MATHEMATICAL GEOSCIENCE.

C5.11.

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LECTURE 1a

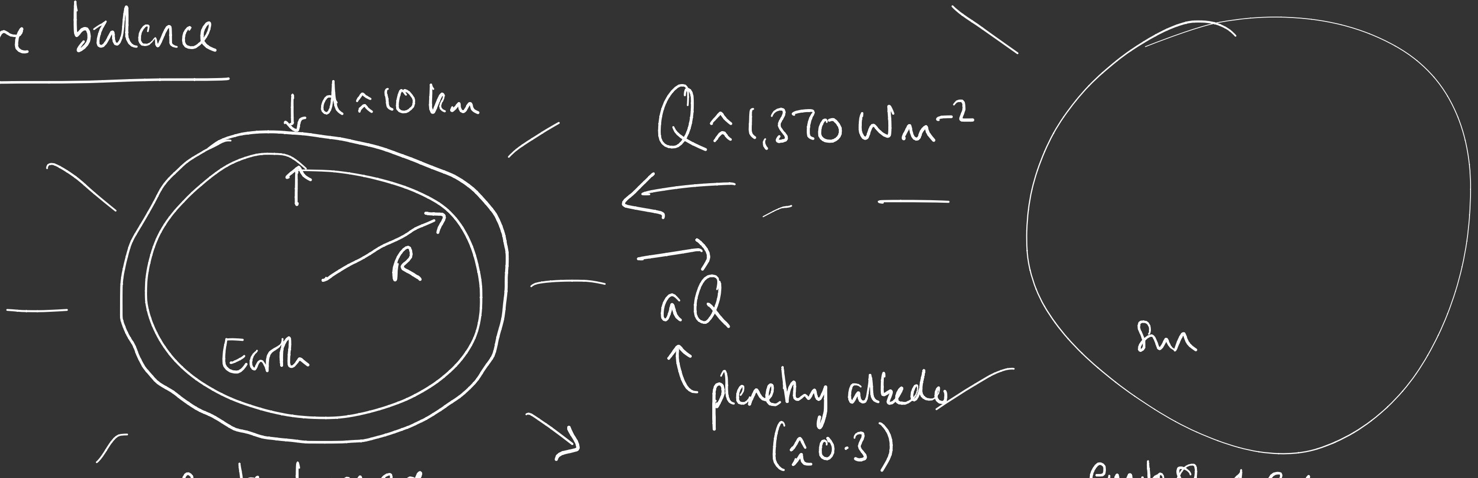
Introduction & Radiative balance

1. CLIMATE

2. RIVERS

3. ICE

Radiative balance



emits longwave radiation (infra-red)

emits shortwave radiation (visible / UV)

$$Q_e = \gamma \sigma T^4$$

γ: greenhouse factor (depends on composition)

σ: Stefan-Boltzmann constant 5.67×10^{-8} $\mathrm{Wm^{-2}K^{-4}}$

Energy balance for atmosphere

$$\boxed{\frac{d}{dt}\left(4\pi R^2 d \rho c_p T\right) = \pi R^2 (1-a) Q - 4\pi R^2 \gamma \sigma T^4}$$

$$\boxed{C \frac{dT}{dt} = \frac{1}{4}(1-a)Q - \gamma\sigma T^4}$$

$C = \rho c_p d \hat{=} 10^7 \text{ J m}^{-2}\text{K}^{-1}$

heat capacity of atmosphere

Steady state $T_0 = \left[\frac{(1-a)Q}{4\gamma\sigma}\right]^{1/4}$

For Earth, with $\gamma = 1$ (no greenhouse effect), $T_0 \hat{=} 255\text{K}$ ($273\text{K} \hat{=} 0\text{C}$)

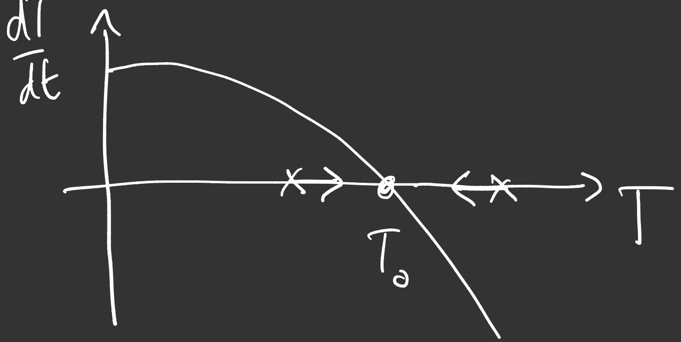
observed temp $\hat{=} 288\text{K} \Rightarrow$ greenhouse factor $\gamma \hat{=} 0.61$ currently.

For Venus, observed temp $\hat{=} 740\text{K} \Rightarrow$ greenhouse factor $\gamma \hat{=} 0.01$

ie. strong greenhouse effect.

The steady state is stable. Two ways to see this:

- graphical



- linear stability – write $T = T_0 + T'$ $\quad |T'| \ll T_0$

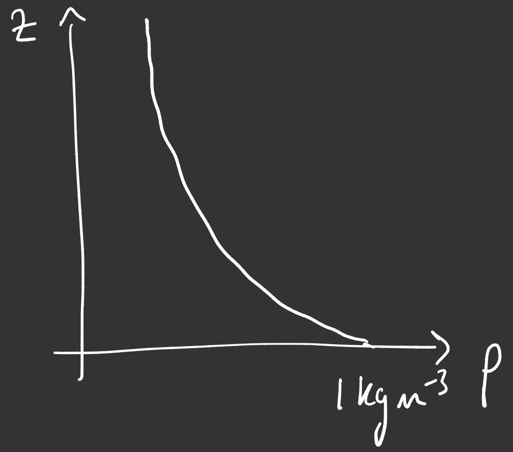
$$\Rightarrow \quad C\frac{dT'}{dt} = \frac{1}{4}(1-a)Q - \gamma\sigma(T_0+T')^4$$

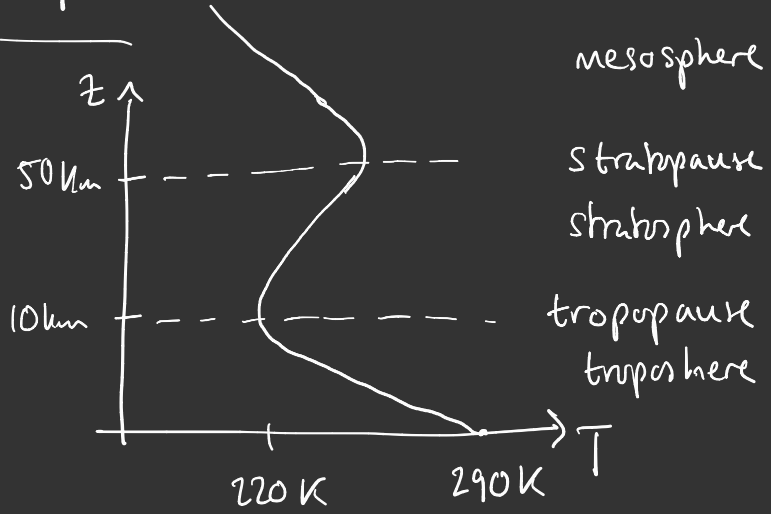
$$= \cancel{\frac{1}{4}(1-a)Q} - \cancel{\gamma\sigma T_0^4} - 4\gamma\sigma T_0^3 T' + \text{h.o.t.}$$

$T' \propto e^{-t/t_0}$ where $t_0 = \dfrac{C}{4\gamma\sigma T_0^3} \approx 30$ days.

