AN EFFECT OF POTASSIUM CYANIDE ON THE OXIDATION-REDUCTION POTENTIAL.

By **Kosaku MASAKI** and **Takuo IKKATAI.**

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On the oxidation-reduction potential of the ferri-ferro complex cyanide solution many researches have been carried out and reported.

The first one who determined the potential was Fredenhagen(1) and in his experiment the ratio of ferricyanide to ferrocyanide was varied. Schaum and Linde,(2) using potassium ferricyanide and sodium ferrocyanide, obtained the following formula as the result of their experiment.

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(1) *Z. anorg. Chem.*, **29** (1902), 396.

(2) *Z. Elektrochem.*, **9** (1903). 407.

$$E = E_0 + 0.0002T \log \frac{\text{(total Ferricyanide)}}{\text{(total Ferrocyanide)}}$$

In their experiment the total concentration of complex cyanide was constant, the ratio only being changed. The addition of some electrolytes displays a powerful influence on the potentials of oxidation-reduction. In acidic solution, potassium ferrocyanide acts as an oxidizing agent and therefore we can determine the concentration of the salt with hydrogen iodide. While in neutral potassium ferrocyanide plays a reducing action to convert iodine to iodide, as follows.

$$2\mathrm{Fe(CN)}_6^{---} + 2\mathrm{I}^- \rightleftarrows 2\mathrm{Fe(CN)}_6^{----} + \mathrm{I}_2$$

Schoch⁽¹⁾ measured the potential in the presence of 0.05 molal hydrochloric acid, varying the ratio of ferricyanide to ferrocyanide. Lewis and Sargent⁽²⁾ showed that the presence of potassium ion added as potassium chloride had a large influence to lift the oxidation potential and explained this result that the added potassium ions decrease the concentration of ferrocyanide ions. Müller⁽³⁾ found that the relation between the potential and the concentration of potassium ion using potassium hydroxide is as follows (at 0°C.).

$$E = E_0 + 0.0546 \log \frac{\text{(total ferricyanide)}(\mathrm{K}^+)}{\text{(total ferrocyanide)}}$$

According to Schoch and Felsing⁽⁴⁾ the relation is as follows;

$$E = E_0 + 0.0591 \log \frac{(\mathrm{Fe(CN)}_6^{---})(\mathrm{K}^+)^x}{(\mathrm{Fe(CN)}_6^{----})}$$

and the value of x varies between 0.725 and 0.75. They obtained these relation using potassium chloride at 25°C. Linhart⁽⁵⁾ also investigated the influence of potassium chloride in the similar manner.

Moreover, on the influence of hydrogen ion, Müller and Kolthoff⁽⁶⁾ reported their results. The former obtained the following equation at 18°C.,

$$E = E_0 - 0.546 \log (\mathrm{H}^+)^2$$

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(1) *J. Am. Chem. Soc.*, **26** (1904), 1422.
(2) *J. Am. Chem. Soc.*, **31** (1909), 355.
(3) *Z. physik. Chem.*, **88** (1914), 46.
(4) *J. Am. Chem. Soc.*, **38** (1916), 1928.
(5) *J. Am. Chem. Soc.*, **39** (1917), 615.
(6) *Z. anorg. Chem.*, **110** (1920), 143.

while the latter at the same temperature,

$$E = 0.416 - 0.0577 \log (H^+)^{2.22}$$

and in the experiments the ratio of ferricyanide to ferrocyanide was 1:1, each concentration being ½(0.025) mol per litre. In this investigation the influence of added potassium cyanide was measured at the various concentration of the salt.

Experimental Part.

The apparatus used is shown in the diagram. A: Hydrogen inlet; B: Thermometer; C: Platinum electrode; D: Solution inlet; E: Hydrogen outlet; F: Salt bridge (0.1 m KCl); G: Salt vessel (0.1 m KCl); H: Calomel electrode. This investigation was carried out in the hydrogen atmosphere. Because in the alkaline solution, as we described above, potassium ferrocyanide behaves as a pretty powerful reducing agent in contact with air as following.

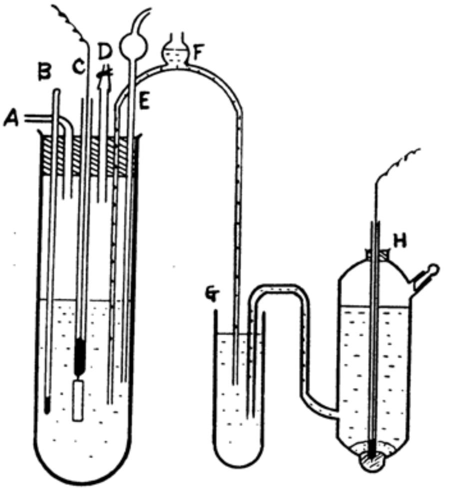

Fig. 1.

$$2Fe(CN)_6^{----} + \frac{1}{2}O_2 + HO \rightleftarrows 2Fe(CN)_6^{---} + 2OH^-$$

Potassium ferricyanide and ferrocyanide employed were of Kahlbaum's, and each was made into 0.05 molal solution with distilled water at the least contact of air. The potassium cyanide was also of high purity and standardised with 0.1 normal silver nitrate solution. Potassium cyanide was added in the mixture of each 10 c.c. of the ferricyanide and ferrocyanide solution and the volume of this solution was enlarged to 50 c.c. with distilled water. Thus the ratio of ferricyanide to ferrocyanide was 1 : 1, and each of these concentration was 0.01 molal. The vessel was filled with hydrogen before the solution was poured into it. The hydrogen gas was prepared by using pure metallic zinc and sulphuric acid, and washed with potassium permanganate and then potassium hydroxide.

