

Solubility of chlorine in aqueous hydrochloric acid solutions

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Abstract

The solubility of chlorine in aqueous hydrochloric acid solutions was studied. The effects of HCl concentration and temperature on the solubility were evaluated, and the thermodynamic parameters of the dissolution were calculated. It was found that the solubility isotherms had a minimum at about 0.5 M HCl concentration at all the temperatures studied and that solubility decreased with the increase of temperature at all the HCl concentration range investigated.

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1. Introduction

Chlorine is an element of the halogen family, but it is never found uncombined in nature. It is estimated to account for 0.15 percent of the earth's crust in the form of soluble chlorides such as common salt (NaCl), carnallite (KMgCl₃·6H₂O) and sylvinit (KCl) [1]. Chlorine gas is especially produced as a by-product in the electrolysis of sodium chloride in the chloroalkali industry. Generally, most producers operate their plants to make chlorine since it is hard to store and is used to product derivatives such ethylene dichloride, phosgene and epichlorhydrine. Caustic soda is generally sold on the merchant market and consumed in a myriad of uses. Little chlorine is traded among countries, but a considerable amount of caustic soda is traded, especially in aqueous form [2].

Chlorine is a very effective disinfectant and has been used in drinking water supplies for nearly 100 years. Risks for certain types of cancer are now being correlated to the use of chlorinated drinking water. Suspected carcinogens make

the human body more vulnerable through repeated ingestion and research indicates the incidents of cancer are 44% higher among those using chlorinated water [3].

On the other hand, chlorine released to atmosphere causes depletion of the ozone layer which absorbs most of the harmful ultraviolet-B radiation from the sun. To prevent the depletion of ozone shield, developed countries have made protocols and some international regulations have arranged. For that reason, new and applicable uses must be found to consume chlorine [4].

When chlorine gas is dissolved in water, it is rapidly hydrolysed and a special type of oxidation–reduction reaction takes place. The chlorine molecule with the sum valence of zero enters into the reaction known as disproportionation reaction with water as following [1]:



This reaction is reversible. It was found that the forward reaction is first order [5]. The rate of this reaction was studied by Lifthitz and Perlmutter-Haymen [6], Shilov and Solodushenkov [7] and Brian et al. [8]. The equilibrium constant

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for Eq. (1), is given by:

$$K = \frac{[\text{H}^+][\text{Cl}^-][\text{HOCl}]}{[\text{Cl}_2]} \quad (2)$$

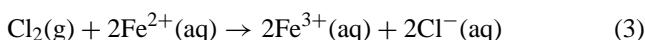
This means that as HCl concentration increases, the equilibrium shifts to left and Cl_2 solubility decreases [5].

Leaist [9] used solubility and diffusion data to describe absorption of chlorine gas into water at 25 °C and 1 atm pressure. The author stated that hydrochloric acid produced by partial hydrolysis of molecular chlorine in according to Eq. (2), diffuses rapidly into the bulk liquid and because the surface of the absorbent is depleted in hydrochloric acid, the solubility of chlorine in the interfacial liquid is significantly higher than the equilibrium solubility at the same chlorine partial pressure.

On the other hand, Islam et al. [10], made an attempt to propose an empirical model describing the solubility versus partial pressure relation over a wide range of concentrations for some reactive gases, including chlorine. As a result, they found out that the solubility of gas is the sum of two components, one fitting the Langmuir isotherm and other fitting Henry's Law.

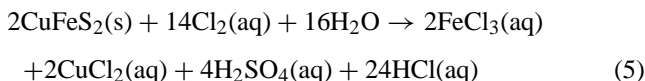
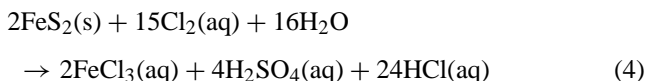
Awakura et al. [11] investigating solubility of chlorine gas in various chloride solutions at 298 K found out that the solubility in aqueous HCl solutions decreases drastically with increasing HCl concentrations up to 0.2 mol L⁻¹, and then, it increases gradually with a further increase in HCl concentration. Also, the authors determined that the solubility of chlorine gas decreases steadily with increasing MClx concentration in aqueous HCl solutions containing MClx [M = Na, K, Ca, Ba, Mg, Ni, Co, Zn, Fe(III)].

Gilliand et al. [12], on the other hand, measured rates of absorption of Cl_2 into FeCl_2 solutions in a wetted-wall column. The overall reaction was



In using chlorine diluted with nitrogen the absorption rates agreed well with predictions based on a second-order reaction between Cl_2 and Fe^{2+} .