Lecture 1b

Vertical structure of the atmosphere





Why? Ideal gas law $p = \rho \frac{RT}{M_a}$

$R \approx 8.3\ \mathrm{J\,K^{-1}\,mol^{-1}}$

$M_a \approx 29 \times 10^{-3}\ \mathrm{kg\,mol^{-1}}$

Hydrostatic equilibrium $\frac{dp}{dz} = -\rho g$ (vertical force balance)

Treat $T \approx T_0$ as constant $\Rightarrow$ $\frac{d\rho}{dz} = -\frac{M_a g}{RT_0}\rho$ $\Rightarrow$ $\boxed{\rho = \rho_0 e^{-z/H}}$ $H = \frac{RT_0}{M_a g} \approx 8\ \mathrm{km}$

Energy eqn

$$\rho c_p \frac{DT}{Dt} - \frac{Dp}{Dt} = \cancel{\nabla\cdot(k\nabla T)} - \cancel{\nabla\cdot\underline{q}} \qquad \left(\frac{DT}{Dt} = \frac{\partial T}{\partial t} + \underline{u}\cdot\nabla T \quad \text{material derivative}\right)$$

adiabatic term

conduction

radiation

In troposphere, convection causes vertical advection to dominate

$$\Rightarrow \boxed{\rho c_p \frac{dT}{dz} - \frac{dp}{dz} \approx 0}$$

adiabatic approximation

$$+\ \text{hydrostatic} \Rightarrow \frac{dT}{dz} = -\frac{g}{c_p} =: -\Gamma_d,$$

the lapse rate $\approx 10\,\mathrm{K\,km^{-1}}$

(this ignores water vapour & condensation - see later)

Lecture 2a

Two-stream approximation

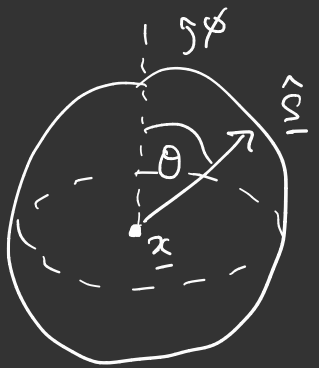
Last time: steady radiation balance

$$\frac{1}{4}(1-a)Q = \underset{\wr}{\gamma\sigma T_s^4} = \sigma T_e^4$$ where $T_e = \gamma^{1/4} T_s$ is the 'effective emitting temperature'

Now: determine γ by modelling longwave radiation within the atmosphere.

We'll assume a 'grey atmosphere', i.e. absorption is independent of frequency.

Define radiative intensity $I(\underline{x}, \hat{\underline{s}})$



radiative transfer equation (RTE)

$$\boxed{\frac{\partial I}{\partial s} = -\kappa\rho(I-B)}$$

emission intensity

$$B = \frac{\sigma T^4}{\pi}$$

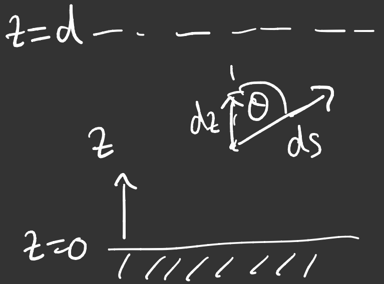
density

absorption coefficient (depends on concentration CO_2, H_2O, CH_4, ...)

$$\hat{\underline{s}} = (\sin\theta\cos\phi, \sin\theta\sin\phi, \cos\theta)$$

$$\left(\frac{\partial I}{\partial s} = \hat{\underline{s}}\cdot\nabla I\right)$$

We assume a one-dimensional atmosphere, so $I(z,\theta)$.



Then $$\frac{\partial I}{\partial s} = \boxed{\cos\theta \frac{\partial I}{\partial z} = -\kappa\rho(I-B)}$$ for $z\in[0,d]$, $\theta\in[0,\pi]$

(note $I=I(z,\theta)$, $B=B(z)$, $\kappa(z)$, $\rho(z)$)

Average intensity over all upwards / downwards directions, I_+ / I_-

$$I_+(z) = \frac{1}{2\pi} \int_0^{2\pi} \int_0^{\pi/2} I(z,\theta) \sin\theta \, d\theta \, d\phi = \int_0^1 I \, d\mu$$

$$\mu = \cos\theta$$
$$d\mu = -\sin\theta \, d\theta$$

$$I_-(z) = \frac{1}{2\pi} \int_0^{2\pi} \int_{\pi/2}^{\pi} I(z,\theta) \sin\theta \, d\theta \, d\phi = \int_{-1}^{0} I \, d\mu$$

Also define the total upwards / downwards fluxes, F_+ / F_-

$$F_+(z) = \int_0^{2\pi} \int_0^{\pi/2} I(z,\theta) \cos\theta \sin\theta \, d\theta \, d\phi = 2\pi \int_0^1 I \mu \, d\mu \overset{\text{approx.}}{\approx} \pi I_+$$

$$F_-(z) = -\int_0^{2\pi} \int_{\pi/2}^{\pi} I(z,\theta) \cos\theta \sin\theta \, d\theta \, d\phi = -2\pi \int_{-1}^{0} I \mu \, d\mu \approx \pi I_-$$

Next, re-write RTE $\mu \frac{\partial I}{\partial z} = -\kappa\rho(I-B)$.

Integrate $\int_0^1 d\mu$ & $\int_{-1}^0 d\mu$, using the same approx. $\left(\int_0^1 I \mu \, d\mu \approx \frac{1}{2} \int_0^1 I \, d\mu \right)$

$$\Rightarrow \boxed{\frac{1}{2}\frac{dI_+}{dz} = -\kappa\rho(I_+ - B) \qquad -\frac{1}{2}\frac{dI_-}{dz} = -\kappa\rho(I_- - B)}$$

This is the two-stream approximation.

