The equilibrium partial pressure of species i is equal to vapor pressure equilibrium constant at T.

$$C\_{w}, aqueous phase species concentration (M)=\frac{P\_{g}, gas phase species partial pressure (atm)}{Henry^{'}s law constant \left(atm M^{-1}\right)}$$

**Adsorption**- surface uptake **Absorption**- distributed uptake **Sorption**- either one or both

sorption isotherms $linear:q\_{e}=K\_{ads}C\_{e} Langmuir: q\_{e}=q\_{max}\frac{bC\_{e}}{1+bC\_{e}} Freundlich: q\_{e}=K\_{f}C\_{e}^{\frac{1}{n}}$

Equations you need for the dissociation of weak acid HA

|  |  |
| --- | --- |
| $$water dissociation: K\_{w}=\left[H^{+}\right]\left[OH^{-}\right]$$$$material balance on A: C\_{total}=\left[A^{-}\right]+[HA]$$$$acid dissociation: K\_{A}=\frac{\left[H^{+}\right]\left[A^{-}\right]}{[HA]}=\frac{\left[H^{+}\right]\left[A^{-}\right]}{C\_{total}-\left[A^{-}\right]}$$ | $$K\_{A}C\_{total}-K\_{A}\left[A^{-}\right]=\left[H^{+}\right]\left[A^{-}\right] \left[A^{-}\right]=\frac{K\_{A}C\_{total}}{K\_{A}+\left[H^{+}\right]}$$$$electroneutrality: \left[H^{+}\right]=\frac{K\_{w}}{\left[H^{+}\right]}+\frac{C\_{total}K\_{A}}{K\_{A}+\left[H^{+}\right]}$$ |
| $CO\_{2}\left(g\right)$ carbon dioxide gas $CO\_{2}\left(aq\right)$ dissolved carbon dioxide $CaCO\_{3}\left(s\right)$ calcium carbonate$H\_{2}CO\_{3}\left(aq\right)$ carbonic acid $HCO\_{3}^{-}\left(aq\right)$ bicarbonate ion $CO\_{3}^{2-}\left(aq\right)$ carbonate ion $$\left[CO\_{2}\left(aq\right)\right]=K\_{H}P\_{CO\_{2}} K\_{H}=0.034\frac{M}{atm} C\_{carbonate}=[H\_{2}CO\_{3}]+\left[HCO\_{3}^{-}\right]+[CO\_{3}^{2-}]$$$$ \frac{\left[H\_{2}CO\_{3}\right]}{[CO\_{2}\left(aq\right)]}=K\_{m}=1.58\*10^{-3} [H\_{2}CO\_{3}\*]=[CO\_{2}\left(aq\right)]+\left[H\_{2}CO\_{3}\right]=[CO\_{2}\left(aq\right)](1+K\_{m})$$$$H\_{2}CO\_{3}\rightarrow H^{+}+HCO\_{3}^{-} K\_{1}=\frac{\left[H^{+}\right]\left[HCO\_{3}^{-}\right]}{[H\_{2}CO\_{3}]}=4.47\*10^{-7}M $$$$HCO\_{3}^{-}\rightarrow H^{+}+CO\_{3}^{2-} K\_{2}=\frac{\left[H^{+}\right]\left[CO\_{3}^{2-}\right]}{[HCO\_{3}^{-}]}=4.68\*10^{-11}M$$$$CaCO\_{3}\rightarrow Ca^{2+}+CO\_{3}^{2-} K\_{sp}=\left[Ca^{2+}\right][CO\_{3}^{2-}]$$$$α\_{H\_{2}CO\_{3}\*}=\frac{[H\_{2}CO\_{3}\*]}{C\_{carbonate}}=\frac{\left[H^{+}\right]^{2}}{\left[H^{+}\right]^{2}+K\_{1}\left[H^{+}\right]+K\_{1}K\_{2}} α\_{HCO\_{3}^{-}}=\frac{\left[HCO\_{3}^{-}\right]}{C\_{carbonate}}=\frac{K\_{1}\left[H^{+}\right]}{\left[H^{+}\right]^{2}+K\_{1}\left[H^{+}\right]+K\_{1}K\_{2}}$$$$α\_{CO\_{3}^{2-}}=\frac{\left[CO\_{3}^{2-}\right]}{C\_{carbonate}}=\frac{K\_{1}K\_{2}}{\left[H^{+}\right]^{2}+K\_{1}\left[H^{+}\right]+K\_{1}K\_{2}}$$ |
| pH of water in a limestone aquifer$$\left[H\_{2}CO\_{3}\*\right]=\frac{\left[HCO\_{3}^{-}\right][H^{+}]}{K\_{1}} \left[HCO\_{3}^{-}\right]=\frac{\left[H^{+}\right]\left[CO\_{3}^{2-}\right]}{K\_{2}}$$$$\left[H^{+}\right]\left[OH^{-}\right]=K\_{w} \left[Ca^{2+}\right]\left[CO\_{3}^{2-}\right]=K\_{sp}$$$$2\left[Ca^{2+}\right]+\left[H^{+}\right]=\left[OH^{-}\right]+\left[HCO\_{3}^{-}\right]+2\left[CO\_{3}^{2-}\right]$$$$\left[Ca^{2+}\right]=\left[H\_{2}CO\_{3}\*\right]+\left[HCO\_{3}^{-}\right]+\left[CO\_{3}^{2-}\right]$$$$\frac{2K\_{sp}}{\left[CO\_{3}^{2-}\right]}+\left[H^{+}\right]=\frac{K\_{w}}{\left[H^{+}\right]}+\frac{\left[H^{+}\right]\left[CO\_{3}^{2-}\right]}{K\_{2}}+2\left[CO\_{3}^{2-}\right]$$$$\left[CO\_{3}^{2-}\right]=K\_{sp}^{\frac{1}{2}}\left(\frac{\left[H^{+}\right]^{2}}{K\_{1}K\_{2}}+\frac{\left[H^{+}\right]}{K\_{2}}+1\right)^{-\frac{1}{2}}$$ | pH of pristine rainwater$$\left[H\_{2}CO\_{3}\*\right]=(1+K\_{m})K\_{H}P\_{CO\_{2}}$$$$\left[HCO\_{3}^{-}\right]=\frac{K\_{1}\left[H\_{2}CO\_{3}\*\right]}{[H^{+}]}$$$$\left[CO\_{3}^{2-}\right]=\frac{K\_{2}\left[HCO\_{3}^{-}\right]}{[H^{+}]}$$$$\left[H^{+}\right]\left[OH^{-}\right]=K\_{w}$$$$\left[H^{+}\right]=\left[OH^{-}\right]+\left[HCO\_{3}^{-}\right]+2\left[CO\_{3}^{2-}\right]$$$$\left[H^{+}\right]=\frac{K\_{w}}{\left[H^{+}\right]} +\frac{K\_{1}(1+K\_{m})K\_{H}P\_{CO\_{2}}}{[H^{+}]}+2\frac{K\_{1}K\_{2}(1+K\_{m})K\_{H}P\_{CO\_{2}}}{\left[H^{+}\right]^{2}}$$ |