Recently, chlorine gas was used as a reactant in the dissolution of various ores in aqueous media [13–17]. Çolak et al. [14] investigated the dissolution of chalcopyrite containing pyrite in Cl_2 saturated water and they gave the dissolution reactions as



Before the tremendous increase of the use of chlorine in chemical industry, most chlorine was used in the textile in-

dustry for bleaching purposes. It is the most unusual and versatile substance with more diverse uses than any other chemical known—from rocket fuels to the manufacture of food products.

However, excessive demand of industry to sodium hydroxide increases inevitably the production of chlorine. This case is required to find new uses for chlorine gas. So, it was thought that the data, which make possible to use chlorine gas especially in hydrometallurgy, could be obtained.

To consume chlorine gas more safely and more environmentally friendly and to stabilize it, it is required to improve industrially the applications such as in Eqs. (3) and (4) in which HCl occurs. For this reason, a fundamental study was undertaken to establish the solubility of chlorine gas in HCl solutions and to predict the some thermodynamic data.

2. Experimental

The experiments were carried out at atmospheric pressure, 81.33 kPa in Erzurum, Turkey by using a glass flask equipped with a gas inlet and outlet tubes and a magnetic stirrer. The flask was immersed in a constant temperature bath. The iodometric titration method was used in determining the concentration of Cl_2 in solution [18]. The titrations were made until the same values was obtained in three or more subsequent determinations at each temperature. The same procedure was repeated at other temperatures and then for other solutions of HCl. The chlorine gas used was obtained from Koruma-Tarım Corp., Turkey. Other chemicals were from Merck.

3. Result and discussion

The obtained experimental data showed that the concentration of HCl and temperature affected the solubility of chlorine in aqueous hydrochloric acid solutions (Figs. 1–3).

3.1. The effect of HCl concentration

The effect of the concentration of HCl on the solubility was investigated in the concentration range 0–7.0 M. The results obtained are shown graphically in Fig. 1.

As seen from this figure, each isotherm consists of two different parts. In the first region, the solubility of Cl_2 decreases with increasing HCl concentration from 0 to 0.5 M. It is known that the presence of any electrolyte causes the reduction of the solubility of a gas in any solvent because the amount of free solvent molecules decreases [19]. Also this means that at HCl concentrations lower than 0.5 M, the solubility of chlorine fits to Eq. (2) given by Brian. According to this equation, as HCl concentration increases, the equilibrium shifts to left and solubility decreases. On the other hand, in the second region in which HCl concentration is bigger than 0.5 M, Eq. (2) is not valid and chlorine solubility increases by increasing HCl concentration. In this region,

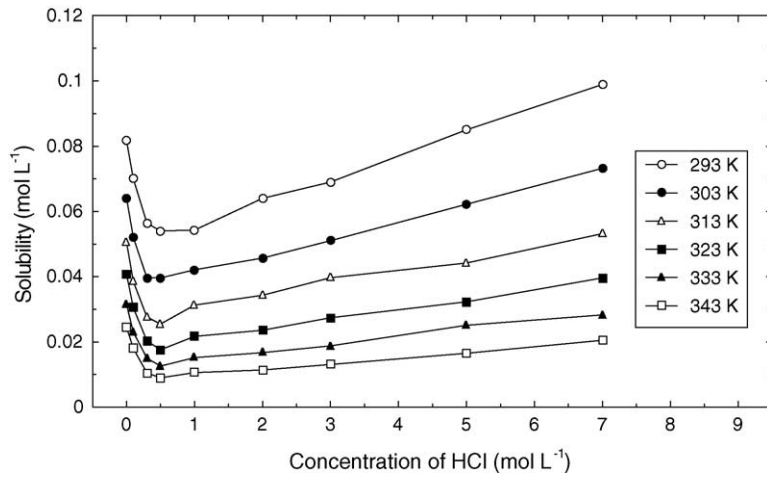
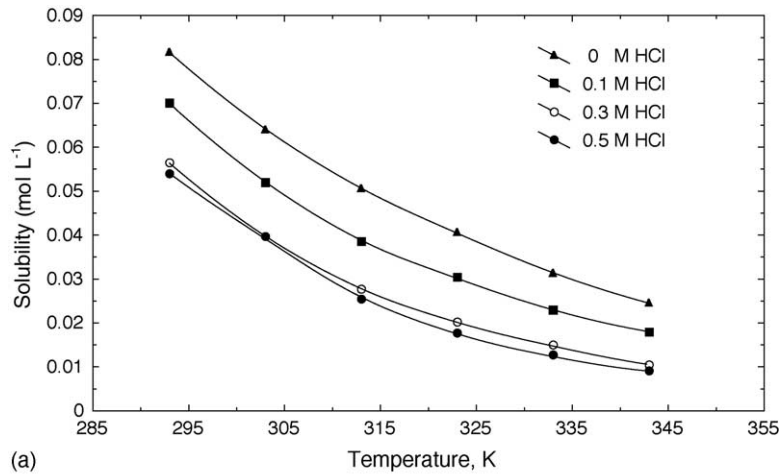
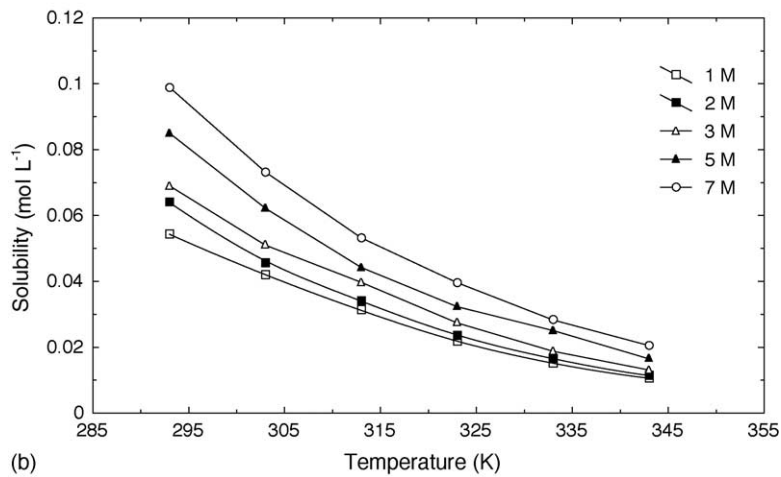