Lecture 2b

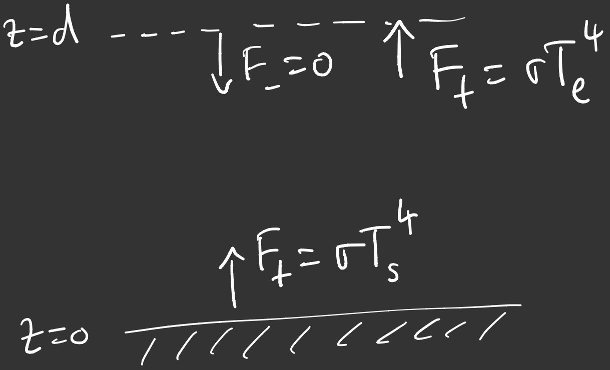
We assume local radiative equilibrium (each point re-emits all the radiation that it absorbs)

$$B = \frac{1}{4\pi}\int_0^{2\pi}\int_0^{\pi} I(z,\theta)\sin\theta\, d\theta\, d\phi = \frac{1}{2}(I_+ + I_-)$$

$$\Rightarrow \quad \frac{dI_+}{dz} = -k\rho\,(I_+ - I_-) = \frac{dI_-}{dz}$$

or

$$\boxed{\frac{dF_+}{dz} = \frac{dF_-}{dz} = -k\rho\,(F_+ - F_-)}$$



At $z=0$, $F_+ = \sigma T_s^4$ (Stefan-Boltzmann)

At $z=d$, $F_- = 0$ (no incoming longwave radiation)

$F_+ = \sigma T_e^4$ (defines T_e)

Note $\frac{dF_+}{dz} = \frac{dF_-}{dz} \Rightarrow (F_+ - F_-)$ is independent of z, so $F_+ - F_- = \sigma T_e^4$

so $\frac{dF_-}{dz} = -\kappa\rho\sigma T_e^4$ with $F_- = 0$ at $z = d$

$\Rightarrow F_- = \sigma T_e^4 \int_z^d \kappa\rho \, dz = \sigma T_e^4 \tau$, where $\tau = \int_z^d \kappa\rho \, dz$ is the optical depth

So $F_+ = \sigma T_e^4 (1 + \tau)$

so, at $z = 0$, $\sigma T_s^4 = \sigma T_e^4 (1 + \tau_s)$ where $\tau_s = \int_0^d \kappa\rho \, dz$ is the optical thickness of the atmosphere

So, we find $\boxed{\gamma = \frac{T_e^4}{T_s^4} = \frac{1}{1 + \tau_s}}$ is the greenhouse factor

Lecture 3a

Runaway greenhouse effect.

Water vapour is a powerful greenhouse gas. It exerts a positive feedback:

$$\begin{tikzcd}
\text{more vapour} \arrow[r] & \text{stronger greenhouse effect} \arrow[r] & \text{higher temperatures} \arrow[r] & \text{more evaporation} \arrow[lll, bend left]
\end{tikzcd}$$

On Earth, this is limited by cloud formation (clouds = condensed water droplets in suspension) and rainfall. On Venus, clouds don't form ⇒ <u>runaway greenhouse effect</u>.

(Clouds also increase the albedo, → negative feedback).

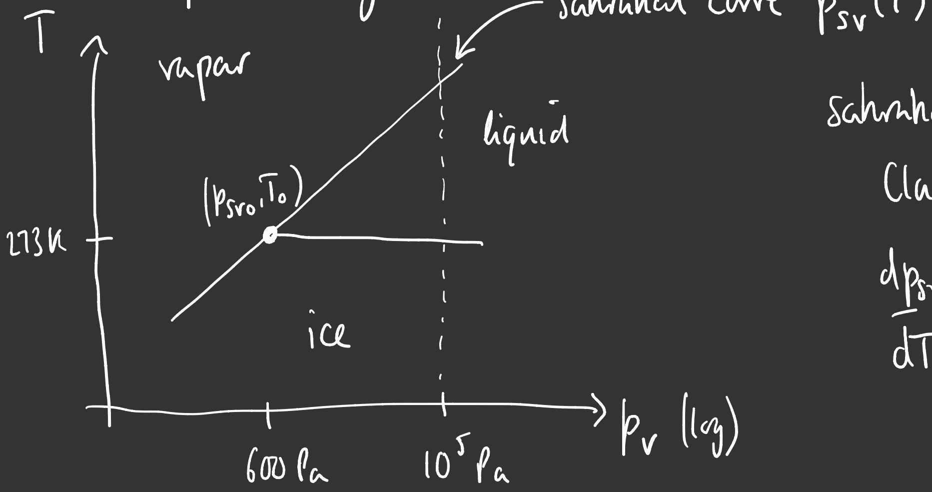
The amount of vapour is described with the density ρ_v, and the partial pressure p_v, related by the ideal gas law:

$$\boxed{p_v = \frac{\rho_v R T}{M_v}}$$

R = gas constant

M_v = molecular weight (18×10^{-3} kg mol^{-1})

The phase diagram:



saturation curve is described by the Clausius-Clapeyron equation

$$\frac{dp_{sv}}{dT} = \frac{\rho_v L}{T}$$

L = latent heat of condensation
$\simeq 2.5 \times 10^6$ J kg^{-1}

$$= \frac{M_v L}{R} \frac{p_{sv}}{T^2}$$

$$\Rightarrow \log\left(\frac{p_{sv}}{p_{sv0}}\right) = \frac{M_v L}{R}\left(\frac{1}{T_0} - \frac{1}{T}\right) \simeq \frac{M_v L}{T_0^2}(T - T_0) \quad (*)$$

for $|T - T_0| \ll T_0$

As atmosphere formed (through volcanism), p_v (and ρ_v) increased. That causes T to increase too, since $T = \left[\frac{Q(1-a)}{4\gamma\sigma}\right]^{1/4}$ with $\gamma = \gamma(\rho_v)$ according to radiative balance.

We assume that initially $p_v < p_{sv}(T)$. Does the atmosphere reach saturation?

