

At least two contributions are believed to be important in these types of mixtures.

1) There is an endothermic term opposing the components to be mixed due to strong oxygen or halogen bridges (covalent forces) present in one of the components.

2) The other term is the exothermic coulombic repulsion term which arises from the reduction in second nearest neighbour coulombic repulsion between the cations. A small cation like Si^{4+} , Be^{2+} or Mg^{2+} strongly favours a large cation of low charge as next nearest neighbour.

The size of these two opposing terms will determine whether the energy of mixing shall be a) only positive, b) both positive and negative and c) only negative.

1. Kracek, F. C. *J. Am. Chem. Soc.* **52** (1930) 1436.
2. Førland, T. In Sundheim, B. R. *Fused Salts*, McGraw, New York 1964, pp. 150–154.
3. Lumsden, J. *Thermodynamics of Molten Salt Mixtures*, Academic, London and New York 1966, pp. 327–330.
4. Holm, J. L., Kleppa, O. J. and Westrum, Jr., E. F. *Geochim. Cosmochim. Acta* **31** (1967) 2289.
5. Kelley, K. K. *U.S. Bur. Mines, Bull.* **584** (1960).
6. *JANAF Thermochemical Tables*, Clearing-house, Springfield, Virginia 1965.
7. De Vries, R. C., Roy, R. and Osborn, E. F. *Trans Brit. Ceram. Soc.* **53** (1954) 531.
8. Holm, J. L. and Kleppa, O. J. *Unpublished results*.
9. Mathews, A. L. and Baes, Jr., C. F. ORNL TM-1129 (1965), Oak Ridge Natl. Lab., Tennessee, USA.
10. Papatheodorou, G. N. and Kleppa, O. J. *J. Chem. Phys.* **47** (1967) 2014.
11. Østvold, T. *Unpublished results*; Report to Norsk Hydros Forskningsfond, Institute of Inorganic Chemistry, The Technical University of Norway, November 1967.
12. Counts, W. E., Roy, R. and Osborn, E. F. *J. Am. Ceram. Soc.* **36** (1953) 14.

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Investigation into the Influence of Electric Charges on the Corrosion of Metals

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When the role of the electron exchange at phase boundary processes — self-evident *per se* — could be subjected to quantitative determinations, it was possible to submit an old theory of one of the authors to the verification of experimental testing.

If a metal rod is charged with electricity, by passing an electric current through it or by some other method, it will be surrounded by a non-homogeneous electric field. A dipole in this field will get a certain orientation and a certain acceleration in the direction towards the metal. It is consequently probable that a corrosive gas consisting of dipoles, *e.g.*, hydrochloric gas, hydrogen sulphide, or water vapour, will react in one fashion if the metal is electrically charged, in another fashion if it is uncharged.

In order to make some preliminary investigations into the question whether our assumptions were correct and whether measurable differences could be observed, silver and copper rods were caused to react with corrosive gases the molecules of which either were permanent dipoles, as

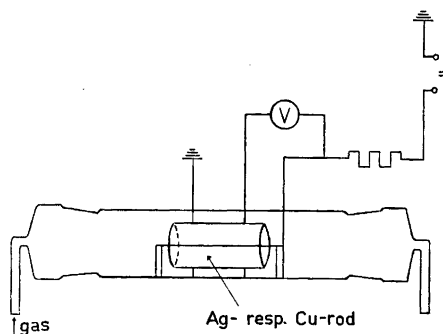


Fig. 1. Experimental apparatus.

hydrogen sulphide, or could be assumed to be slightly polarized, as iodine vapour (I_2).

An apparatus constructed as shown in Fig. 1 was used. We avoided current flow in these experiments, which had the advantage that there was no need to consider the influence of a possible rise of temperature in the conducting rod. One end of a metal rod is connected with one pole of a direct current generator. The other pole of the d.c. generator is earthed. The metal rod is surrounded by an earthed metal cylinder and the surrounding field consequently assumed a cylindrical shape. Gas of known composition flowed in the direction of the rod. The whole apparatus was kept at 25°C by means of a thermostat.

We had originally meant to measure the tarnishing film by interferometry, but the effect was actually large enough to permit weighing. The weight of the metal rod was consequently registered by means of a microbalance at uniform intervals. The accuracy at the weighing was 5×10^{-6} g.

The results of experiments with a copper rod and hydrogen sulphide mixed with nitrogen are shown in Table 1. The partial

Table 1. Reaction between hydrogen sulphide gas and copper rod.

