Environmental Chemistry

Most environmental engineering problems require familiarity & comfort with chemistry.

Stoichiometry

Measurement of how chemicals combine with each other in reactions. Reaction equivalent of mass balance.

Reactants & Products. Conservation of mass requires that at atomic level masses of products equal masses of reactants.

Oxidation of methane (sewer gas) $CH_4 + O_2 \rightarrow CO_2 + H_2O$ (+ heat) left side is not balanced with right because there are 4H vs 2H and 2O vs 3O.

A balanced equation has equal numbers of atomic species on each side. One approach that works for simple organic reactions is: ① balance carbon with carbon
② balance H with water ($H_2O$)
③ balance O with O.

$$CH_4 + O_2 \rightarrow CO_2 + H_2O$$

① Carbons balanced

② 4H on left, balance with $2H_2O$

$$CH_4 + O_2 \rightarrow CO_2 + 2H_2O$$

③ balance 4O on right with $2O_2$

$$CH_4 + 2O_2 \rightarrow CO_2 + 2H_2O$$

Now if want to know masses involved, can use stoichiometric relationships and the atomic weight of each species to determine the masses.

$C = 12$, $O = 16$, $H = 1$

$$CH_4 + 2O_2 \rightarrow CO_2 + 2H_2O$$

$$\underbrace{16g \quad 2(32g)}_{80g} = \underbrace{44g \quad 2(18g)}_{80g} \quad \therefore \text{mass balance}$$

Many environmental problems involve substances dissolved in water, one concentration unit is moles/Liter (M or mol/L)

- One measure of water pollution is the oxygen demand – it represents the ability of water to assimilate waste.

One kind of oxygen demand is the theoritical oxygen demand (ThOD) – it is the amount of oxygen required to exactly oxidize a compound.

Example

1.67 mmol/L solution of glucose ($C_6H_{12}O_6$). Complete oxidization of a carbohydrate should produce $CO_2$ and $H_2O$. Find the amount of oxygen required to completely oxidize the solution (ThOD)

$$C_6H_{12}O_6 + O_2 \rightarrow CO_2 + H_2O$$

① balance carbons (add $6CO_2$)

$$C_6H_{12}O_6 + O_2 \rightarrow 6CO_2 + H_2O$$

② balance Hydrogen (add $6H_2O$)

$$C_6H_{12}O_6 + O_2 \rightarrow 6CO_2 + 6H_2O$$

③ balance Oxygen (add $6O_2$)

$$C_6H_{12}O_6 + 6O_2 \rightarrow 6CO_2 + 6H_2O$$

It takes 6 mole $O_2$ to oxidice 1 mol of $C_6H_{12}O_6$

$\therefore$ Need $6(1.67)$ mmol/L of $O_2$ to oxidize the solution

10.02 mmol/L of $O_2$

Convert to mass basis

$$10.02\,\frac{mmol}{L}\,O_2\;\frac{.032\,g}{1\,mmol\,O_2} = 0.32\,g/L\;O_2 \text{ required}$$

$$= 320\,mg/L\;O_2$$

Enthalpy in Chemical Systems

The balance of energy in chemical reactions is generally explained using enthalpy. $U_1 + Q_{heat} = U_2 + W_{work}$

Most chemical reactions of practical interest are constant pressure reactions. Recall earlier that a constant pressure process

$\Delta H = \Delta U + \underbrace{P\Delta V}_{\text{work done by system}}$

Substitute back into chemical enthalpy equation

$$U_1 + Q = U_2 + W = U_2 + \Delta H - \Delta U$$

So $$Q = \underbrace{U_2 - U_1}_{\Delta U} + \Delta H - \Delta U$$

$$\therefore Q_{heat} = \Delta H$$

In a constant pressure reaction the change in enthalpy is equal to the added heat.

If $\Delta H > 0$, heat is added (absorbed) and the reaction is called endothermic

$\Delta H < 0$, heat is liberated (released) and the reaction is called exothermic.

