Technical Paper

Conductivity of Concentrated KCl Solution*

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Electrolysis of NaCl solutions has a large share in the chlor-alkali industry, but the capacity of KCl electrolysis is also increasing. While both processes are essentially the same, details such as voltage balance are different due to the difference in physico-chemical properties between two salts¹⁻³.

For the performance of electrolytic cells, a general formula for calculating the conductivity of the aqueous solutions of KCl electrolysis is required.

The 3-5 M KCl solutions are usually used as the electrolytes at the temperature range of 50-100°C. Thus, the formula shown below covers a range of conditions which include the above ranges of interest: 1-5 M KCl from room temperature to 100°C.

1 Pure KCl Solution

Equipment and method for measurement was conventional, and the cell constant was obtained from various data published.

Solutions were prepared with extra pure potassium chloride and water which had been deionized and then

Fig. 1 Specific conductivity of 5 moles/lit KCl aqueous solution at various temperatures

distilled twice. An example of the conductivity vs. temperature curve is shown in Fig. 1. However, representation of specific conductivity as a function of the KCl concentration at various temperatures, such as

Fig. 2 Specific conductivity of concentrated KCl aqueous solutions at high temperature ranges

shown in Fig. 2, is more feasible for use. Thus, we may put:

$$\kappa = a + bm + cm^2 \quad (1)$$

where κ conductivity mho/cm
 m molality moles/l

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Three coefficients, a , b , and c , are the functions of temperature as follows:

$$a = \alpha_0 + \alpha_1 \left(\frac{t}{100} \right) + \alpha_2 \left(\frac{t}{100} \right)^2 + \alpha_3 \left(\frac{t}{100} \right)^3 \quad (2)$$

$$b = \beta_0 + \beta_1 \left(\frac{t}{100} \right) + \beta_2 \left(\frac{t}{100} \right)^2 \quad (3)$$

$$c = \gamma_0 + \gamma_1 \left(\frac{t}{100} \right) + \gamma_2 \left(\frac{t}{100} \right)^2 \quad (4)$$

$$\begin{aligned} \alpha_0 &= +0.06714771 & \beta_0 &= -0.02683625 & \gamma_0 &= +0.02169544 \\ \alpha_1 &= -0.27901096 & \beta_1 &= +0.59002202 & \gamma_1 &= -0.11169075 \\ \alpha_2 &= +0.21209696 & \beta_2 &= -0.28912264 & \gamma_2 &= +0.06978237 \\ \alpha_3 &= +0.00089866 & & & & \end{aligned}$$

Minimum deviation of this formula is 1.5%, and is enough for engineering use.

2 Acidic and Alkaline Solutions

The slope of the potential vs. distance curve near the working electrode depends on the conductivity of solution, that is,

$$\Delta E = \frac{dE}{dx} = i/\kappa \quad (5)$$

where ΔE potential gradient V/cm
 x distance cm
 i current density A/cm²

Fig. 3 shows an example of the potential vs. distance curve near the graphite anode polarized in KCl solution at various current densities. The potential gradient vs. current density well agrees with Eq. (5) as shown in Fig. 4, thus the conductivity can be evaluated. However, the data obtained in this manner are about 50% larger than one of pure solution calculated by Eq. (1) as shown in Table 1. The pH of the

Fig. 3 Potential vs. distance near the working electrode

Fig. 4 Potential gradient vs. current density near the working electrode

Table 1 Specific conductivity of 4 M KCl

Temperature (°C)	Specific conductivity (mho/cm)	
	From Eq. (5)	From Eq. (1)
30	0.645	0.413
50	0.877	0.504

Fig. 5 Conductivity vs. pH of 1 M KCl at constant temperatures

solution near the graphite anode lowers exceedingly during electrolysis due to dissolution of chlorine, and excess H^+ may associate the conduction. Chlorine bubbles disturb passage of electric current at very high current density, and the superficial conductivity of

Fig. 6 Conductivity vs. pH of 3M KCl at constant temperature

Fig. 7 Conductivity vs. HCl concentration of a mixed solution of HCl and KCl (3M)

solution near the working electrode decreases in practical cell.

Fig. 5 and 6 are the conductivity of KCl at various conditions of concentration, temperature, and pH. The conductivity of both acidified and alkaline solutions is large in comparison with neutral solution due to large mobility of H^+ and OH^- .