Fig. 1. Dependence of solubility of Cl₂ on initial concentration of HCl.



(a)



(b)

Fig. 2. (a) The effect of temperature on the solubility of Cl₂ in aqueous HCl solutions. (b) The effect of temperature on the solubility of Cl₂ in aqueous HCl solutions.

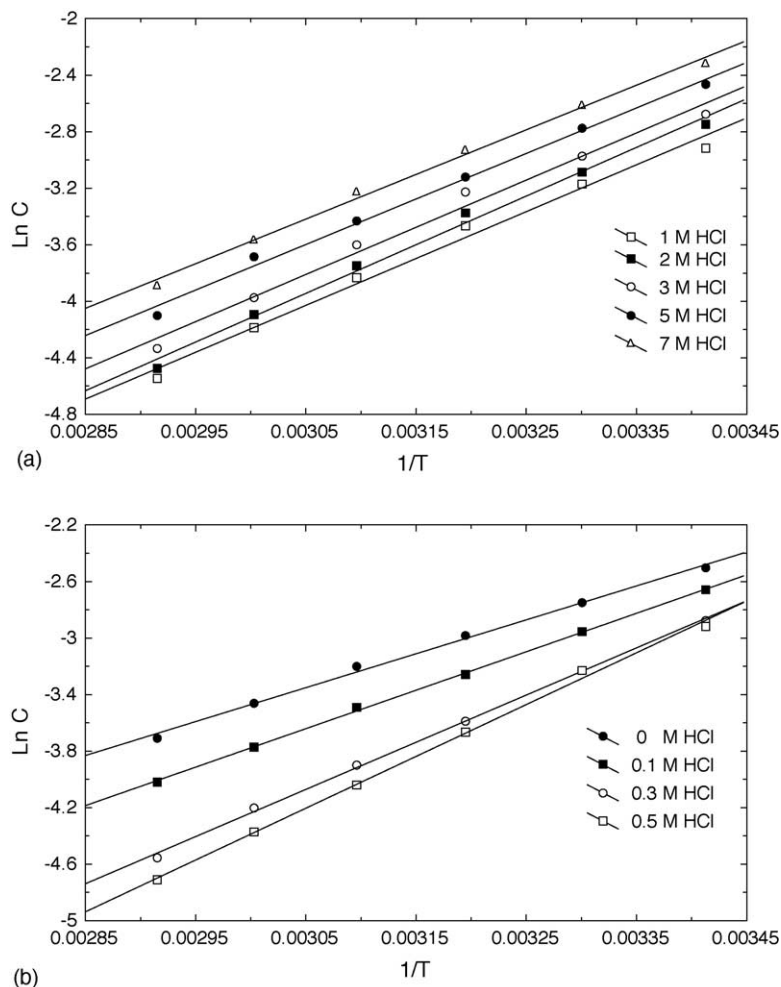


Fig. 3. (a) $\ln C$ vs. $1/T$ plots of results obtained. (b) $\ln C$ vs. $1/T$ plots of results obtained.

increase in the solubility is probably due to the formation of complex ion, Cl_3^- , in the medium, according to the following equation [19]:



Results from Awakura et al. [11] also confirm this sight. But, these authors found out a minimum point at 0.2 M of HCl concentration, graphically. In the present study, this minimum was obtained in 0.5 M of HCl concentration. This case was attributed to the fact that solubility changes were very small in 0.1–0.5 M HCl concentration range and Awakura et al. had studied at only one temperature. Because, in the present investigation, solubility was studied at six various temperatures and found out that the minimum point was 0.5 M HCl concentration for all the temperatures.

