Process Design Technical Note

TECHNICAL NOTE

CHLORINE SCRUBBING

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1.0 Chlorine Scrubbing

Atomic weight	35.45
Melting point	-101°C
Boiling point	-34.9 °C

1.1 Reactions of Cl_2

1.1.1 Dissolution

$$Cl_2 + H_2O \leftrightarrow HCl + HOCl$$

Equilibrium concentrations @ 25°C: Cl_2 : 0.061 mol/litre i.e. 4.3 g/l Cl_2
HOCl: 0.030 mol/litre i.e. 1.6 g/l HOCl

1.1.2 Alkaline Scrubbing

a. $$Cl_2 + 2\,XOH \xrightarrow{< 20^oC} \underset{\text{chloride}}{XCl} + \underset{\text{hypochlorite}}{XOCl} + H_2O$$

b. $$3\,Cl_2 + 6\,XOH \xrightarrow{\sim 75^oC} 5\,XCl + \underset{\text{chlorate}}{XClO_3} + 3\,H_2O$$

Therefore, scrubbing reaction depends on temperature. XOCl solutions are stable below room temperature and reasonably pure solutions can be prepared. The disproportionation reaction to ClO_3^- is slower than for bromine and requires a temperature of >75°C to give good yields.

The stoichiometry is similar for both reactions i.e. 2 moles XOH per mole Cl_2

Further disproportionation can take place but it is slow even at 100°C

c. $$4\,ClO_3^- \longrightarrow Cl^- + \underset{\text{perchlorate}}{3\,ClO_4^-}$$

The reactions outlined above take place with NaOH and KOH.

1.1.3 Solubilities

	Solubility in water @ 0°C g/l	Solubility in water @ 100°C g/l
NaCl	357	398
NaClO	260	1580
$NaClO_3$	790	2300
$NaClO_4$	1700	3200
KCl	276	567
KClO	?	
$KClO_3$	33	570
$KClO_4$	7.5	218

1.2 Heat of Reaction

1.2.1 NaOH Liquor

Heats of formation, ΔH_f @25°C

$Cl_{2\ (g)}$	0	kcal/mole
$NaOH_{\ (aq)}$	-112.19	
$NaCl_{\ (aq)}$	-97.32	
$NaOCl_{\ (aq)}$	-82.8	
$NaClO_{3\ (aq)}$	-78.42	
$NaClO_{4\ (aq)}$	-97.66	
$H_2O_{\ (l)}$	-68.32	

a. $Cl_2 + 2\ NaOH \longrightarrow NaCl + NaOCl + H_2O$

Heat of reaction = -(0 + (2 x -112.19)) + (- 97.32 +(-82.8) + (- 68.32))
= 224.38 - 248.44
= -22.06 kcal

i.e. **22 kcal/mole chlorine** exotherm

b. $3\ Cl_2 + 6\ NaOH \longrightarrow 5\ NaCl + NaClO_3 + 3\ H_2O$

Heat of reaction = -(0 + (6 x -112.19)) + ((5 x - 97.32) + (- 78.42) + (3 x - 68.32)) kcal
= 673.14 - 769.98 = -96.84 kcal

i.e. 96.84/3 = **32.3 kcal/mole chlorine** exotherm

1.2.2 KOH Liquor

Heats of formation, ΔH_f @25°C

$Cl_{2\ (g)}$	0	kcal/mole
$KOH_{\ (aq)}$	-114.96	
$KCl_{\ (aq)}$	-100.16	
$KOCl_{\ (aq)}$	*-86*	*estimated*
$KClO_{3\ (aq)}$	- 81.34	
$KClO_{4\ (aq)}$	- 101.14	
$H_2O_{\ (l)}$	- 68.32	

a. $Cl_2 + 2\ KOH \longrightarrow KCl + KOCl + H_2O$

Heat of reaction = -(0 + (2 x -114.96)) + (-100.16 + (-86) + (-68.32))
= 229.92 – 254.48
= -24.56 kcal

i.e. **24.6 kcal/mole chlorine** exotherm

b. $3\ Cl_2 + 6\ KOH \longrightarrow 5\ KCl + KClO_3 + 3\ H_2O$

Heat of reaction = -(0 + (6 x -114.96)) + ((5 x -100.16) + (-81.34) + (3 x - 68.32)) kcal
= 689.76 – 787.10 = -97.34 kcal

i.e. 97.34/3 = **32.4 kcal/mole chlorine** exotherm