Dissolution of ammonium chloride involving a phase change

$$electroneutrality: \left[H^{+}\right]+\left[NH\_{4}^{+}\right]=\left[OH^{-}\right]+\left[Cl^{-}\right] water dissociation: K\_{w}=\left[H^{+}\right]\left[OH^{-}\right]$$

$$Henry^{'}s law:\left[NH\_{3}\left(aq\right)\right]=K\_{H}P\_{NH\_{3}} acid dissociation: K\_{A}=\frac{\left[NH\_{3}\left(aq\right)\right]\left[H^{+}\right]}{\left[NH\_{4}^{+}\right]}$$

$$mass balance on NH\_{3}:n\_{NH\_{3}}=\left(\left[NH\_{4}^{+}\right]+\left[NH\_{3}\left(aq\right)\right]\right)V\_{w}+\frac{P\_{NH\_{3}}V\_{air}}{RT} mass balance on Cl: n\_{Cl}=n\_{NH\_{3}}$$

$$\left[NH\_{4}^{+}\right]=\frac{n\_{NH\_{3}}-\left[NH\_{3}\left(aq\right)\right]V\_{w}-\frac{P\_{NH\_{3}}V\_{air}}{RT}}{V\_{w}}=\frac{n\_{NH\_{3}}-\frac{K\_{A}\left[NH\_{4}^{+}\right]V\_{w}}{\left[H^{+}\right]}-\frac{K\_{A}\left[NH\_{4}^{+}\right]V\_{air}}{\left[H^{+}\right]RTK\_{H}}}{V\_{w}}=\frac{n\_{NH\_{3}}}{V\_{w}+\frac{K\_{A}V\_{w}}{\left[H^{+}\right]}+\frac{K\_{A}V\_{air}}{\left[H^{+}\right]RTK\_{H}}}$$

$$\left[H^{+}\right]+\frac{n\_{NH\_{3}}}{V\_{w}+\frac{K\_{A}V\_{w}}{\left[H^{+}\right]}+\frac{K\_{A}V\_{air}}{\left[H^{+}\right]RTK\_{H}}}=\frac{K\_{w}}{\left[OH^{-}\right]}+\frac{n\_{NH\_{3}}}{V\_{w}}$$

