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Metastability of CuCl$_2$ in H$_2$O-HCl for the Copper-Chlorine Thermochemical Cycle of Hydrogen Production

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Abstract

In this paper, metastability of CuCl$_2$ in H$_2$O-HCL for applications to the Cu-Cl thermochemical cycle is experimentally investigated to decrease crystallizing (precipitating) temperature and reduce thermal energy requirements of the cycle. Metastability delays the phase transition by altering the phase transition temperature, depending on direction (heating or cooling). The dissolving temperature is increased if the solution is heated and decreased if the solution is cooled, whereas a typical simple solubility model assumes dissolving and crystallizing occur at the same temperature. The solution temperature is controlled using an ethylene-glycol heater/chiller and measured with a thermocouple. The results of this paper show the metastable zone width increases with cooling rate and is unaffected by HCL concentration. The solubility product constant is calculated for CuCl$_2$ dissolving in various concentrations of HCL and decreases with increasing temperature and HCL concentration.

Keywords: Hydrogen production; Copper-Chlorine cycle; Metastability; Solubility

Nomenclature

c	Concentration, g solute/100 g solvent
dc'/dT	Temperature coefficient of solubility, K/s
K_N	Nucleation rate constant, dimensionless
K_{sp}	Solubility product constant, dimensionless
M	Molarity, mol/L
m	Nucleation order, dimensionless
MSZW	Metastable zone width, K
P	Pressure, kPa
R	Ideal gas constant, J/mol·K
R_{ha}	Ratio of molecular weights of hydrate to anhydrous components, dimensionless
Q̇	Cooling rate, K/s
T	Temperature, K
T_d	Saturation temperature, K
$T_{initial}$	Initial temperature, K
$T_{lowered}$	Lowered temperature, K
T_{met}	Metastable temperature, K
ΔG°	Difference in Gibbs free energy, kJ/kg
ΔH°	Difference in enthalpy, kJ/kg
ΔS°	Difference in entropy, kJ/kg K
A	Greek Symbols
ε	Conversion factor, dimensionless

Introduction

Crystallization is a promising method to recover solids in the copper-chlorine cycle for hydrogen production during the drying step of CuCl$_2$(aq)→CuCl$_2$(s). Crystallization's main advantage is the relatively low energy requirements compared to other drying techniques. A simple solubility model assumes precipitation and dissolution occur at the same temperature, regardless of the rate and direction of temperature change (heating or cooling). However, experiments have shown that this is not the case [1]. Crystals begin to form at colder temperatures and dissolve at lower temperatures than predicted by a simple solubility model. The difference between these two temperatures is the metastable zone width (MSZW=TdITmet). Thus, metastability delays phase change compared to a simple solubility model prediction and the dissolution and precipitation temperatures dependent on the direction, as well as rate of temperature change.

As illustrated in Figure 1, metastability is a type of chemical hysteresis and a critical parameter for optimal design of a crystallization system. The main importance of metastability to the copper-chlorine cycle is that precipitation (e.g., crystallization) occurs at a lower temperature and reduces thermal energy requirements. Barrett and Glennon [1] cooled a solution of potash alum (Kal(SO$_4$)$_2$ · 12(H$_2$O)) at various rates and used FBRM (Focused Beam Reflectance Method) and PVM (Particle Vision and Measurement) to determine the MSZW. The particle count significantly increases when T_{met} is reached (nucleation begins) and decreases when Td is reached (particles re-dissolve). Kubota [2] examined the roughly linear relationship between log(MSZW) and log (Q), which is similar to the paper by Barrett and Glennon's [1]. Mersmann and Bartosch [3] presented a theoretical model to predict MSZW and that optimum supersaturation is less than the metastable supersaturation [4,5].

S (entropy). The variable Ksp is usually calculated in terms of concentration, but the equations given in Euler, Kirschenbaum and Ruekberg [6,7] are essential for calculating Ksp as a function of temperature.

The objectives of the research presented in this paper are to

investigate the relationship between cooling rate and MSZW for CuCl$_2$-H$_2$O-HCl (ternary) systems, as well as to determine Ksp values for CuCl$_2$ dissolving in H$_2$O-HCl systems. The values of Ksp have not previously been determined for CuCl$_2$ dissolving in H$_2$O-HCl systems.

Experimental Methods

In this paper, the metastable zone is determined by cooling an unsaturated solution until a crystal appears, and then the solution is gradually heated until the crystal re-dissolves. The temperatures of crystal disappearance and appearance are recorded and the difference between them is the metastable zone width. To measure MSZW, an HCL solution of known molarity is prepared in a jacket vessel by diluting an HCL solution (12 M) with the corresponding volume of water to make 200 ml of solution. The specified amount of CuCl$_2$ is weighed and added to the jacket vessel. The solution is continuously stirred at 300 to 350 RPM with a magnetic stirrer. A programmable heater / chiller that circulate ethylene-glycol solution through the jacket vessel control the solution temperature, as well as the heating / cooling rates. The temperature of the solution is measured with a digital thermocouple [8,9].