The change in enthalpy is called the heat of reaction

Change in enthalpy is more important than absolute enthalpy, so most discussions are referenced against a set of standard enthalpies.

$$H^{o}_{298} = \text{enthalpy @ 1 atm and } 298°K \quad (kJ/mol)$$

A table of standard enthalpies can be used to determine if a reaction requires heat, or liberates heat.

$$CH_4 + 2O_{2(g)} \rightarrow CO_{2(g)} + 2H_2O_{(l)}$$

$$-74.9 \qquad 0 \qquad -393.5 + 2(-285.8)$$

$$\text{Net (reactants - products)} = -890.2 \text{ kJ/mol } CH_4$$

Since $\Delta H < 0$, the reaction liberates heat.

Enthalpy is also used to explain energetics in photochemical reactions. Such reactions are fundamental in understanding air pollution.

In a photochemical reaction the added energy (heat) is light.
One kind of PC reaction is photolysis photo - light; lysis - split

$$E(J/\text{photon}) = h\nu = \frac{hc}{\lambda}$$

↑ Planck's constant

This equation relates energy to wavelength. Use $\Delta H$ to determine energy required.

Use $E = \frac{hc}{\lambda}$ to find largest wavelength. to activate reaction
Need $6.02 \cdot 10^{23}$ photons to energize one mole of reactant.

Photolysis of Ozone

Find $\lambda_{max}$ that can photolyze $O_3$ to $O_2 + O$.

$$\underset{(142.9)}{O_3} \xrightarrow{h\nu} \underset{(0)}{O_2} + \underset{(247.5)}{O}$$

$\Delta H = 247.5 - 142.9 = 104.6\ kJ/mol$

$\Delta H > 0$ ∴ reaction requires energy (heat)

$$\frac{hc}{\lambda} \cdot \left(\frac{6.02 \cdot 10^{23}\ \text{photons}}{mol}\right) = E/mol$$

Rearrange & solve for $\lambda$

$$\frac{hc(6.02 \cdot 10^{23})}{104.6 \cdot 10^3} \geq \lambda \Rightarrow \frac{(6.6 \cdot 10^{-34} J \cdot s/\text{photon})(3 \cdot 10^8 m/s)(6.02 \cdot 10^{23}\ \text{photons}/mol)}{104.6 \cdot 10^3 J/mol} =$$

$$\frac{1.19 \cdot 10^{-1} J \cdot m/mol}{104.6 \cdot 10^3 J/mol} = 1.1 \cdot 10^{-6} m$$

∴ $\lambda \leq 1.1 \mu m$ to energize $O_3$ to $O_2 + O$

This reaction illustrates how high altitude, ozone protects the Earth's surface from high energy, short wavelength radiation

Chemical Equilibria

The reactions so far have been written as proceeding in one direction — most reactions are reversible to some extent. When the forward reaction rates equal the reverse rates the reaction is in equilibrium — we observe no change in quantities on either side of the reaction

A generic reaction is $aA + bB \rightleftharpoons cC + dD$
We could study the rate of change of any species as

$-\frac{dA}{dt}$; $-\frac{dB}{dt}$; $\frac{dC}{dt}$; $\frac{dD}{dt}$ all 4 are "rates" — not all 4 rates are the same. Stoiochiometry provides a noramalization procedure

$$-\frac{a}{a}\frac{dA}{dt} = -\frac{a}{b}\frac{dB}{dt} = \frac{a}{c}\frac{dC}{dt} = \frac{a}{d}\frac{dD}{dt}$$

$$\underbrace{aA}\ \rightarrow\ cC$$

$$\frac{\Delta A}{\Delta t} \overset{?}{=} \frac{\Delta C}{\Delta t}$$

a units of A react with $\frac{a}{c}$ units of C in one unit $\Delta t$

At equilibrium the rates vanish $\frac{dA}{dt} = \frac{dB}{dt} = \cdots = 0$ and a concept called the Law of Mass Action is used to study the relationship of products and reactants.

$$Q = \frac{[\text{Products}]}{[\text{Reactants}]} = \frac{[C]^c[D]^d}{[A]^a[B]^b}$$

The quotient Q is the ratio of products to reactants — at equilibrium $Q = K$

K is called the equilibrium constant. If for a given reaction $Q < K$, then the reaction is not at equilibrium, and will proceede forward as written, if $Q > K$, then the reaction will proceede backward as written. At equilibrium $Q = K$

$$K = \frac{[C]^c[D]^d}{[A]^a[B]^b}$$

the terms in [ ] are called activites, in dilute systems activites & molar concentrations are roughly equivalent.