**Oxidation states**

|  |  |  |  |
| --- | --- | --- | --- |
| Sulfur (S) | Oxygen (O) | Carbon | Hydrogen |
| 0 in elemental form-2 in sulfide+6 in sulfate or sulfur trioxide+4 in sulfur dioxide | -2 in all except-1 in peroxide0 in elemental form | -4 in all organic compounds0 in elemental form+2 in CO+4 in CO2 | 0 in elemental form+1 in proton-1 in hydride |
| Nitrogen (N) | Chlorine (Cl) |
| 0 in elemental form-3 in ammonia/ammonium+2 in NO+4 in NO2+5 in nitrate and N2O5+3 in nitrite | 0 in elemental form-1 in chloride+1 in HOCl (hypochlorous acid)+7 in HClO4 (perchloric acid) |

$$species+radical\rightarrow products R=kY\_{species}Y\_{radical} τ\_{rxn}=\frac{Y\_{species}}{R}=\frac{1}{kY\_{radical}}$$

|  |  |
| --- | --- |
| Photosynthesis $CO\_{2}+H\_{2}O\rightarrow \left\{CH\_{2}O\right\}+O\_{2}$Nitrification $NH\_{4}^{+}+2O\_{2}\rightarrow NO\_{3}^{-}+2H^{+}+H\_{2}O$ | Aerobic respiration $\left\{CH\_{2}O\right\}+O\_{2}\rightarrow CO\_{2}+H\_{2}O$Methane formation $2\left\{CH\_{2}O\right\}\rightarrow CO\_{2}+CH\_{4}$ |

Nitrogen fixation $\left\{CH\_{2}O\right\}+2N\_{2}+3H\_{2}O+4H^{+}\rightarrow 3CO\_{2}+4NH\_{4}^{+}$

Denitrification $5\left\{CH\_{2}O\right\}+4NO\_{3}^{-}+4H^{+}\rightarrow 5CO\_{2}+7H\_{2}O+2N\_{2}$

Sulfate reduction $2\left\{CH\_{2}O\right\}+2H^{+}+SO\_{4}^{2-}\rightarrow 2CO\_{2}+2H\_{2}O+H\_{2}S$

$$\frac{dX}{dt}=μX=r\_{g}X \left(growth term\right)-k\_{d}X \left(decay term\right)$$

S- limiting substrate concentration (mg/L), km- the maximum substrate degradation rate (mg S/mgX/d)s

Ks- half saturation degradation rate (mg S/L), Y- cell-yield coefficient (mg S/mg X)

$$r\_{g}=Y\frac{k\_{m}S}{K\_{s}+S} \frac{dS}{dt}=-\frac{r\_{g}}{Y}X=-\frac{k\_{m}S}{K\_{s}+S}X μ=\frac{1}{X}\frac{dX}{dt}=Y\frac{k\_{m}S}{K\_{s}+S}-k\_{d}=Y\frac{1}{X}\frac{dS}{dt}-k\_{d}$$

$r\_{g}=Y\frac{k\_{m}S}{K\_{s}+S} $ If $K\_{s}\gg S$ $r\_{g}=Y\frac{k\_{m}S}{K\_{s}}$ 1st order If $S\gg K\_{s}$ $r\_{g}=Yk\_{m}$ 0th order

|  |  |
| --- | --- |
| BOD + OD -> oxidized products1. Measure the initial DO content of water, call DO(0)
2. Fill a 300 mL glass bottle with a sample of the water, seal it.
3. Incubate in dark at 20 degrees for 5 days
4. Measure DO content on day 5, DO5
5. Compute BOD5=DO(0) - DO5
 | $$\frac{d\left[BOD\right]}{dt}=-k\_{BOD}\left[BOD\right]$$$$ \left[BOD\right]\left(t\right)=\left[BOD\right]\left(0\right)\*e^{-k\_{BOD}t}$$$$\frac{d\left[DO\right]}{dt}=-k\_{BOD}\left[BOD\right]$$$$ \left[DO\right]\left(t\right)=\left[DO\right]\left(0\right)-\left[BOD\right]\left(0\right)\*(1-e^{-k\_{BOD}t})$$ |

