

Kelvin Equation

→ Applies to curved surfaces relate vapor pressure over flat w.r.t curved surfaces.

→ we define a Gibbs Free energy per unit mol of substance g .

Two phases → gas, liquid

$g_l = g_{gas}$ when the interface is planar

let's call that g^*

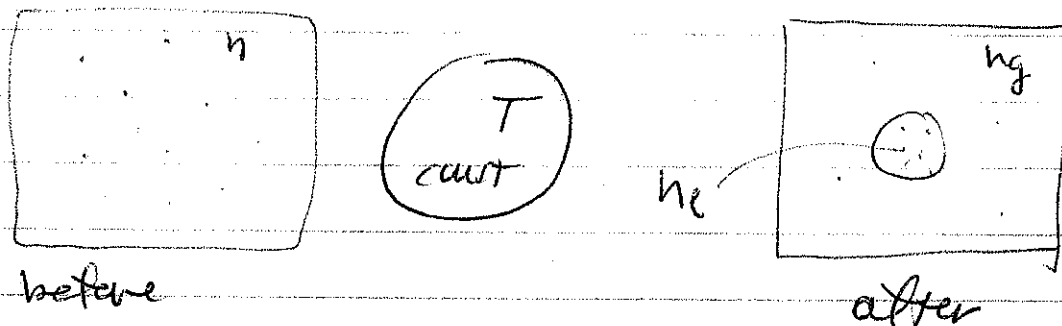
$g_l \neq g^*$, b/c of the effect of surface tension
 ↖ curved surface

How much? e const. T, p

$$\int_{g^*}^{g_l} dg = \int_0^A \sigma dA \Rightarrow g_l = g^* + \underbrace{\sigma A}_{\text{enhancement in chem. p. from s.t.}}$$

So let's see how the s.t. change affects vapor pressure

1. Take two states (before/after drop formation)
closed system, constant P, T



$$G_b = n g_g$$

$$G_f = n_g g_g + n_l g_l + \underbrace{4\pi R_p^2 \sigma}_A$$

$$\Delta G = G_f - G_b = n_g g_g + n_l g_l + 4\pi R_p^2 \sigma - n g_g$$

but $n = n_l + n_g$ (conservation of mass)

$$\Rightarrow \Delta G = \cancel{n_g g_g} + n_l g_l + 4\pi R_p^2 \sigma - n_l g_l - \cancel{n_g g_g} =$$

$$= -n_l (g_g - g_l) + 4\pi R_p^2 \sigma \quad (2)$$

we said before that $g_g - g_l \neq 0$ (b/c we are talking about curved interfaces. So what we do is relate g_l to the curved surface and

g_g to a flat surface in equilibrium with it:

$$dg = -s dx + v dp = \frac{RT}{P} dp \Rightarrow \int_{g_0}^{g_g} dg = \int_{P_0}^P \frac{RT}{P} dP \Rightarrow$$