If the reaction is the dissolution of a solid, then K is called the solubility product.

If the reaction is the dissociation of an ionic compound (salt for exam K is called the ionization constant.

The constants are often expressed as their negative base-10 logarithim.

$$pK = -\log K \qquad K = 10^{-pK}$$

Acid – Base Reactions

Water dissociates slightly $H_2O \rightleftharpoons H^+ + OH^-$

$$K = \frac{[H^+][OH^-]}{[H_2O]}$$

$[H_2O] \approx 55\ mol/L$ and is nearly constant

$$\therefore K[H_2O] = K_W = \underbrace{[H^+][OH^-] = 1 \cdot 10^{-14}}_{\text{fundamental equation of aqueous chemistry}}$$

Expressed in $-\log$ form

$$pH + pOH = pK_w = 14$$

In a neutral solution $[H^+] = [OH^-]$ ; $pH = pOH$

$$\therefore pH + pH = pK_w = 14 \rightarrow 2pH = 14 \quad pH = 7$$

An <u>acidic</u> solution is where $[H^+] > [OH^-]$

$pH < pOH \Rightarrow pH < 7$

A <u>basic</u> solution is where $[H^+] > [OH^-]$

$pH > pOH \Rightarrow pH > 7$

pH is central in environmental engineering – its control is sometimes a major process feature.

Example: Ammonia Stripping

Ammonia gas is relatively insoluble in water – one way to remove ammonium from water is to alter pH so that the gas concentration is large (and thus the water is supersaturated with ammonia

$$NH_3 + H_2O \rightleftharpoons NH_4^+ + OH^-$$

← we want to shift reaction to left

$$\frac{[NH_4^+][OH^-]}{[NH_3]} = K_{NH_3} = 1.82 \cdot 10^{-5}$$

to shift to left we want $Q > K$, we want the denominator large & the numerator small

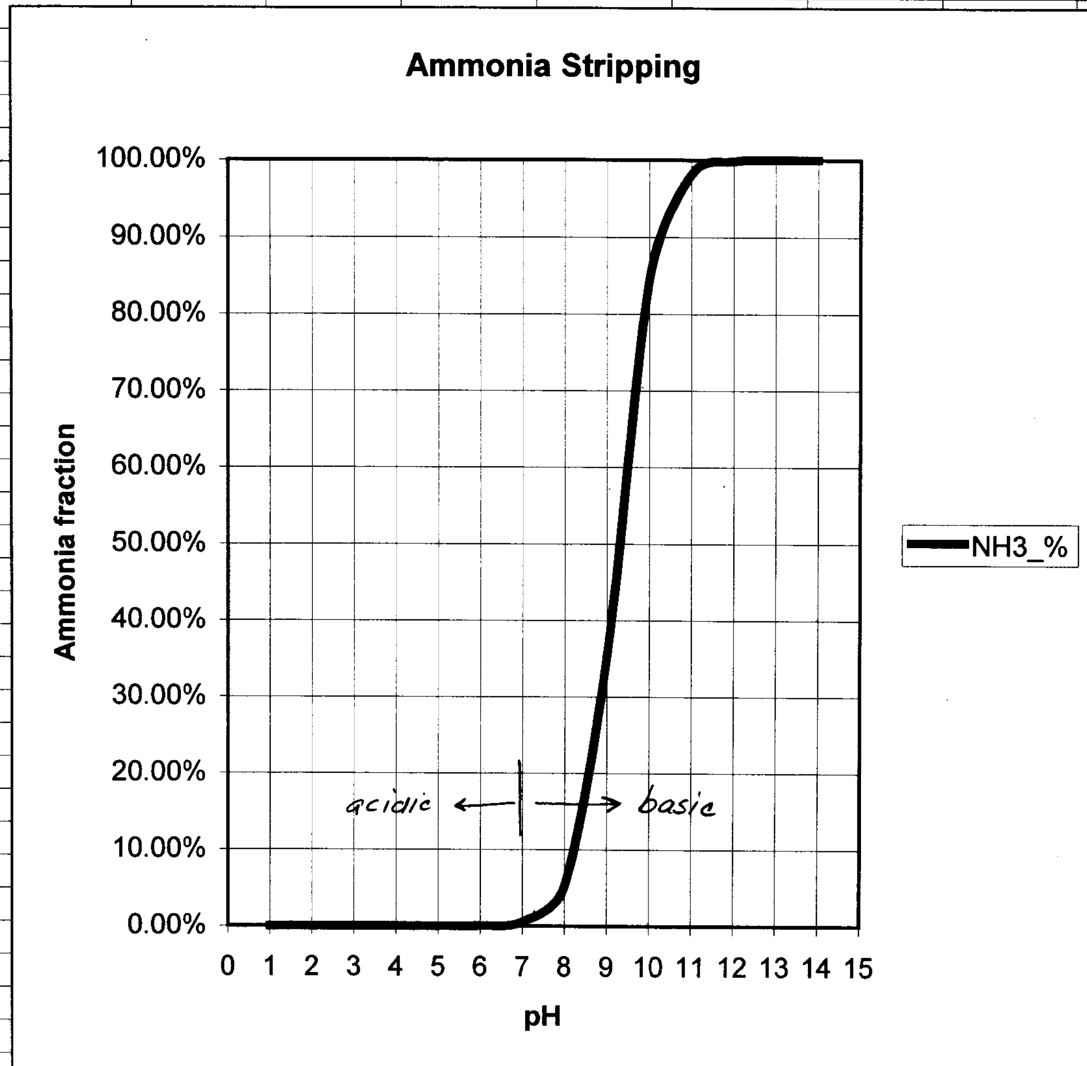
One can develop a design curve to express equilibrium relationships