Dispersion is concentrations spread out in space. Diffusivity: big species ↓, small species ↑, water ↓, air ↑, low T ↓, high T ↑

|  |  |  |
| --- | --- | --- |
| Molecular diffusion: $J=-D\frac{dC}{dx}$ D [=] m2/s | Turbulent diffusion: $J=-ε\frac{dC}{dx}$ $ε$[=] m2/s | Advection:$ J \left[\frac{mol}{m^{2}s}\right]=u\left[\frac{m}{s}\right]C [\frac{mol}{m^{3}}] $ |

$$x=\sqrt{2Dt}$$

$$Re\_{p}=\frac{d\_{p}V\_{\infty }}{v \left(kinematic viscosity\right)}=\frac{d\_{p}V\_{\infty }ρ\_{f}}{μ (dynamic viscosity)}$$

Two properties of a fluid that contribute to drag: viscosity, density. Particles reach terminal velocity quickly, Fnet = 0

Drag on particles

|  |  |
| --- | --- |
| $$Re\_{p}<0.3$$ | $$C\_{d}=\frac{24}{Re\_{p}} F\_{d}=3πμd\_{p}V\_{\infty } v\_{t}=\frac{gd\_{p}^{2}}{18}\left(\frac{ρ-ρ\_{f}}{μ}\right)$$ |
| 0.3~1000 | $$C\_{d}=\frac{24}{Re\_{p}}\left(1+0.14Re\_{p}^{0.7}\right) v\_{t}=\left[\frac{4}{3}\frac{gd\_{p}}{C\_{d}}\left(\frac{ρ-ρ\_{f}}{ρ\_{f}}\right)\right]^{\frac{1}{2}} ρ>ρ\_{f} v\_{t}=\left[\frac{4}{3}\frac{gd\_{p}}{C\_{d}}\left(\frac{ρ\_{f}-ρ}{ρ\_{f}}\right)\right]^{\frac{1}{2}} ρ\_{f}>ρ$$ |
| 1000~35000 | $$C\_{d}=0.445 F\_{d}=0.173ρ\_{f}d\_{p}^{2}V\_{\infty }^{2} v\_{t}=\left[\frac{4}{3}\frac{gd\_{p}}{C\_{d}}\left(\frac{ρ\_{f}-ρ}{ρ\_{f}}\right)\right]^{\frac{1}{2}}$$ |

Gravitational settling $F\_{g}=F\_{b}+F\_{d}$

$F\_{g}=mg=ρ\frac{π}{6}d\_{p}^{3}g F\_{b}=ρ\_{f}\frac{π}{6}d\_{p}^{3}g F\_{d}=\left(\frac{π}{4}d\_{p}^{2}\right)\left(\frac{1}{2}ρ\_{f}V\_{\infty }^{2}\right) $ $V\_{\infty }$ is the speed of the particle relative to the fluid

|  |  |
| --- | --- |
|  | $$J\_{b}=k\_{m}\left(C-C\_{i}\right)=\frac{D\left(C-C\_{i}\right)}{L\_{f}} C\_{i}=interface C k\_{m}=\frac{D}{L\_{f}}$$$$J\_{gl}=D\_{w}\frac{C\_{i}-C}{L\_{w}}=D\_{a}\frac{(P-P\_{i})/RT}{L\_{a}}=k\_{gl}(C\_{s}-C)$$C = bulk Cs = equilibrium with bulk Ci = interface$$C\_{i}=K\_{H}P\_{i} C\_{s}=K\_{H}P$$$$D\_{w}\frac{C\_{i}-C}{L\_{w}}=D\_{a}\frac{(C\_{s}-C\_{i})}{RTK\_{H}L\_{a}}=k\_{gl}(C\_{s}-C)$$$$k\_{gl}=\frac{D\_{w}}{L\_{w}}\left(\frac{D\_{a}L\_{w}}{D\_{w}L\_{a}RTK\_{H}+D\_{a}L\_{w}}\right)=\frac{1}{\frac{L\_{w}}{D\_{w}}+\frac{L\_{a}}{D\_{a}}RTK\_{H}}$$$$\frac{1}{k\_{gl}}=\frac{1}{k\_{l}}+\frac{RTK\_{H}}{k\_{g}} k\_{l}=\frac{D\_{w}}{L\_{w}} k\_{g}=\frac{D\_{a}}{L\_{a}}$$If $k\_{l}<\frac{k\_{g}}{RTK\_{H}}$ liquid film resistance dominatesIf $k\_{l}>\frac{k\_{g}}{RTK\_{H}}$ gas film resistance dominates |

