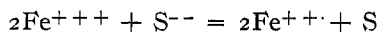


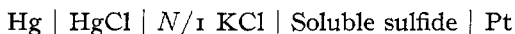
THE ELECTROMOTIVE BEHAVIOR OF SOLUBLE SULFIDES

BY ROGER C. WELLS¹

One of the most characteristic properties of soluble sulfides, aside from their ability to form insoluble precipitates with many metals, is their reducing power. This is shown in the familiar reactions with ferric salts, chromates, ferri-cyanides, the halogens, nitro groups, nitric acid, and even sulfuric acid. If we consider this property to be essentially a property of sulfide ions the reduction of a ferric salt, for example, may be indicated by the equation



According to this equation the sulfide ions give up their negative charges while an equal number of positive charges are neutralized; free sulfur remains; no other ions appear to be directly concerned with the reducing action. The tendency of sulfide ions to give up their charges may also be shown by the production of an electric current when any unattacked conductor, such as platinum, is immersed in a soluble sulfide and properly connected to some other half cell such as the calomel electrode, yielding a cell combining two single potentials of this sort.



The single potentials created by soluble sulfides under these circumstances may be designated sulfide potentials and the experiments to be described consisted in measurements of such potentials.

The single values were obtained by assigning the value 0.56 to the calomel electrode and neglecting diffusion potentials. Some of these values are shown in Table I, the positive sign indicating that the platinum was positive to the solution.

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TABLE I
Potentials of soluble sulfides

Solution in half cell	Sulfide potential
1 mole HCl per liter saturated with H_2S	+0.40
1 mole acetic acid saturated with H_2S	+0.29
KCl saturated with H_2S	+0.20
1 mole NaSH	-0.14
1 mole Na_2S	-0.27

Previous Work

In his measurements on oxidation cells Bancroft, in 1890, made a determination of the potential of a fifth molal solution of Na_2S , which by reference to a normal calomel electrode would yield the single potential -0.091 .¹ This value does not fit in very well with my measurements. While studying the behavior of polysulfides Küster² obtained the value -0.239 for a normal solution of Na_2S with which my measurements agree to a few centivolts. Only a few other data, and these largely of an incidental character, have come to my attention.³ In addition to the important contributions of Küster, however, there is one other suggestive paper by I. Bernfeld⁴ in which it is shown that under certain conditions the sulfide potential observed can be calculated from the partial pressure of hydrogen sulfide in equilibrium with the solution used in the half-cell.

Chemistry of the Sulfide Electrode

It will be observed from Table I that when the sulfide electrode is coupled with the calomel electrode the potential of which is 0.56 volt, the current in every case tends to flow in a direction to make the platinum an anode, and hence to

¹ Bancroft: Ueber Oxydationsketten, *Zeit. phys. Chem.*, **10**, 387 (1892); cf. Neumann: Ueber das Potential des Wasserstoffs und einiger Metalle, *Ibid.*, **14**, 228 (1894).

² *Zeit. anorg. Chem.*, **44**, 445 (1905).

³ Hittorf: *Zeit. phys. Chem.*, **10**, 612 (1892). Two observations yielded -0.10 and -0.04 for 2.77 *N* KSH.

⁴ Bernfeld: "Studien über Schwefelmetallelektroden," *Zeit. phys. Chem.*, **25**, 46 (1897).

reduce mercurous ions to mercury. In other words the sulfide ions give up their negative charges, leaving free sulfur. This appears to be the primary action. When a feeble current (0.1 milliampere) was passed into a solution of hydrogen sulfide through a platinum anode a white cloud of sulfur was observed forming on the platinum and in the solution near the platinum; when sodium hydrosulfide or sodium sulfide was employed, however, sulfur was not a visible product nor was any gas evolved but after a time the solution turned yellow, indicating the formation of a polysulfide. The formation of a polysulfide may be considered a secondary effect due to the solution of sulfur freed by the current in the sodium hydroxide present, or it may be that polysulfide ions are an oxidation product of sulfide ions. Since polysulfides are not stable in acid solution we may postpone a consideration of them while we consider certain relations in acid solutions.