The solution is heated to the initial temperature, $T_{initial}$, and held until all CuCl$_2$ is dissolved (homogenous mixture), and then the solution is cooled at a constant cooling rate, until the first crystal appears, T_{met}. The solution is then heated at a constant heating rate, until the crystal disappears (re-dissolves), T_d. The magnitude of cooling and heating rates may be different. The solubility product constant is determined by calculations made from the MSZW experimental data and reference data.

Formulation of Metastability and Equilibrium

The most general form of the equation relating cooling rate to MSZW is

$$\ln(Q)=m \ln(\Delta T_{max})+\ln(k_N)+(m-1) \ln(dc^*/dT)-\ln\varepsilon \quad (1)$$

Where Q is the cooling rate, m is the nucleation order, ΔT_{max} is the MSZW, k_N is a nucleation rate constant, dc^*/dT is the temperature coefficient of solubility and ε is a conversion factor, such that

$$E=(100R_{ha})/(100-c(R_{ha}-1))^2 \quad (2)$$

where R_{ha} is the ratio of molecular weight of hydrate to anhydrous and c is the concentration. If the last two terms of Equation (1) are assumed negligible [10,11], the equation reduces to:

$$\ln(Q)=m \ln(\Delta T_{max})+\ln(k_N) \quad (3)$$

Barrett and Glennon found the relation between ln(Q) and ln(MSZW) to be approximately linear. The slope of, m, corresponds to the nucleation order. The y-intercept (y-int) is equal to $\ln(K_N)$, therefore, K_N (nucleation rate constant) is equal to

$$\ln(Q)=m \ln(MSZW)+y\text{-int} \quad (4)$$

The exact equation proposed by Barrett and Glennon is an empirical correlation (from potash alum data), has values of m=2.03 and y-int=-8.967, which vary depending on the chemistry of the solution.

The solubility equilibrium is determined in the following way. The variable Ksp is calculated by first calculating the Gibbs Free Energy ($\Delta G°$),

$$\Delta G°=-RT \ln(Ksp) \quad (5)$$

$$\Delta G°=\Delta H°-T\Delta S° \quad (6)$$

where R=8.314 J/mol · K. The weighted-average equations (7) and (8) are used to calculate the overall (i.e., weighted-average by mass) enthalpy (H) and entropy (S) of the ternary system. Mass ratio is used as the weighting factor,

$$\Delta H°=(M_{HCL})H_{HCLl} \times (1-M_{HCL}) H_{Water} \quad (7)$$

The weighted-average entropy (S) is calculated with a similar method

$$\Delta S°=(M_{HCL})S_{HCL}\times(1 M_{HCL})S_{Water} \quad (8)$$

Since the solution is ternary, it has three components, including (i) water (H$_2$O), (ii) hydrogen chloride (HCl), and (iii) copper II chloride (CuCl$_2$). Enthalpy and Entropy are determined from thermophysical data as a weighted average between water (data from [12-14]) and hydrogen chloride (data from Engineering Equation Solver).

Results and Discussion

In this section the results of the metastability experiments and equilibrium constants are presented. As presented in Table 1, to determine the unknown variables in Equation (4) and ensuring independence of concentration, average and weighted-average values for m, and y-int are calculated. The calculation uses the number of data points per concentration divided by the total number of data points as the weights.

As presented in Figure 2, the nucleation order and nucleation rate constants are almost all within 1 of a weighted average. Cooling rate has a dominant influence on MSZW, whereas concentration has a minor influence on MSZW. It is likely that HCl acts as a crystallization inhibitor since higher ln(MSZW) are found at lower HCL concentrations.

The relation between MSZW (dependent variable) and concentration (independent variable) is plotted in Figure 3, for various cooling rates. Linear fits are applied for 0.25 K/s and 0.5 K/s. For the 0.5 K/s dataset, point (4,5) is probably an outlier, thus two linear fits are applied for 0.5 K/s, one fit including the outlier and the other without. The linear fit without the outlier has a stronger linear correlation. Further experimentation is required to determine if the point at (4,5) is an outlier.