$$\frac{[NH_4^+][OH^-]}{[NH_3]} = \frac{[NH_4^+]}{[NH_3]} \cdot \frac{(1 \cdot 10^{-14})}{(1 \cdot 10^{-pH})} = 1.82 \cdot 10^{-5} \qquad [OH^-] = \frac{1 \cdot 10^{-14}}{[H^+]} = \frac{1 \cdot 10^{-14}}{1 \cdot 10^{-pH}}$$

$$\therefore \frac{[NH_4^+]}{[NH_3]} = \frac{(1.82 \cdot 10^{-5})(1 \cdot 10^{-pH})}{(1 \cdot 10^{-14})}$$

$$NH_3 \text{ fraction} = \frac{[NH_3]}{[NH_3] + [NH_4^+]} = \frac{1}{1 + \frac{[NH_4^+]}{[NH_3]}}$$

| | A | B | C | D |
|---|---|---|---|---|
| 1 | Ammonia Stripping | | | |
| 2 | | | | |
| 3 | K1 | 1.82E-05 | | |
| 4 | Kw | 1.00E-14 | | |
| 5 | | | | |
| 6 | | | | |
| 7 | | | | |
| 8 | pH | [H] | [NH4/NH3] | NH3_% |
| 9 | 1 | 0.1 | 1.82E+08 | 5.49E-09 |
| 10 | 2 | 0.01 | 1.82E+07 | 5.49E-08 |
| 11 | 3 | 0.001 | 1.82E+06 | 5.49E-07 |
| 12 | 4 | 0.0001 | 1.82E+05 | 5.49E-06 |
| 13 | 5 | 0.00001 | 1.82E+04 | 5.49E-05 |
| 14 | 6 | 0.000001 | 1.82E+03 | 5.49E-04 |
| 15 | 7 | 1E-07 | 1.82E+02 | 5.46E-03 |
| 16 | 8 | 1E-08 | 1.82E+01 | 5.21E-02 |
| 17 | 9 | 1E-09 | 1.82E+00 | 3.55E-01 |
| 18 | 10 | 1E-10 | 1.82E-01 | 8.46E-01 |
| 19 | 11 | 1E-11 | 1.82E-02 | 9.82E-01 |
| 20 | 12 | 1E-12 | 1.82E-03 | 9.98E-01 |
| 21 | 13 | 1E-13 | 1.82E-04 | 1.00E+00 |
| 22 | 14 | 1E-14 | 1.82E-05 | 1.00E+00 |




Finally one plots $NH_3$ vs pH. Observe at neutral pH or acidic, very little $NH_3$ is is solution. One needs to shift pH up, to make a basic solution that is enriched with $NH_3$. Then the ammonia can be stripped from solution. pH control is very important when metals are [illegible]