Let us consider the reversibility of the sulfide electrode. The spontaneous process sets sulfur free. The reverse process therefore appears to demand that sulfur should ionize. Several experiments were made to see if free sulfur under any circumstances in contact with platinum could be made to ionize. A platinum electrode coated with sulfur was allowed to stand in normal potassium chloride in a closed half-cell for a long period. The effect was in the direction expected but it would have required several weeks to reach a correct sulfide potential in that way, if it ever could be reached. A similar electrode in caustic soda gave low values in the course of two days but as it is well known that sulfur dissolves in alkali hydroxides at an appreciable speed the production of a low potential in this way may be regarded wholly as a "chemical" action and the electromotive effect secondary. The experiments were therefore inconclusive as to whether the platinum assisted the ionization of the sulfur at all.

Effect of Hydrogen

On the other hand, if a current is passed in a direction to make the platinum a cathode hydrogen is probably set free

under ordinary circumstances. Even if it is not visibly evolved it is probably dissolved somewhat by the platinum or it may combine with sulfur to form hydrogen sulfide. No difficulty was ever experienced, using a Lippman electrometer, in approaching the point of balance from either direction although I preferred to approach it from the side to set sulfur free. The object of this procedure was to have the solution saturated with sulfur.

TABLE II

Effect of hydrogen in platinized electrodes used in sulphide solutions

Electrode	Time	Cell Hg+	Platinum	Remarks
A freshly platinized electrode, soaked an hour in hot water then touching $N/1$ NaOH in bottle H_2 turned on	1.23	0.12	+0.44	
	1.32	0.13	+0.43	An oxygen value
	1.37	1.06	-0.50	Correct hydrogen value
	1.40	1.07	-0.51	
Electrode now touched to colorless $N/1$ Na_2S	3.07	1.07	-0.51	A variable intermediate value
	4.00	0.96	-0.40	
	4.02	0.90	-0.36	
	4.07	0.88	-0.32	
	5.00	0.86	-0.30	
Smooth electrode	next day,			
	9.00	0.88	-0.32	Correct sulfide potential
	10.00	0.80	-0.24	
	10.30	0.79	-0.23	
	11.00	0.80	-0.24	

Ordinary hydrogen sulfide made from commercial ferrous sulfide contains considerable hydrogen. A number of experiments were therefore made to find out if hydrogen could cause an error in the determination of sulfide potentials. It was found that hydrogen might easily cause an error in acid solutions where the concentration of sulfide ion is small but that it was of doubtful influence in alkaline solutions containing a high concentration of sulfide. In fact it seemed of assistance in the alkaline solutions in preventing oxidation. It is generally assumed that smooth electrodes are best for

measuring most oxidation potentials but that platinized electrodes are desirable for hydrogen, iodine, bromine and chlorine electrodes. I was therefore somewhat surprised to find that hydrogen showed its effect rather quickly even with smooth electrodes in acid solution, whereas in the alkaline sulfide solutions I found it impossible to obtain correct hydrogen potentials even with well-platinized electrodes. The variability of a platinized electrode in sodium sulfide is shown in Table II.

When an error from hydrogen was feared pure hydrogen sulfide was employed instead, prepared from alkali sulfide and hydrochloric acid and washed with sodium hydrosulfide.

Relation between Concentration and Potential

In seeking for a mathematical elucidation of sulfide potentials we may assume the process at the electrode, at least in one direction, to be



which would yield as the most general expression possible for the potential

$$E = E_0 - \frac{0.059}{2} \log \frac{[S^{--}]}{[S]} \quad (2)$$

in which the bracketed symbols stand for concentrations.

