under the influence of fast electrons, it has been observed visually that aerosols are formed, these being liquid products of the radiochemical reactions suspended in the irradiated gas.

The extent of formation of such aerosols varied both with the nature of the reactants (methane, ethane, propane, butane, ethylene, and mixtures of methane or ethylene with oxygen) and with the experimental conditions. Such aerosols have not yet been described in the literature. They are of considerable interest in the radiochemistry of gases, since radiochemical reactions obviously occur not only in the gas phase but also in the mixture of gas and liquid droplets; we therefore decided to investigate some of the properties of such aerosols.

EXPERIMENTAL

The aerosol was prepared by exposing various gases to a stream of fast electrons in a brass reaction vessel of 2-litre capacity. Samples of the aerosol were then taken for investigation. In some experiments they were diluted with methane. Exposure was carried out in an accelerator which gave a current of electrons with a mean energy of 112 keV and an intensity up to 100 μA . The electrons, accelerated by a potential difference of 125 kV, passed out of the accelerator through an aluminium foil into the brass reaction vessel, which was thermostatted with a water jacket. The properties of the aerosol were studied from the absorption of a beam of light in the brass reaction vessel 1 (Fig. 1) containing the aerosol. Light from a 70-W car headlamp bulb 2 passed through the optical system 3, the glass windows 4 fastened with plasticine, and the layer of aerosol in the chamber, and then fell on the selenium photocell 5. The