3.2. Modeling the solubility

Some semi-empirical models have been derived for solubilities of gases in liquids. These models generally are non-reactive gases and can not be applied to the system here, especially second part of solubility isotherms.

For this, a new equation representing the dependence of the solubility on the concentration of HCl and temperature was derived by using PC as follows:

$$C = 4.46 \times 10^{-8} \exp \left[\frac{2927}{T} \right] \left[-10.73[\text{HCl}]^{3/2} + 63.55[\text{HCl}] - 89.41[\text{HCl}]^{1/2} + 92.02 \right] \quad (7)$$

where C is the solubility in water and HCl solutions in mol L^{-1} , T the temperature (K), $[\text{HCl}]$ the HCl concentration. To test the agreement between the experimental conversion values and the values calculated from Eq (7), a plot of the observed solubility values versus predicted solubility values for 0–7 M acid concentration range was drawn in Fig. 4. The agreement between the experimental and calculated conversion values were found to be very good.

3.3. The effect of temperature

This effect was studied at the temperatures of 293, 303, 313, 323, 333 and 343 K. As shown in Fig. 2a and b, the

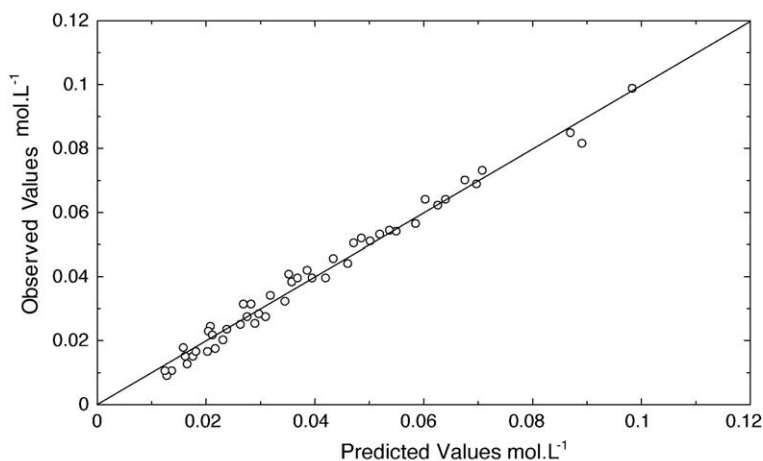


Fig. 4. Agreement between observed solubility values and predicted solubility values from the Eq. (7).

Table 1

Thermodynamic characteristics of dissolution of Cl_2 in hydrochloric acid solutions

Concentration of HCl (mol L^{-1})	ΔH (kJ mol^{-1})	ΔS ($\text{J mol}^{-1} \text{K}^{-1}$)
0	-19.75	-88.02
0.1	-22.45	-98.66
0.3	-27.45	-116.29
0.5	-29.73	-125.55
1.0	-27.48	-117.21
2.0	-28.35	-119.11
3.0	-27.62	-115.81
5.0	-26.44	-110.42
7.0	-26.31	-108.63

solubility of Cl_2 decreases as the temperature increases at all the HCl concentrations studied.

3.4. Thermodynamic parameters

The thermodynamic parameters of the dissolution process were also determined. The heat and entropy change of the solution were calculated graphically [20] by plotting $\ln C$ versus $1/T$ in terms of the following equation (Fig. 3a and b):

$$\ln C = -\Delta H/RT + \Delta S/R \quad (8)$$

The results obtained are summarized in Table 1. The analysis of thermodynamic parameters shows that the enthalpies and entropies of Cl_2 dissolution in solution of HCl are lower than those in water, indicating the formation of more highly ordered structures in solution [21].

4. Conclusions

Investigation of the solubility of Cl_2 in HCl solutions (0–7.0 M) in the temperature range 293–343 K showed that the Cl_2 solubility isotherms had minimum in the region 0.5 M HCl. The solubility of Cl_2 decreases with the increase of

temperature at all the HCl concentration range studied. The thermodynamic parameters of Cl_2 dissolution in HCl solutions were calculated and show evidence that enthalpies and entropies of solubility of chlorine gas in HCl solutions are lower than those in water.

These data will be useful in the use of chlorine gas in metallurgical and electrowinning processes in future.

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