For illustration, suppose $\gamma = K/\rho_v = \frac{KR}{M_v}\frac{T}{p_v}$ $\Rightarrow$ $\boxed{T = \left[\frac{(1-a)QM_v}{4\sigma KR}\right]^{1/5} p_v^{1/5}}$

The runaway greenhouse effect occurs if this radiative balance curve $T(p_v)$ stays above the saturation curve $p_{sv}(T)$ ⊛

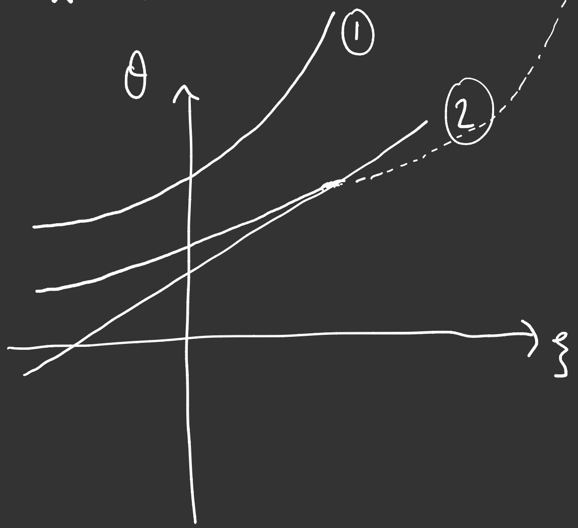
Lecture 3b

Write $\theta = \frac{T}{T_0}$ & $\xi = \frac{1}{5}\log\left(\frac{p_v}{p_{svo}}\right)$. Then radiative balance ⇒

$$\boxed{\theta = \beta e^{\xi}} \quad ① \qquad \text{where } \beta = \left[\frac{(1-a)QM_v\, p_{svo}}{4\sigma K R T_0^5}\right]^{1/5}$$

& the saturation curve becomes

$$\boxed{\theta = 1 + \alpha \xi} \quad ② \qquad \text{where } \alpha = \frac{5RT_0}{M_v L}$$



The lines will not intersect (⇒ runaway) if

$\beta > \beta_c$, where β_c is the critical value at which the two curves meet tangentially.

$$\left.\begin{aligned} \beta e^{\xi} &= 1 + \alpha\xi \\ \beta e^{\xi} &= \alpha \end{aligned}\right\} \quad \xi = \frac{\alpha - 1}{\alpha} \quad \Rightarrow \beta_c = \alpha e^{(1-\alpha)/\alpha}$$

On Venus, $\beta > \beta_c$. On Earth, $\beta < \beta_c$.

The wet adiabat / lapse rate

Recall that $T(z)$ in the atmosphere was determined from the energy eqn.
Accounting for the latent heat release by condensation, this becomes

$$\rho c_p \frac{dT}{dz} - \frac{dp}{dz} + \rho L \frac{dm}{dz} \hat{=} 0, \qquad \text{where } m = \frac{\rho_v}{\rho} \text{ is the moisture content.}$$

If atmosphere is saturated, then

$$m = \frac{\rho_v}{\rho} \underset{\substack{\uparrow \\ \text{ideal gas law}}}{=} \frac{M_v}{M_a}\frac{p_v}{p} \underset{\substack{\uparrow \\ \text{saturation } p_v = p_{sv}(T)}}{=} \frac{M_v}{M_a}\frac{p_{sv}}{p}$$

$$\Rightarrow \frac{dm}{dz} = \frac{M_v}{M_a}\left[\frac{dp_{sv}}{dT}\frac{dT}{dz}\frac{1}{p} - \frac{p_{sv}}{p^2}\frac{dp}{dz}\right] \underset{\substack{\uparrow \\ \text{Clausius-Clapeyron}}}{=} \frac{M_v}{M_a}\left[\frac{\rho_v L}{Tp}\frac{dT}{dz} - \frac{p_{sv}}{p^2}\frac{dp}{dz}\right]$$

Inserting into the energy eqn & using $\frac{dp}{dz} = -\rho g$, gives

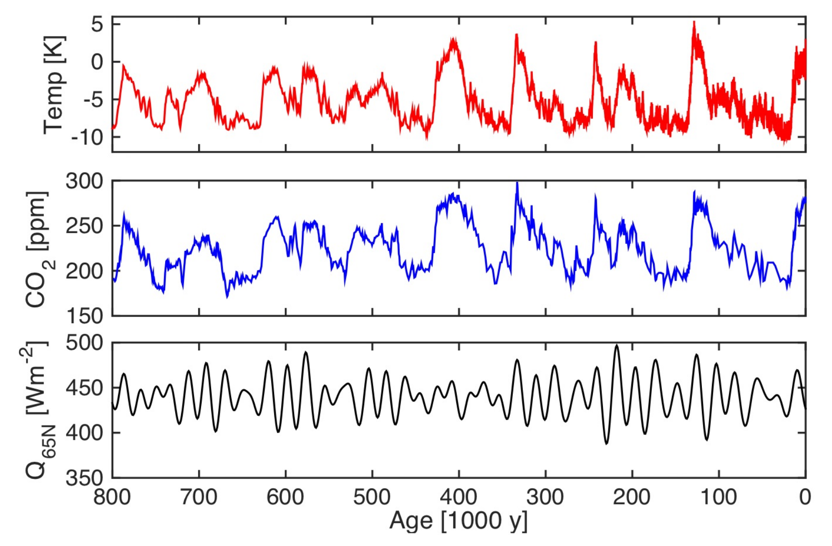
$$\frac{dT}{dz} = -\frac{c_p}{g} \, \frac{1 + \frac{\rho_v L}{p}}{1 + \frac{\rho_v L}{p}\frac{M_v}{M_a}\frac{L}{c_p T}} = -\Gamma_w \overset{\wedge}{\sim} -6\ \mathrm{K\,km^{-1}}$$

for typical values of ρ_v, p, T.

Lecture 4a

Ice-albedo feedback.

Ice-core records

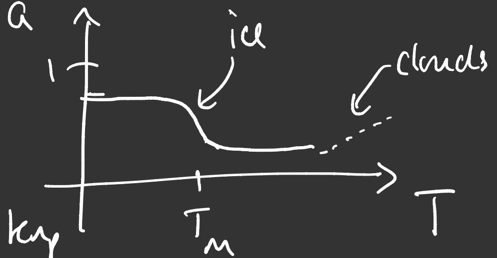


Over the last 2.5 My (the Pleistocene) there has been a succession of ice ages, recently with period ~100 ky. The last glacial maximum (LGM) was ~18 ky ago, and sea level was ~130m lower than today.