|  |  |  |  |
| --- | --- | --- | --- |
| Batch reactor $\frac{d\left(CV\right)}{dt}=rV$ | Zeroth order$$C\left(t\right)=C\left(0\right)-k\_{o}t $$$$until C runs out$$$$τ=\frac{C\left(0\right)}{k\_{0}}$$ | First order$$C\left(t\right)=C\left(0\right)e^{-k\_{1}t}$$$$τ=\frac{1}{k\_{1}}$$ | Second order$$C\left(t\right)=\frac{C\left(0\right)}{1+2k\_{2}C(0)t}$$$$τ=\frac{1}{2k\_{2}C(0)}$$ |
| CMFR$$\frac{d\left(CV\right)}{dt}=QC\_{in}-QC+rV$$$$ \frac{dC}{dt}=\frac{1}{τ}\left(C\_{in}-C\right)+r$$ | Zeroth order$$\frac{dC}{dt}=\frac{1}{τ}\left(C\_{in}-C\right)-k\_{o}$$$$C=C\_{in}-k\_{o}τ$$ | First order$$\frac{dC}{dt}=\frac{1}{τ}\left(C\_{in}-C\right)-k\_{1}C$$$$C=\frac{C\_{in}}{1+k\_{1}τ}$$ | Second order$$\frac{dC}{dt}=\frac{1}{τ}\left(C\_{in}-C\right)-2k\_{2}C^{2}V$$$$C=\frac{\left(8k\_{2}C\_{in}τ+1\right)^{0.5}-1}{4k\_{2}τ}$$ |
| PFR $$U\frac{dC(x)}{dx}=r$$ | Zeroth order$$C(x)=C(0)-\frac{k\_{o}x}{U}$$ | First order$$C(x)=C\left(0\right)e^{-\frac{k\_{1}}{U}x}$$ | Second order$$C(x)=\frac{UC\left(0\right)}{U+2k\_{2}C\left(0\right)x}$$ |

Ci, Q into CMFR 🡪 C1, Q into PFR 🡪 C2,Q (both first order) $C\_{1}=\frac{C\_{i}}{1+kτ\_{CMFR}} C\_{2}=C\_{1}e^{-kτ\_{PFR}} C2=\frac{C\_{i}}{1+kτ\_{CMFR}}e^{-kτ\_{PFR}}$

|  |  |
| --- | --- |
|  | $$τ\_{r}=\frac{V}{Q\left(1+R\right)}=\frac{τ}{1+R} R is recycle ratio $$$$ C\_{in}Q+C\_{out}RQ-C\_{in}^{\*}\left(Q+RQ\right)=0 C\_{in}^{\*}=\frac{C\_{in}+RC\_{out}}{1+R}$$$$C\_{out}=\frac{C\_{in}+RC\_{out}}{1+R}e^{-\frac{kτ}{1+R}}=\frac{e^{-\frac{kτ}{1+R}}}{1+R[1-e^{-\frac{kτ}{1+R}}]}$$ |
|  | $$\frac{d\left(CV\right)}{dt}=C\frac{dV}{dt}+V\frac{dC}{dt}=Q\_{in}C\_{in}-Q\_{out}C-kVC V\left(t\right)=V\_{0}+\left(Q\_{in}-Q\_{out}\right)t$$$$C\left(Q\_{in}-Q\_{out}\right)+\left(V\_{0}+\left(Q\_{in}-Q\_{out}\right)t\right)\frac{dC}{dt}=Q\_{in}C\_{in}-Q\_{out}C-k\left[V\_{0}+\left(Q\_{in}-Q\_{out}\right)t\right]C$$$$\frac{dC}{dt}=\frac{Q\_{in}\left(C\_{in}-C\right)}{\left(Q\_{in}-Q\_{out}\right)t+V\_{0}}-kC$$ |