Fig. 8 Conductivity vs. KOH concentration of a mixed solution of KOH and KCl (3M)

The increment of conductivity is plotted against the HCl concentration as shown in Fig. 7. K and K^* in the figure represent the conductivity of the sample solution and of neutral KCl, respectively. Therefore, the line with triangular points shows the increment due to H^+ in acidified solution. It is parallel to the conductivity of pure HCl but small somewhat, probably due to decrease in the activity of H^+ in concentrated solution. In alkaline solution, similar results are obtained as shown in Fig. 8. The gap between two parallel lines is considerably large in comparison with Fig. 7.

In conclusion, the specific conductivity of pure KCl in a range between room temperature and $100^\circ C$ was measured. A general formula and the coefficients were obtained. Deviation of the conductivity of KCl solution in a range $pH < 2$ and $pH > 11$ was discussed. Excess H^+ and OH^- associate to increase the conductivity of KCl.

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☆会誌「電気化学および工業物理化学」英文要旨の書き方☆

1. 英文要旨のまとめ方

英文要旨は 200 語以内にまとめるものとし、論文の内容および結論の要約で、新情報や新知見を読者に示し得るものとする。要旨にもとづいて読者がその論文の内容を読むべきか否かの判断ができるようにしなければならない。そのためには次の諸点に留意して論文の主眼となる項目を中心に記述すること。

- i) 研究の目的および範囲が表題から明らかに理解できる場合は、要旨の中にそれを繰り返さないこと。表題によって内容を明確に表現しきれないときは、研究の目的およびその概要を示すこと。
- ii) 新しい考え方、理論、研究方法、装置、反応、物質、データ（精度を含めて）、既存の知識の新分野への応用など、研究上新らしい点を述べること。
- iii) 実験方法について簡単に述べること。
- iv) 研究結果—新事実を強調する—
- v) 研究結果についての著者の考察。
- vi) たとえ主題から離れていても新発見については言及すること。

2. 英文を作成するときの注意

- (1) 文案は簡潔な表現を用いること。しかし完全な文章でなければならない。電文のような見出語の羅列ではいけない。
- (2) 国際的に認められている略号や用語以外を用いないこと。また固有名、商品名ではなく一般名を用いること。
- (3) 英文要旨それ自身で内容の豊富なものであること。数字などを用いて本文や文献からの引用は原則として避けること。
- (4) 文章のスタイルは「われわれは……を行なった(We …….)」としなくて、第三者的に「……が行なわれた」とすること。もし著者に言及する必要があるときは、誤解を生じる恐れがない限り三人称とすること(we とはしないで the author(s) のように)。
- (5) 冠詞を適切に用いることにより文章を明確にすること。
- (6) アラビア数字は文頭に用いないこと。また As, He, I, In のようにまぎらわしい元素記号も文頭に用いないこと。
- (7) 動詞はなるべく主語に近い位置におく方がわかりやすい。

(8) 時制は現在形、過去形、現在完了形などを用いるが、とくべつの場合を除いては、時制は混合して用いない方がよい。

原則的にはその論文で行なっている動作は現在形を(……is discussed.……is described.……is shown.)、実験内容として行なった過去の動作は過去形を用いる(the mixture was distilled)。しかし研究の全般的な目的にかかわる動作には現在、過去形のほか、現在完了形を用いてもよい(……has been studied,……has been developed.)。結果、結論については過去、現在のいずれを用いてもよいが、過去を用いた場合は単に結果を紹介する感じであるのに対して、現在を用いるとその結果が不変の事実であるとの強い感じとなることが多い。

(9) 主語が単数から複数に変化するような重文においては、動詞は省略しないこと。たとえば次の文章の is は省略できない。

The two liquids are mixed and the mixture is heated to boiling

(10) 物の単位を示すような集合名詞は単数動詞をとること。“10 g are added”ではなく、“10 g is added.” data とか、spectra のように複数名詞は複数動詞をとる。

(11) 懸垂分詞(文の主語と文法的に結合されないまま用いられている分詞)は用いない方がよい。たとえば“N was determined using the kjeldahl method.”ではなく、“N was determined by the kjeldahl method.”とすること。

(12) 3 コ以上の言葉をならべて用いる場合、最後の2語を結ぶ“and”, “or”, “nor”の前にはカンマをつけること。

“benzene, toluene, and xylene.”

“either Cu, Ag, or Au.”

(13) 本誌の要旨においてはパラグラフは設けないことにする(改行を行わない)。

—参考文献—

1. UNESCO “Guide for the preparation and publication of synopses” (1949).
2. ISO Recommendation R 214 “Abstracts and synopses” (1961).
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