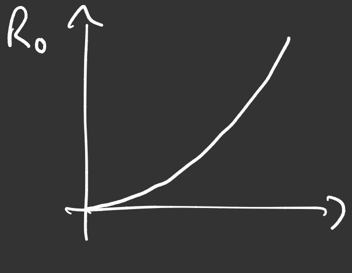
Recall the global energy balance model:

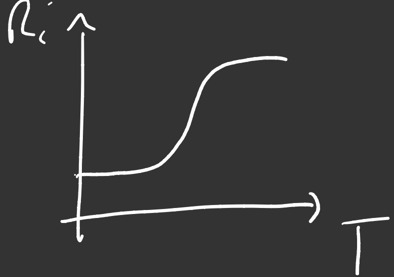
$$C\frac{dT}{dt} = \underbrace{\frac{1}{4}Q(1-a)}_{R_i} - \underbrace{\gamma\sigma T^4}_{R_o}$$

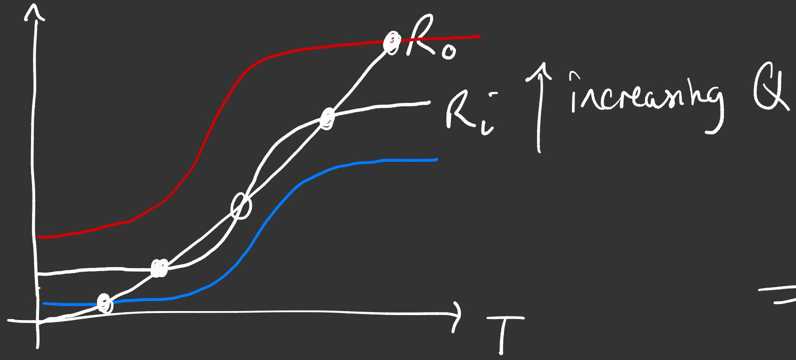
Both γ and a can vary with temperature



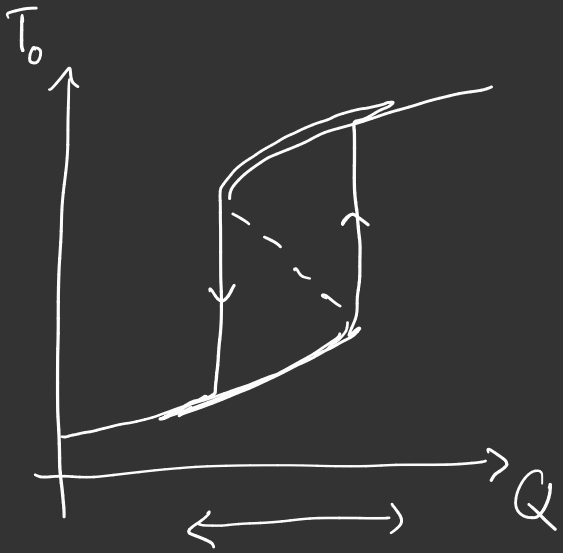
So both incoming and outgoing radiation vary with temp

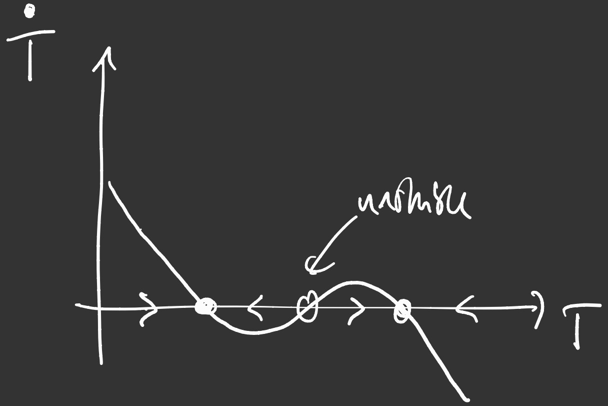






$\Longrightarrow$





Milanković theory – variations in Earth's orbit cause changes in Q that result in appearance / disappearance of different equilibrium temperatures.

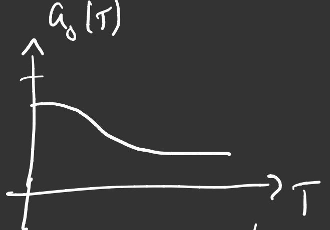
Lechre 4 b

The model just studied assumed a to be an instantaneous function of T. In fact, the growth of ice sheets takes millenia.

A better model is:

$$C\frac{dT}{dt} = \frac{1}{4}Q(1-a) - \gamma\sigma T^4$$

$$t_i\frac{da}{dt} = a_0(T) - a$$



where $a_0(T)$ is the 'equilibrium' albedo, and t_i is the timescale on which a evolves ($t_i \hat{=} 10^4$ y)

Non-dimensionalise: $T = \underbrace{[T]}_{[T]=\left(\frac{[Q]}{4\gamma\sigma}\right)^{1/4}}\hat{T}$, $t = \underbrace{[t]}_{t_i}\hat{t}$, $Q = \underbrace{[Q]}_{1{,}370\ \mathrm{W\,m^{-2}}}\hat{Q}$ $\quad \hat{a}_0(\hat{T}) = a_0([T]\hat{T})$

$$\frac{C[T]}{[t]}\frac{d\hat{T}}{d\hat{t}} = \frac{1}{4}[Q]\hat{Q}(1-a) - \gamma\sigma[T]^4\hat{T}^4, \quad \boxed{\frac{t_i}{[t]}}\frac{da}{d\hat{t}} = \hat{a}_0(\hat{T}) - a$$

$$\Rightarrow \boxed{\begin{aligned} \varepsilon \frac{dT}{dt} &= Q(1-a) - T^4 \\ \frac{da}{dt} &= a_0(T) - a \end{aligned}}$$

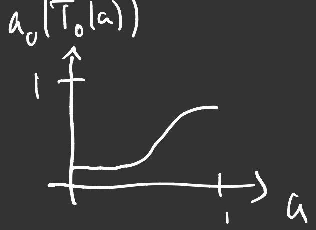
$$\varepsilon = \frac{4C[T]}{[Q][t]} = \frac{C}{\sigma\gamma[T]^3[t]}$$

$$\approx \frac{4\,10^7\,290}{1{,}370\;3\,10^{11}} \qquad \frac{\cancel{J}\,\cancel{K^{-1}}\,\cancel{m^{-2}}\,\cancel{K}}{\cancel{W}\,\cancel{m^{-2}}\,\cancel{s}}$$

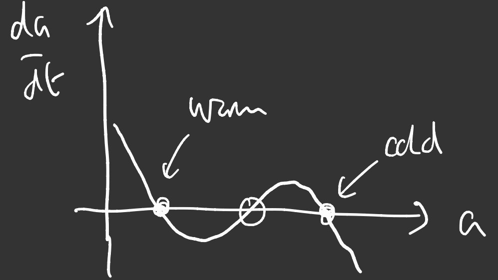
$$\approx \frac{10^{10}}{5\,10^{14}} \approx 2\times10^{-5} \ll 1$$

$\varepsilon \ll 1 \Rightarrow$ temperature is quasi-static $T = T_0(a) = [Q(1-a)]^{1/4}$