We are uncertain about the number of atoms in a molecule of sulfur but it is obvious that the proper equation would yield the same value of E_0 whatever the complexity of the sulfur molecule. Further, we know that the concentration of free sulfur soluble in water is exceedingly small, so small that a very small current must suffice to liberate enough to form a saturated solution. If we take the concentration of free sulfur in a saturated solution to be constant and part of E_0 the only remaining variable is the concentration of sulfide ions. Let us calculate values of E_0 therefore from sulfide ion concentrations so far as they are known.

Fortunately the sulfide ion concentrations of the salts

concerned have already been deduced by Knox.¹ The essential equation is

$$[S^{--}] = \frac{1.1 \times 10^{-23}}{[H^+]^2} \quad (3)$$

an expression giving the sulfide ion concentration for any solution whose hydrogen ion concentration is known. Table III gives the sulfide ion molality of the solutions investigated, the potential observed, the value of E_o calculated by equation (2) taking the concentration of free sulfur as unity and also the value of E calculated from the mean value of E_o .

TABLE III

Solution	Sulphide ion concentration	E_o calculated	E observed	E calc. from E_o
1 mole HCl + H ₂ S	1.1×10^{-23}	-0.27	+0.40	+0.41
1 mole acetic acid + H ₂ S	0.6×10^{-18}	-0.24	+0.29	+0.27
1 mole KCl + H ₂ S	1.2×10^{-15}	-0.23	+0.20	+0.17
1 mole NaSH	3.6×10^{-5}	-0.27	-0.14	-0.13
1 mole Na ₂ S	0.09	-0.30	-0.27	-0.23
	mean	-0.26		

There is fair approach to constancy in the values of E_o . Equation (2) is therefore significant in view of the enormous range of the sulfide ion concentration and appears to be applicable to the determination of sulfide ion concentrations under some conditions. Of the values in Table III, those for NaSH and Na₂S are the least certain and the behavior of these two salts must therefore be considered further.

Preparation of Sodium Hydrosulfide

Küster and Heberlein² recommend metallic sodium as the best substance with which to start if for any reason sodium hydroxide will not suffice. If it is desired to avoid all oxidized products it is advisable to pass a current of hydrogen through

¹ J. Knox: "A Study of the Sulfur Anion and of Complex Sulfur Anions." Trans. Faraday Soc., 4, 47 (1908).

² Küster and Heberlein: Zeit. anorg. Chem., 3, 55 (1905).

the sodium hydroxide before introducing hydrogen sulfide, at the same time having a piece of platinum in the bottle to make the hydrogen more effective through electrolytic action. The saturation of sodium hydroxide with H_2S yields a solution containing a considerable excess of H_2S . Part of this excess may be removed from a solution as concentrated as normal by bubbling a stream of hydrogen through it for some hours. Since both Na_2S and NaSH yield an alkaline reaction the neutral point is passed while there is still a slight excess of H_2S . The changes in the solution from the first introduction of H_2S to saturation and expulsion of excess may be followed with advantage by potential measurements. The results of one experiment in which the excess of H_2S in normal NaSH was neutralized by adding NaOH from a burette are shown in Fig. 1.

