TECHNICAL NOTE

HYDROGEN CYANIDE SCRUBBING

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Hydrogen cyanide scrubbing

Atomic weight	27.03
Melting point	-3.2^{o}C
Boiling point	26^{o}C
Specific gravity	0.687 @ 18^{o}C
Soluble in water	

1. Dissolution

HCN behaves as a very weak acid pK 9.0 in aqueous solution, which means it will not readily ionise in aqueous solution.

However, as with normal protonic acids direct reaction with bases occurs without participation of water.

i.e. $HCN + NaOH \longrightarrow NaCN + H_2O$

2. Vapour pressure of HCN

Temperature ^{o}C	**Vapour pressure** kPa
-29.5	6.7
-5.3	26.7
0	35.2
10.2	53.3
25.9	101.3

3. Chemistry : **Reactions of HCN**

HCN is scrubbed using hypochlorite solution, preferably sodium hypochlorite, for cost reasons.
This is the same treatment as used in the treatment of aqueous wastes containing HCN i.e. an alkaline chlorination to yield a non-toxic cyanate.

The pH is critical and must be maintained in the **region pH 9-11**. A 10% hypochlorite solution is used.

$$HCN + NaOH \longrightarrow NaCN + H_2O$$

Hypochlorite solution *{ $2NaOH + Cl_2 \longrightarrow 2NaOCl + H_2O$ }*

$$NaCN + (2NaOH + Cl_2) \longrightarrow NaCNO + 2NaCl + H_2O$$

Further reaction can take place as follows:-

$$2NaCNO + (4NaOH + 3Cl_2) \longrightarrow 6NaCl + N_2\uparrow + 2H_2O + 2CO_2$$

$$\{CO_2 + 2NaOH \longrightarrow Na_2CO_3 + H_2O\}$$

If the pH is allowed to fall below pH 9 the highly reactive and explosive NCl_3 can be formed at lower pH, as can the poisonous cyanogen chloride (B.pt. 13^{o}C) by the reaction

$$NaCN + Cl_2 \longrightarrow NaCl + CNCl$$

4. Caustic solutions

The reaction schemes outlined above takes place with NaOH, KOH and $Ca(OH)_2$.
Na_2CO_3 solution can also be used to absorb HCN.

5 Heat of Reaction

5.1 NaOCl solution

Heats of formation, ΔH_f @25°C

$HCN_{(g)}$	+31.1	kcal/mole
$HCN_{(aq)}$	+24.2	
$NaOH_{(aq)}$	-112.19	
$NaCl_{(aq)}$	-97.32	
$NaOCl_{(aq)}$	-82.8	
$NaCNO_{(aq)}$	-91.7	
$CO_{2\,(g)}$	-94.05	
$H_2O_{(l)}$	- 68.32	
$N_{2\,(g)}$	0	

$$HCN_{(g)} \longrightarrow HCN_{(aq)}$$

$$HCN_{(aq)} + NaOH_{(aq)} \longrightarrow NaCN_{(aq)} + H_2O$$

Hypochlorite solution *{ 2NaOH + Cl_2 ⟶ NaOCl + NaCl + H_2O }*

$$NaCN_{(aq)} + (NaOCl_{(aq)} + NaCl_{(aq)} + H_2O) \longrightarrow NaCNO_{(aq)} + 2NaCl_{(aq)} + H_2O$$

$$HCN_{(g)} + NaOH_{(aq)} + NaOCl_{(aq)} \longrightarrow NaCNO_{(aq)} + NaCl_{(aq)} + H_2O$$

Heat of reaction = - (+ 31.1 + (-112.19) + (-82.8)) + (- 91.7 + (-97.32) + (-68.32))
= - (- 163.89) + (- 257.34)
= <u>- 93.45 kcal</u>

i.e. **93 kcal/mole hydrogen cyanide** exotherm

5.2 NaOH solution

Heats of formation, ΔH_f @25°C

$HCN_{(g)}$	+31.1	kcal/mole
$HCN_{(aq)}$	+24.2	
$NaOH_{(aq)}$	-112.19	
$NaCN_{(aq200)}$	-22.29	
$H_2O_{(l)}$	- 68.32	

$$HCN_{(g)} \longrightarrow HCN_{(aq)}$$

$$HCN_{(aq)} + NaOH_{(aq)} \longrightarrow NaCN_{(aq)} + H_2O$$

$$HCN_{(g)} + NaOH_{(aq)} \longrightarrow NaCN_{(aq)} + H_2O$$

Heat of reaction = - (+ 31.1 + (-112.19)) + (- 22.29 + (-68.32))
= - (- 81.09) + (- 90.61)
= <u>- 9.52 kcal</u>

i.e. **10 kcal/mole hydrogen cyanide** exotherm

6. Notes

1. If there is a chance of methanol being present in the gas stream containing hydrogen cyanide there is a risk of an explosive atmosphere being formed in the presence of sodium hypochlorite. This was attributed to the formation of extremely unstable methyl hypochlorite. (ICI Mond Division, 1968)

The presence of acids (organic or inorganic) or other esterification catalysts is to be avoided.

In these circumstances caustic soda solution would be used as the scrubbing medium. However, the consequence of this is subsequent risk from the downstream handling of the sodium cyanide solution formed during the scrubbing, which must be undertaken with extreme caution.

Acidification must be avoided to prevent the release of hydrogen cyanide.

2. The presence of ethanol or higher alcohols is unlikely to remove the risk of explosion but it might well reduce it as compared with methanol. No information is to hand, at present.