& a evolves according to $\boxed{\frac{da}{dt} = a_0(T_0(a)) - a}$



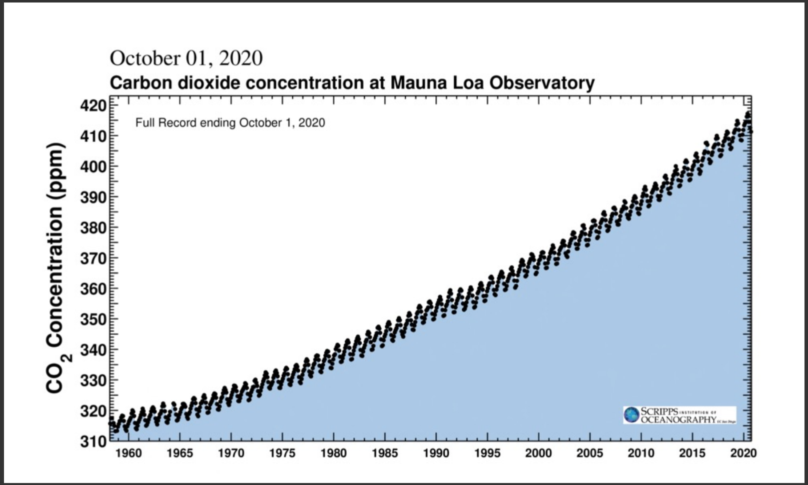
This has multiple steady states, as before



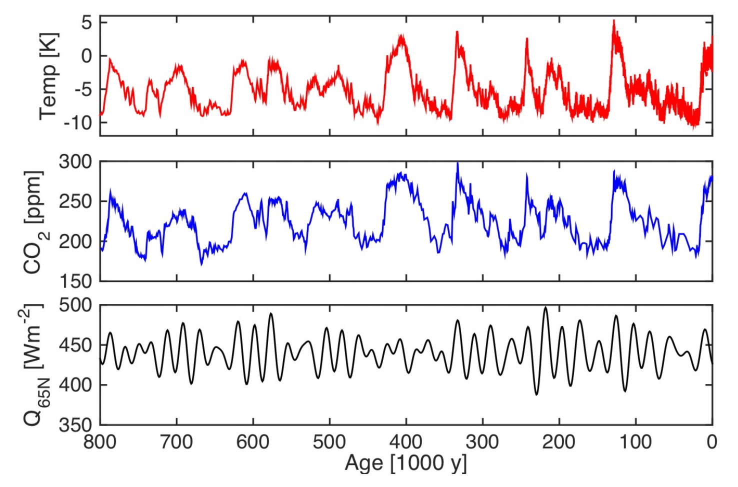
Lecture 5a

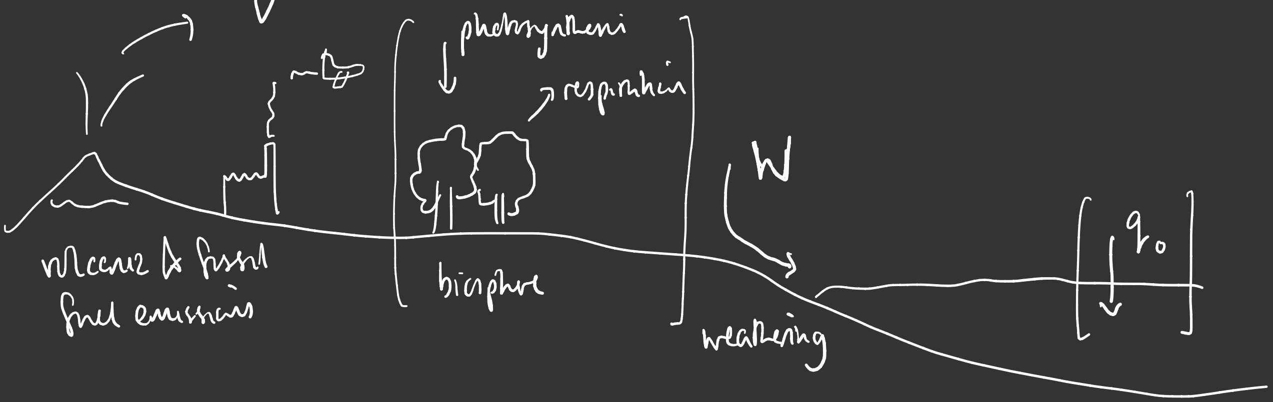
The Carbon Cycle

measurements of atmospheric CO_2 in Hawaii



ice core records →





Atmospheric CO_2: $$\frac{dm_{CO_2}}{dt} = V - W$$

V is the volcanic & fossil fuel emissions ($V \approx 0.3$ Gt y^{-1} pre-industrial
≈ 30 Gt y^{-1} current day)

W is the weathering rate (CO_2 dissolves in rain water, reacts with silicate rocks in the crust, and runs off to the ocean)

We want to relate m_{CO_2} to the partial pressure p_{CO_2} at the Earth's surface.

$$m_{CO_2} = \underset{\substack{\uparrow \\ \text{Total mass of atmosphere}}}{m}\left(\frac{p_{CO_2}}{p}\right) = m\,\frac{M_{CO_2}}{M_a}\,\frac{p_{CO_2}}{p} = \frac{M_{CO_2}A_E}{M_a g}\,p_{CO_2}$$

at the Earth's surface, hydrostatic balance $\frac{\partial p}{\partial z} = -\rho g \Rightarrow p = \int_0^d \rho g\,dz = \frac{mg}{A_E}$

area of Earth's surface.

We take an empirical expression for the weathering rate

$$W = W_0\left(\frac{p_{CO_2}}{p_0}\right)^{\mu}\exp\left(\frac{T-T_0}{\Delta T_c}\right)$$

where $W_0, p_0, T_0, \Delta T_c, \mu$ are constants.

$$\Rightarrow \quad \frac{M_{CO_2} A_E}{M_a g} \frac{dp_{CO_2}}{dt} = v - W_0 \left(\frac{p_{CO_2}}{p_0}\right)^{\mu} \exp\left(\frac{T - T_0}{\Delta T_c}\right) \qquad \text{③}$$

For fixed v & T, this shows that p_{CO_2} adjusts to an equilibrium in which weathering balances emissions.

Combine with the ice-albedo model from last lecture, and take $\gamma = \gamma_0 - \gamma_1 p_{CO_2}$,

$$C \frac{dT}{dt} = \frac{1}{4}(1-a) Q - (\gamma_0 - \gamma_1 p_{CO_2}) \sigma T^4 \qquad \text{①}$$

$$t_i \frac{da}{dt} = a_0(T) - a \qquad \text{②}$$

This is a 3-dimensional dynamical system. Simplify by non-dimensionalising.