	Time (h)	Mean weight increase (g) ($\times 10^4$)
Zero potential	3	0.40
	5	0.60
	10	1.00
	16	1.30
	22	1.70
Negative potential	3	0.25
	5	0.50
	10	0.80
	16	1.05
	22	1.20
Positive potential	2.5	0.80
	5	1.70
	9	2.30
	13	2.70
	17	3.40
	22	3.80

pressure of the hydrogen sulphide gas was constant at 4.4×10^{-3} bars, the potential of the copper rod towards earth (zero) was +100 V and -100 V, respectively. The reaction with hydrogen sulphide gas took

a considerably more rapid course when the copper rod had a positive potential than when it was uncharged. When the copper rod had a negative potential to earth the reaction was slightly slower than when the rod was neutral.

There was reason to expect this result. When the metal rod is positively charged the number of hydrogen sulphide atoms with the sulphur atom directed towards the metal is increased. The activation entropy of the system gets more advantageous. The reverse conditions obtain when the metal rod is negatively charged.

The result of the reaction between saturated iodine vapour mixed with nitrogen and a silver rod is shown in Table 2.

Table 2. Reaction between iodine vapour and copper rod.

	Time (min)	Mean weight increase ($\times 10^4$ g)
Zero potential	20	5.80
	30	6.80
	60	8.60
	75	9.10
	100	9.90
	180	11.40
	290	11.90
Negative potential	30	4.40
	60	6.10
	90	7.80
	150	9.60
	210	10.50
	290	11.20
Positive potential	15	2.00
	30	2.80
	60	3.90
	135	5.60
	210	6.90
	290	7.30

When the silver rod was electrically uncharged, the reaction between silver and the iodine molecule took a faster course than if the rod carried a negative charge, and a considerably faster course than if it was positively charged. These circumstances seem to indicate that the reaction between iodine vapour and silver takes a course *via* the formation of iodine ions. The experimental material is too small, however, to

permit any profound discussion of the reaction mechanism.

The conclusion that the original assumption was correct opens up an interesting and technically important field of research, including, for instance, the corrosion of high tension transmission lines and transformers. The influence of various factors has naturally to be studied, *e.g.* the difference of potential and strength of current flow, as well as the choice of metal and gas.

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A Lamellar Mesophase with Single Amphiphile Layers

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The usual neat soap structure with double amphiphile layers occurs in, for instance, the ternary systems of an ionic association colloid, water, and an alkanol having a long enough hydrocarbon chain. A lamellar mesophase of the neat soap type also appears in these systems when the univalent alcohol is replaced by a bivalent straight chained alcohol with terminal hydroxyl groups, but in this case the structure displays a number of different features. This will be illustrated by experimental results obtained for the lamellar mesophase in the sodium caprylate—1,8-octanediol—water system.

Here a lamellar mesophase occurs at 20°C in the region denoted D in Fig. 1. (The complete phase equilibria diagram will be published in an other connection.) This mesophase has the typical mosaic texture characteristic of the neat soap phase (No. 122.1 in the Rosevear system¹) (Fig. 2). The Bragg spacing ratio of 1:1/2 is indicative of a lamellar structure (Table 1). Assuming that all the diol is contained in the amphiphile layers and using experimental values for the volume fraction of the amphiphilic substance, we obtain values

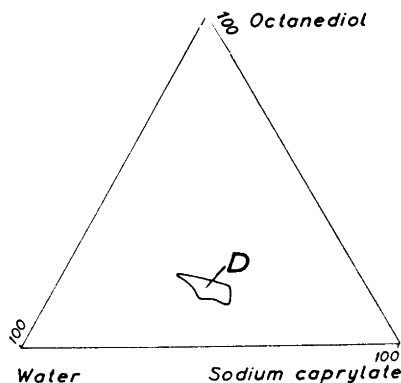


Fig. 1. Phase diagram showing the location of the region with lamellar mesophase in the sodium caprylate—1,8-octanediol—water system.

between 13.5 and 14.7 Å for the layer thickness. These are considerably lower than those for the amphiphile layers in the corresponding mesophase in the sodium caprylate—decanol—water²⁻⁴ and the sodium caprylate—octanol—water⁵ systems, namely 22 and 20 Å. As the molecules of sodium caprylate and octanediol are about 13 and 14 Å in length the observed values would be incompatible with a double-layered structure of the amphiphile layers

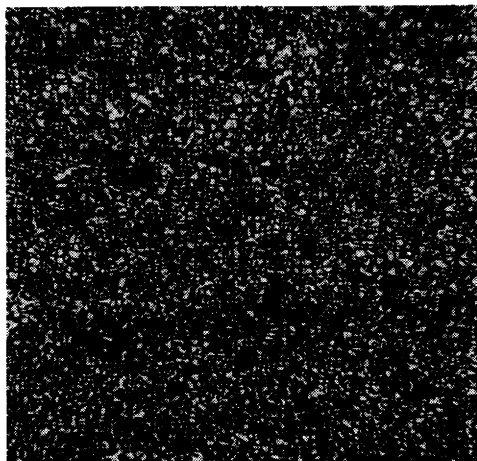


Fig. 2. Photomicrograph of the mesophase in region D. Crossed nicols 150 ×.