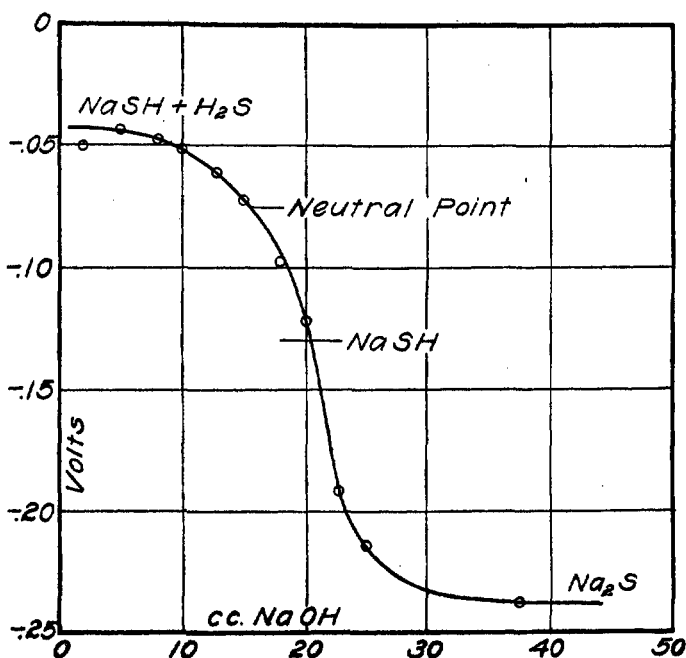


Fig. 1

It is evidently impossible to decide from the figure just what is the proper potential for NaSH . The value -0.14

was chosen before the relations described above were worked out, but was omitted in deriving the average for E_0 . The potential calculated for NaSH by equation (2) is -0.13 .

Behavior of Sodium Sulfide

It is rather difficult to obtain potentials corresponding to pure Na_2S solutions. Equation (2) suggests that this variability may be due to an uncertain concentration of free sulfur. In action an electrode bathed by Na_2S may generate polysulfide and there is not the same limitation set by the saturation with sulfur as appears to obtain in acid solutions. Moreover, it has been found that polysulfides are reduced by the reverse current instead of hydrogen being set free. Solutions containing polysulfides therefore give very definite potentials and their behavior is somewhat like that of ferro-ferricyanide mixtures. It was found, however, that the potential varies considerably with the dilution, depending on the amount of polysulfide present. These results are shown graphically in Fig. 2.

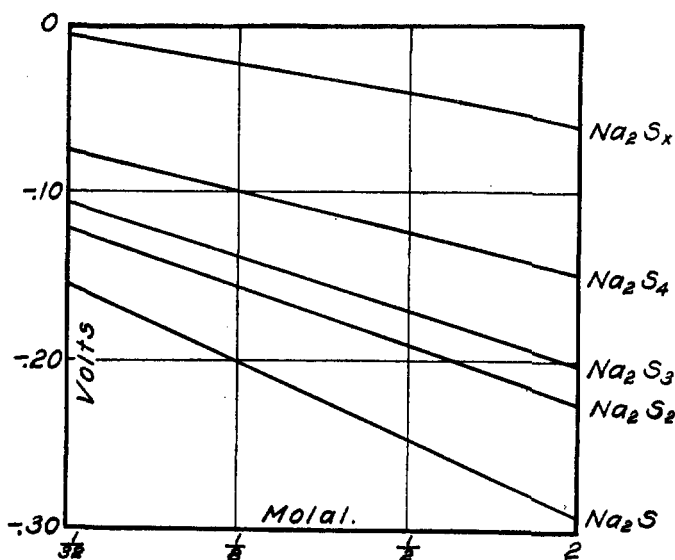


Fig 2

A little calculation shows that the behavior of the saturated polysulfides, Na_2S_x , on dilution is more in harmony with equation (2) than that of the other solutions. Many attempts were made to express the behavior of the other solutions by an equation involving only two molecular species, like ferro-ferricyanide mixtures, but without complete success. Doubtless there are more than two molecular species possible. It appears, however, that there is some basis for neglecting the species Na_2S_2 and Na_2S_3 , and considering such solutions to be chiefly mixtures of Na_2S and Na_2S_4 . The grounds for this will be somewhat evident from a consideration of Fig. 3 in which are shown the changes in potential as the composition of the solution is varied from Na_2S to Na_2S_x .