Lecture 5b

To scale the model, write $T = T_0 + \Delta T_c\, \theta$, $p_{CO_2} = p_0\, \hat{p}$, $t = t_i\, \hat{t}$

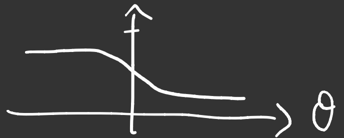
$\Rightarrow$ (dropping hat)

① $$\varepsilon \frac{d\theta}{dt} = (1-a)q - (1-\nu\lambda p)\left(1 + \frac{1}{4}\nu\theta\right)^4$$

$$\varepsilon = \frac{C\Delta T_c}{t_i \sigma \gamma_0 T_0^4} \qquad \nu = \frac{4\Delta T_c}{T_0}$$

② $$\frac{da}{dt} = B(\theta) - a \qquad B(\theta) = a_0(T + \Delta T_c \theta)$$

$$q = \frac{Q}{4\sigma\gamma_0 T_0^4} \qquad \lambda = \frac{\gamma_1 p_0}{\gamma_0 \nu}$$



③ $$\frac{1}{\alpha}\frac{dp}{dt} = 1 - wp^{\mu}e^{\theta}$$

$$\alpha = \frac{v M_a g t_i}{M_{CO_2} A_E p_0} \qquad w = \frac{W_0}{v}$$

Using typical values (see online notes), with $v = 3 \times 10^{11}\,\mathrm{kg\,y^{-1}}$

$\Rightarrow$ $\varepsilon \approx 1.6 \times 10^{-6}$, $\nu \approx 0.18$, $q = 1.4$, $\lambda \approx 0.25$, $\alpha \approx 1.1$, $w \approx 1$

Make use of $\varepsilon \ll 1$, $\nu \ll 1$ (expand in small ν, neglect ε)

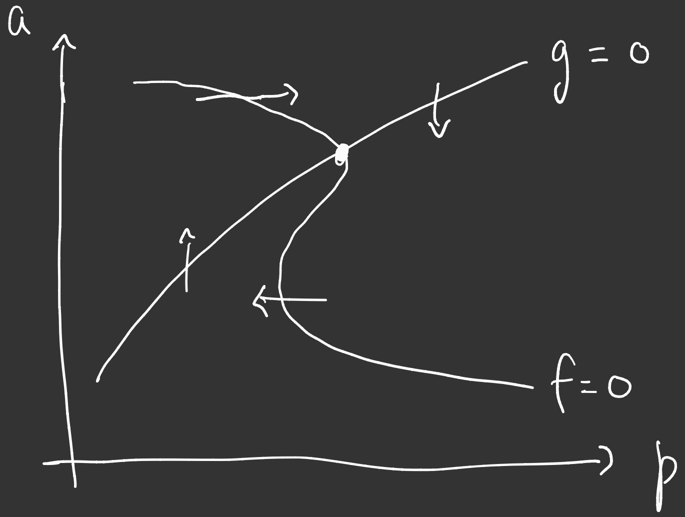
① $\Rightarrow$ $$0 \approx (1-a)q - 1 + \nu\lambda p - \nu\theta$$

$$\Rightarrow \theta = \lambda p + \frac{q(1-a)-1}{\nu} =: \Theta(a,p)$$ quasi-steady temperature.

② & ③ become a two-dimensional dynamical system:

$$\boxed{\begin{aligned} \dot{a} &= B(\Theta(a,p)) - a &&=: f(a,p) \\ \dot{p} &= \alpha\left(1 - w p^{\mu} e^{\Theta(a,p)}\right) &&=: g(a,p) \end{aligned}}$$

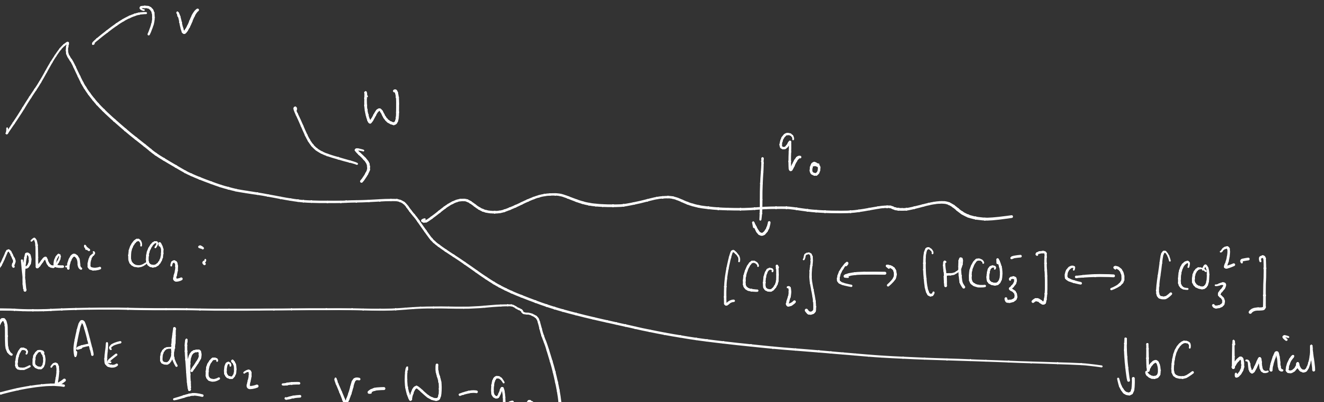
This can be analysed using phase plane methods, eg. steady states, nullclines, stability states, periodic solutions. (see problem sheet)



There is a possibility of limit cycles (even with fixed q)

Lecture 6a

Ocean carbon



Atmospheric CO_2:

$$\boxed{\frac{M_{CO_2} A_E}{M_a g}\frac{dp_{CO_2}}{dt} = v - W - q_0}$$

q_0 is the exchange flux with the ocean, depends on p_{CO_2} and the concentration of dissolved CO_2 in the ocean, $[CO_2]$ (where $[\ ]$ = concentration, mol kg^{-1}).

$$q_0 = h\left(p_{CO_2} - \frac{[CO_2]}{K_H}\right)$$

K_H = solubility (decreases with increasing temp)

h = transfer coefficient

Dissolved CO_2 rapidly reacts with water to form bicarbonate and carbonate ions, HCO_3^- & CO_3^{2-}.