The electrode used was non-platinized platinum plate of about 1 cm. × 3 cm. The construction of the cell was as follows;

$$\mathrm{Pt} \mid K_4Fe(CN)_6,\ K_3Fe(CN)_6,\ KCN \mid 0.1\,mKCl \mid 0.1\,mKCl,\ Hg_2Cl_2 \mid Hg$$

The temperature of the cell was kept constant at 30° ± 0.05°C. in a thermostat. The results are shown in the table.

$K_4Fe(CN)_6$	$K_3Fe(CN)_6$	KCN	E_c	E_h*	E_h (calc.)
0.01	0.01	0	0.0684	0.4094	
0.01	0.01	0.0321	0.0747	0.4157	0.4130
0.01	0.01	0.0642	0.0798	0.4208	0.4238
0.01	0.01	0.0963	0.0855	0.4265	0.4300
0.01	0.01	0.1284	0.0892	0.4302	0.4344
0.01	0.01	0.1605	0.0920	0.4330	0.4379
0.01	0.01	0.1926	0.0953	0.4363	0.4409
0.01	0.01	0.0922	0.0872	0.4282	0.4294
0.01	0.01	0.1844	0.0950	0.4360	0.4400
0.01	0.01	0.2766	0.1040	0.4450	0.4468
0.01	0.01	0.3688	0.1113	0.4523	0.4507
0.01	0.01	0.4610	0.1165	0.4575	0.4541
0.01	0.01	0.5532	0.1182	0.4592	0.4569
0.01	0.01	0.2895	0.1052	0.4461	0.4469
0.01	0.01	0.5730	0.1194	0.4604	0.4576
0.01	0.01	0.7238	0.1220	0.4630	0.4610
0.01	0.01	0.8685	0.1242	0.4652	0.4633
0.01	0.01	1.0132	0.1252	0.4662	0.4662
0.01	0.01	1.1580	0.1257	0.4667	0.4663

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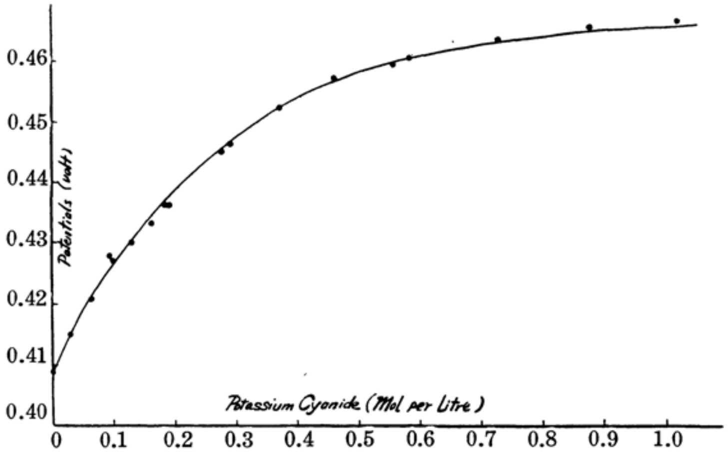
* Potential of 0.1 normal KCl-calomel electrode : $0.3387 + 7.9 \times 10^{-4}\,(t - 25)$.
Kust Arudt, Physikalische-chemie Tecknik, (1923) 795.
Auerbach, *Z. Elektrochem.*, **18** (1912), 13.
Lewis and Brighton, Sebastian. *J. Am. Chem. Soc.*, **39** (1917), 2245.
Fales and Vasbargh, ibid., **40** (1918), 291.

In the table E_c is the measured potential against a decinormal calomel electrode and E_h is the potential against a hydrogen electrode at 25°C. and Fig. 2 shows the value of E_h by the changes of concentrations of potassium cyanide.



From the data, we obtained the following approximate formula

$$E = 0.4660 + 0.0601 \log K^{0.59}$$

where K is the concentration of the potassium cyanide added. The last column in the above table shows the calculated values by this equation.

Under sunlight, we practised many investigations, but all those were worthless giving no systematic results. This is probably due to the decomposition of double cyanide by sun beams. So the author carried out this investigation in the dark room. The effect of more concentrated cyanide is more or less uncertain giving the fluctuation of potential by some disturbance.

Summary.

(1) The effect of the existence of potassium cyanide upon the oxidation-reduction potential of potassium ferricyanide and ferrocyanide was investigated.

(2) The investigation was performed in the hydrogen atmosphere in the dark room to avoid the atmospheric oxidation and the photochemical decomposition.

(3) The result can be expressed approximately by the following empirical formula at 30°C.

$$E = 0.4660 + 0.0601 \log K^{0.59}$$

where K is the concentration of potassium cyanide, and each concentration of potassium ferricyanide and potassium ferrocyanide is 0.01 mol. respectively.

Yokohama Higher Technical School,
Yokohama.