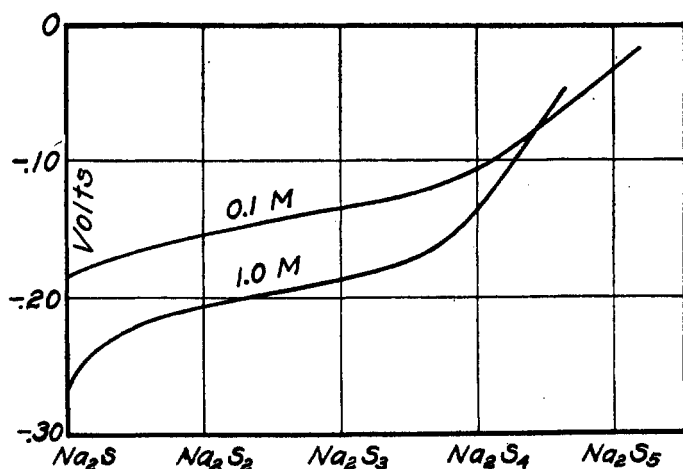
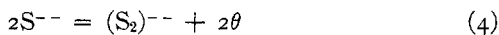


Fig. 3

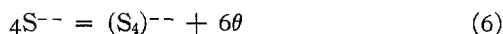
Starting with pure Na_2S we may assume that the first oxidation product is disulfide according to the reaction



We should then have a relation for the oxidation-reduction potential like

$$E = E_0 - \frac{0.059}{2} \log \frac{[\text{S}^{--}]^2}{[(\text{S}_2)^{--}]} \quad (5)$$

A test of this equation was made by resolving solutions of compositions between Na_2S and Na_2S_2 into the proper mixtures of the two species and assuming the ionic concentrations to be proportional to the molal. Suffice it to say that the equation did not yield a constant value of E_o . In fact the shape of the potential curve suggests that the second species must be more complex than Na_2S_2 . Apparently an excess of sulfur forms at once a higher polysulfide than Na_2S_2 . The nearest approach to a uniform slope in the curve falls between Na_2S_2 and Na_2S_3 indicating that if Na_2S is one member the other is nearly as complex as Na_2S_4 . The electrical oxidation would then be



giving for the potential the expression

$$E = E_o - \frac{0.059}{6} \log \frac{[\text{S}^{--}]^4}{[(\text{S}_4)^{--}]} \quad (7)$$

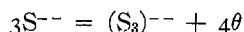
An evaluation of E_o by this equation is shown in Table IV.

TABLE IV

Composition, x in Na_2S_x	Formal concentrations of		Potential observed	E_o calculated by (7)
	Na_2S	Na_2S_4		
1.50	0.83	0.17	—0.220	—0.215
1.75	0.75	0.25	—0.212	—0.211
2.00	0.67	0.33	—0.206	—0.208
2.25	0.58	0.42	—0.201	—0.207
2.50	0.50	0.50	—0.197	—0.206
2.75	0.42	0.58	—0.192	—0.205
3.00	0.33	0.67	—0.188	—0.205
3.25	0.25	0.75	—0.183	—0.205
3.50	0.17	0.83	—0.175	—0.204

It will be seen on referring to the table that equation (7) gives a fairly constant value of E_o from Na_2S_2 to Na_2S_3 . No equation as complicated as this has to my knowledge been applied to potential measurements before, although Freden-

hagen suggested such equations.¹ An equation corresponding to the intermediate possibility, namely,



was found less satisfactory than equation (7).

The conclusions from the preceding discussion are then as follows: The electromotive behavior of the polysulfides resembles that of other oxidation-reduction potentials in a general way. Although it is impossible to account for the behavior without assuming that several species are present in a rather complicated equilibrium it appears unnecessary to consider Na_2S_2 one of them or possibly even Na_2S_3 . The potentials may be calculated as if they depended on the relative concentrations of the two species Na_2S and Na_2S_4 for the range from Na_2S_2 to Na_2S_3 . On reaching a composition near Na_2S_4 a rapid shift to a much higher sulfide is suggested. The excess sulfur is of course presumed to form complex anions.

On the other hand, in solutions which are easily saturated with sulfur the simple equation

$$E = -0.26 - 0.029 \log [S^{--}]$$

appears to express the electromotive behavior of soluble sulfides very well.

Washington, D. C.

April, 1914

¹ C. Fredenhagen: "Zur Theorie der Oxydations- und Reductions-ketten," Zeit. anorg. Chem., 29, 444 (1902).