So we must conserve the total dissolved inorganic carbon (DIC)

$$\boxed{C = [CO_2] + [HCO_3^-] + [CO_3^{2-}]}$$

$$\boxed{\underbrace{\rho_0 V_0}_{\text{mass of ocean}} \frac{dC}{dt} = \frac{q_0 + W}{M_{CO_2}} - bC}$$

Next: relate $[CO_2]$ to C

Reactions: $CO_2 \, (+ \, H_2O) \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} HCO_3^- + H^+$ $\qquad R_1 = k_1[CO_2] - k_{-1}[HCO_3^-][H^+]$

$HCO_3^- \underset{k_{-2}}{\overset{k_2}{\rightleftharpoons}} CO_3^{2-} + H^+$ $\qquad R_2 = k_2[HCO_3^-] - k_{-2}[CO_3^{2-}][H^+]$

Rapid reaction $\Rightarrow$ equilibrium $[HCO_3^-] = \dfrac{K_1[CO_2]}{[H^+]}$ $\qquad K_1 = \dfrac{k_1}{k_{-1}} \mathrel{\hat{=}} 1.3 \times 10^{-6} \text{ mol kg}^{-1}$

$$[CO_3^{2-}] = \frac{K_2[HCO_3^-]}{[H^+]} \qquad K_2 = \frac{k_2}{k_{-2}} \mathrel{\hat{=}} 9.1 \times 10^{-10} \text{ mol kg}^{-1}$$

$$C = [CO_2] + [HCO_3^-] + [CO_3^{2-}] = \underbrace{\left(1 + \frac{K_1}{[H^+]} + \frac{K_1K_2}{[H^+]^2}\right)}_{\hat{=}\, 200}[CO_2]$$

$\Rightarrow$ exchange flux $\boxed{q_0 = h\left(p_{CO_2} - \dfrac{C}{K}\right)}$ where $K = K_H\left(1 + \dfrac{K_1}{[H^+]} + \dfrac{K_1K_2}{[H^+]^2}\right)$

Lecture 6b

$$\frac{M_{CO_2} A_E}{M_a g} \frac{dp_{CO_2}}{dt} = v - W - h\left(p_{CO_2} - \frac{C}{K}\right)$$

$$M_{CO_2} \rho_0 V_0 \frac{dC}{dt} = W + h\left(p_{CO_2} - \frac{C}{K}\right) - M_{CO_2} b C$$

Timescales: $t_p = \frac{M_{CO_2} A_E}{M_a g h} \approx 100\,y$. $t_C = \frac{\rho_0 V_0}{b} \approx 10^5\,y$

Non-dimensionalise: $t = t_p \hat{t}$, $W = W_0 \hat{W}$, $v = W_0 \hat{v}$, $C = \frac{W_0}{M_{CO_2} b} \hat{C}$, $p_{CO_2} = \frac{W_0}{M_{CO_2} b K} \hat{p}$

$\Rightarrow$ (dropping hats)

$$\boxed{\begin{aligned} \frac{dp}{dt} &= \frac{v}{\alpha} + \frac{W}{\alpha} - p + C \\ \frac{1}{\varepsilon}\frac{dC}{dt} &= W + \alpha(p - C) - C \end{aligned}}$$

$$\alpha = \frac{h}{M_{CO_2} b K}$$

$$\varepsilon = \frac{t_p}{t_C} \ll 1$$

Suppose initially in steady state with $v = v_1$ (pre-industrial), then suddenly increase to $v_2 > v_1$.

$$\boxed{\begin{aligned} \frac{dp}{dt} &= \frac{v}{\alpha} + \frac{W}{\alpha} - p + C \\ \frac{1}{\varepsilon}\frac{dC}{dt} &= W + \alpha(p - C) - C \end{aligned}}$$

Initial condition: $C = C_0 = v_1$, $p = p_0 = \frac{v_1}{\alpha} + \frac{W}{\alpha} + C_0$

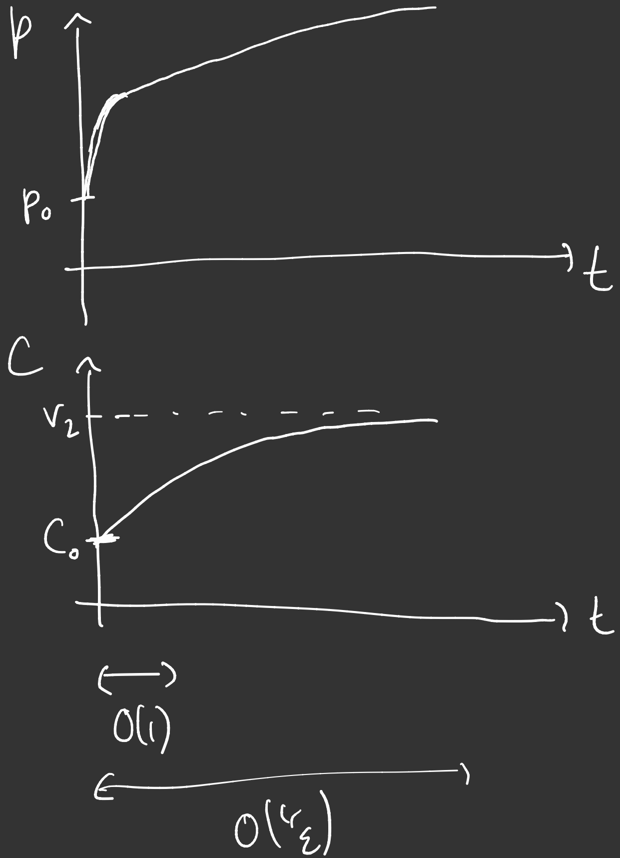
$O(1)$ timescale: $\frac{dC}{dt} \simeq 0 \Rightarrow C = C_0$

$$\frac{dp}{dt} \simeq \frac{v_2}{\alpha} + \frac{W}{\alpha} - p + C_0 \Rightarrow p = \frac{v_2}{\alpha} + \frac{W}{\alpha} + C_0 + \left(p_0 - \frac{v_2}{\alpha} - \frac{W}{\alpha} - C_0\right)e^{-t}$$

$O(\frac{1}{\varepsilon})$ timescale: $0 \simeq \frac{v_2}{\alpha} + \frac{W}{\alpha} - p + C \Rightarrow p = \frac{v_2}{\alpha} + \frac{W}{\alpha} + C$ (quasi-steady)

$t = \frac{1}{\varepsilon}\tau$

$$\frac{dC}{d\tau} \simeq v_2 - C \Rightarrow C = v_2 + (C_0 - v_2)e^{-\tau}$$



Currently (century timescale) increased v causing p_{CO_2} to increase, and increase transfer to the ocean.

Longer term (many millenia), the ocean carbon concentration increases significantly.

Ocean acidification $[H^+]$ is related to the pH of the ocean $\left(pH = -\log_{10}([H^+]) \approx 8.2 \right)$

There is no reason to assume this is fixed (as assumed above). In fact, it is better to assume that there is conservation of total alkalinity

$$A = 2[CO_3^{2-}] + [HCO_3^-]$$

If we revisit the equilibrium reaction & assume $K_2 \ll K_1$, then we find

$$[H^+] \approx K_2 \frac{2C-A}{A-C}, \qquad [CO_2] \approx \frac{K_2}{K_1} \frac{(2C-A)^2}{A-C} \qquad \left(\text{currently } \frac{C}{A} \approx 0.85\right)$$

As C increases, $[H^+]$ increases (ocean acidification), and $[CO_2]$ increases more than linearly with C.