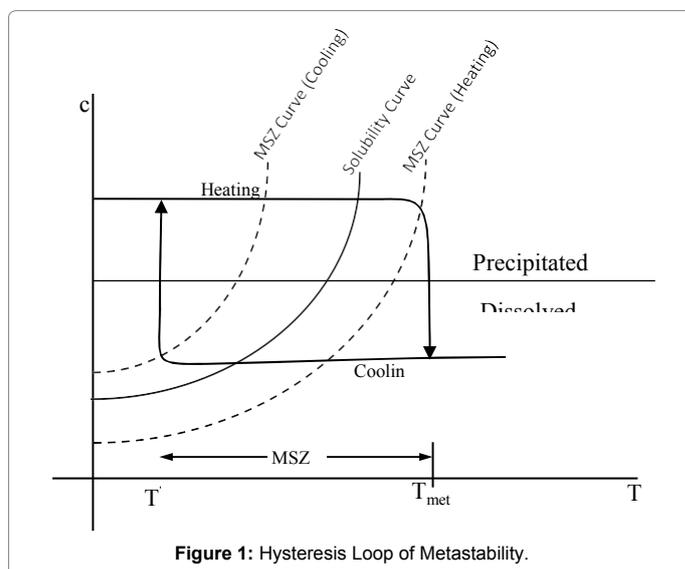As illustrated in Figure 3, MSZW decreases with concentration

Figure 1: Hysteresis Loop of Metastability.

and MSZW increases with faster cooling rates, which agrees well with previous experimental results [15,16]. This is likely caused by higher cooling rates, producing a lower temperature before observing the first crystal, thus lowering T_{met} and increasing MSZW. If the temperature is decreasing too rapidly, T_{met} may be passed because the solution was unable to crystallize at the maximum value of T_{met} due to the rapid cooling rate. When the cooling rate is slower, the solution has time to begin crystallizing at the maximum value of T_{met}.

A higher nucleation order (m) means that the nucleation mode of crystallization (creating new crystals, thus increasing the integer count of crystals), dominates over the growth mode of crystallization (increasing the average size of crystals). As presented in Table 2, values of m and y-int are determined for a ternary system, a correlation is not apparent between the concentration of HCL and the nucleation order.

As illustrated in Figure 4, the relation between HCL concentration, T_{inital} and Ksp is investigated for a ternary system. The effect of CuCl₂ is neglected because it is not a fluid. Linear extrapolation is performed for hydrogen chloride data when T ≥ 60°C. The pressure is assumed to be 100 kPa for thermophysical data. The variable Ksp increases with temperature, since at higher temperatures there is more Brownian motion and more molecular interaction, and hence the solubility increases. The variable Ksp also decreases with HCL concentration, because HCL acts as an anti-solvent, reducing the solubility of CuCl₂ in higher concentrations of HCL solution. The surface can be modelled by,

$$Ksp = 0.9968 - 0.005882(C_{Hcl}) + 0.0001015(T_{inital}) + 0.000131(C_{Hcl})^2 + 2.776 \times 10^{-6}(C_{Hcl})(Tinitial) + 1.393 \times 10^6 (Tinitial)^2$$

Uncertainty Analysis

The main source of measuring MSZW is observing the first crystal at T_{met}. This was done observationally using the unaided eye. The disadvantage of this method is microscopic particles cannot be detected. Thus, it can be assumed that nucleation would consistently occur slightly systematic error when before the unaided eye detects it. Therefore, the reported value of T_{met} might consistently be slightly lower than its true value. Barrett and Glennon overcame this problem, by using highly-sensitive and costly FBRM (Focused Beam Reflectance Method) to detect the first crystal (usually 0-20 μm).

A significant source of error when measuring MSZW is noise, which is seen in Figures 2 and 3. The noise causes the value of the MSZW to differ substantially for the same cooling rate and concentration. It is not precisely known why the noise occurs.

Sources of error for Ksp include the possibility of impurities of the chemicals, slight variations in concentration when diluting HCL to prepare multiple instances of the same molarity solution (e.g., 4 M HCL solution might range from 3.95 M-4.05 M), and random variations in temperature (affecting H and S (and therefore G)).

Conclusion

In this paper, metastability and equilibrium constant were investigated for crystallization in the Cu-Cl cycle. For metastabilty, there is a substantial positive correlation between cooling rate and MSZW. If the crystallization process is not gradual, it is likely maximum T_{met} will be surpassed (reducing T_{met} and increasing MSZW). The results on MSZW should be treated as only tentative, due to significant noise. Further experimentation (ideally with more sophisticated nucleation detection methods) is required to identify the cause of the noise and to overcome the noise, that is, have sufficient points so that noise does not
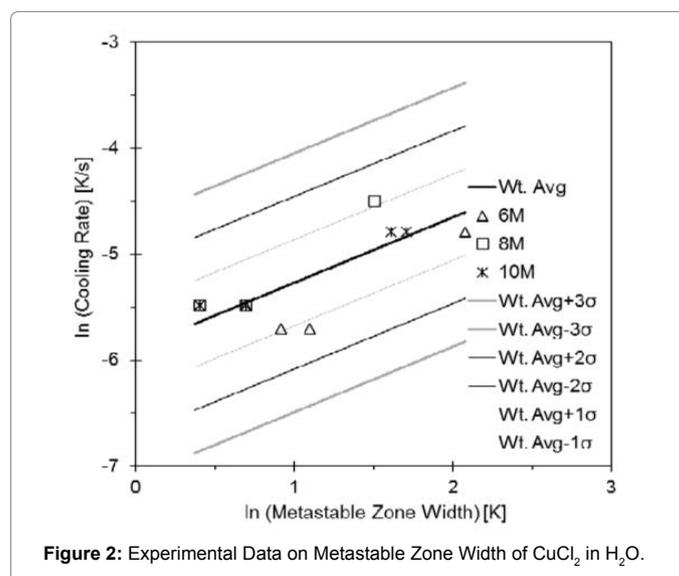

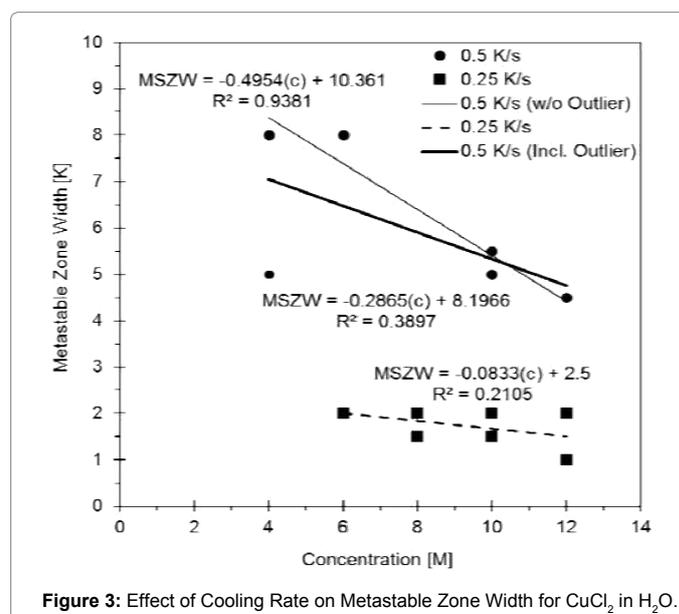**Figure 2:** Experimental Data on Metastable Zone Width of CuCl₂ in H₂O.

Figure 3: Effect of Cooling Rate on Metastable Zone Width for CuCl₂ in H₂O.
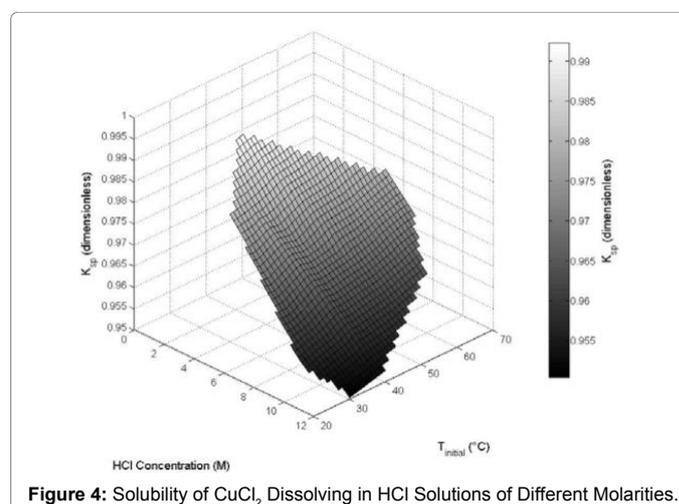

Figure 4: Solubility of CuCl₂ Dissolving in HCl Solutions of Different Molarities.

HCl Concentration [M]	m	y-int	k$_N$	Number of Data Points
6	0.621	-6.162	2.107 × 10^{-3}	4
8	0.998	-6.056	2.343 × 10^{-3}	4
10	0.362	-5.592	3.728 × 10^{-3}	5
Mean	0.66	-5.937	2.640 × 10^{-3}	2.726 × 10^{-3}
Wt. Avg	0.637	-5.91	2.711 × 10^{-3}	2.803 × 10^{-3}

Table 1: Nucleation Order and Nucleation Rate Constants for Several HCL Concentrations.

M$_{HCL}$ [M]	m	y-int
2	n/a	n/a
4	0	-4.787
6	0.621	-6.162
8	0.998	-6.056
10	0.362	-5.592
12	0.472	-5.595

Table 2: Nucleation order and rate for CuCl$_2$ in H$_2$O-HCL.

significantly affect the data.

For solubility equilibrium, Ksp increased with temperature (as expected) and decreased with HCL concentration (the effect of HCL concentration on Ksp was previously unknown). The results of this paper provide useful new experimental data for crystallization and metastability in the Cu-Cl cycle.

Acknowledgments

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