$$\Rightarrow g_g - g_l = RT \ln \frac{P}{P^*} \quad (1)$$

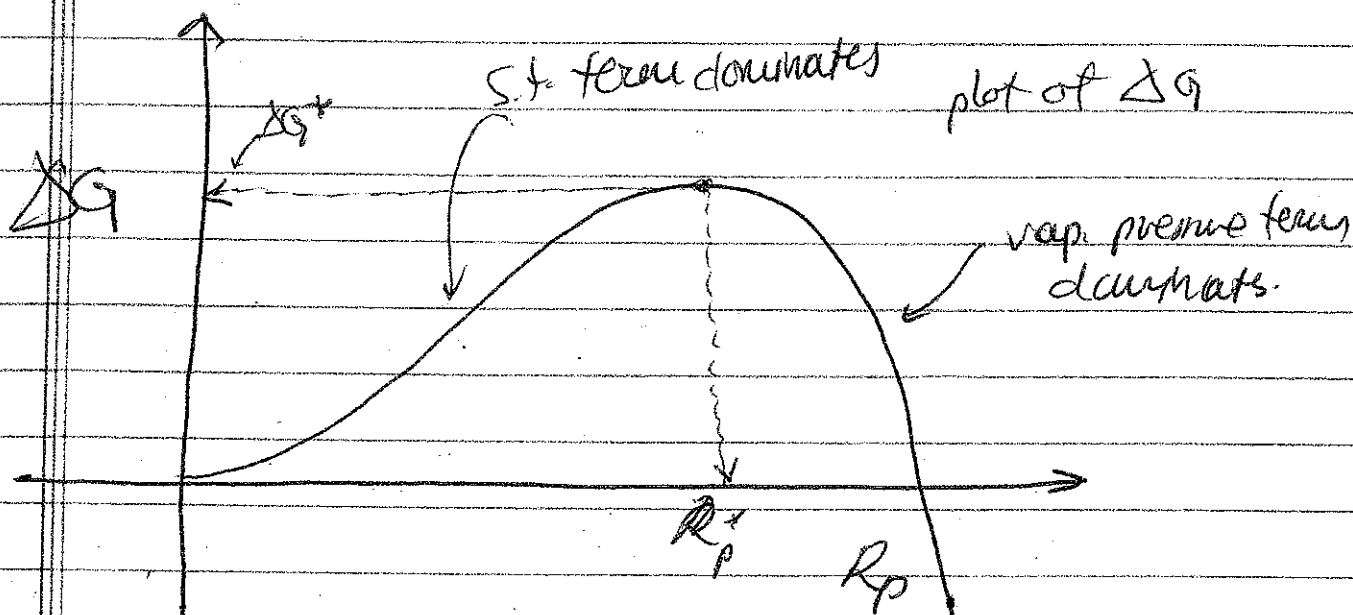
$$\begin{aligned} (1) + (2) \Rightarrow \Delta G &= -n_l RT \ln \frac{P}{P^*} + 4\pi R_p^2 \sigma \\ &= -n_l RT \ln \frac{P}{P^*} + 4\pi R_p^2 \sigma \quad (3) \end{aligned}$$

P^* equil. vap. pressure over flat surface
 P vap. pressure when $R = R_p$

$$n_l = \frac{\text{Volume of drop}}{\text{molar volume of } H_2O(l)} = \frac{\frac{4}{3}\pi R_p^3}{\frac{V_l}{N_l}} \quad (4)$$

(4) + (3):

$$\Delta G = \frac{4}{3} \frac{\pi R_p^3}{V_l} RT \ln \frac{P}{P^*} + 4\pi R_p^2 \sigma$$



@ equilibrium, $\frac{\partial \Delta G}{\partial R_p} = 0$. If where the two terms balance each other

$$\frac{\partial \Delta G}{\partial R_p} = \frac{4\pi R_p^2}{\beta v_l} \ln \frac{P}{P^*} + 2\pi R_p \sigma = 0 \Rightarrow$$

$$\Rightarrow -\frac{R_p}{v_l} \ln \frac{P}{P^*} + 2\sigma = 0$$

where R_p^* is the R_p for which $\frac{\partial \Delta G}{\partial R_p} = 0$.

$$\ln \frac{P}{P^*} = \frac{2\sigma v_l}{RT R_p^*} \Rightarrow \boxed{P = P^* \exp\left(\frac{2\sigma v_l}{RT R_p^*}\right)}$$

Kelvin Equation.

$$v_l = \frac{M}{\rho}$$

so E.E becomes

$$P = P^* \exp\left(\frac{2\sigma M}{RT \rho} \frac{1}{R}\right) \leftarrow \text{Curvature Effect.}$$

Vapor pressure over
convex surface

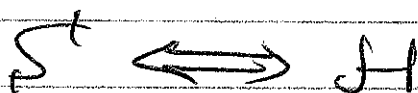
Vapor pressure over flat
surface

$$So \frac{P}{P^*} > 1$$

↑

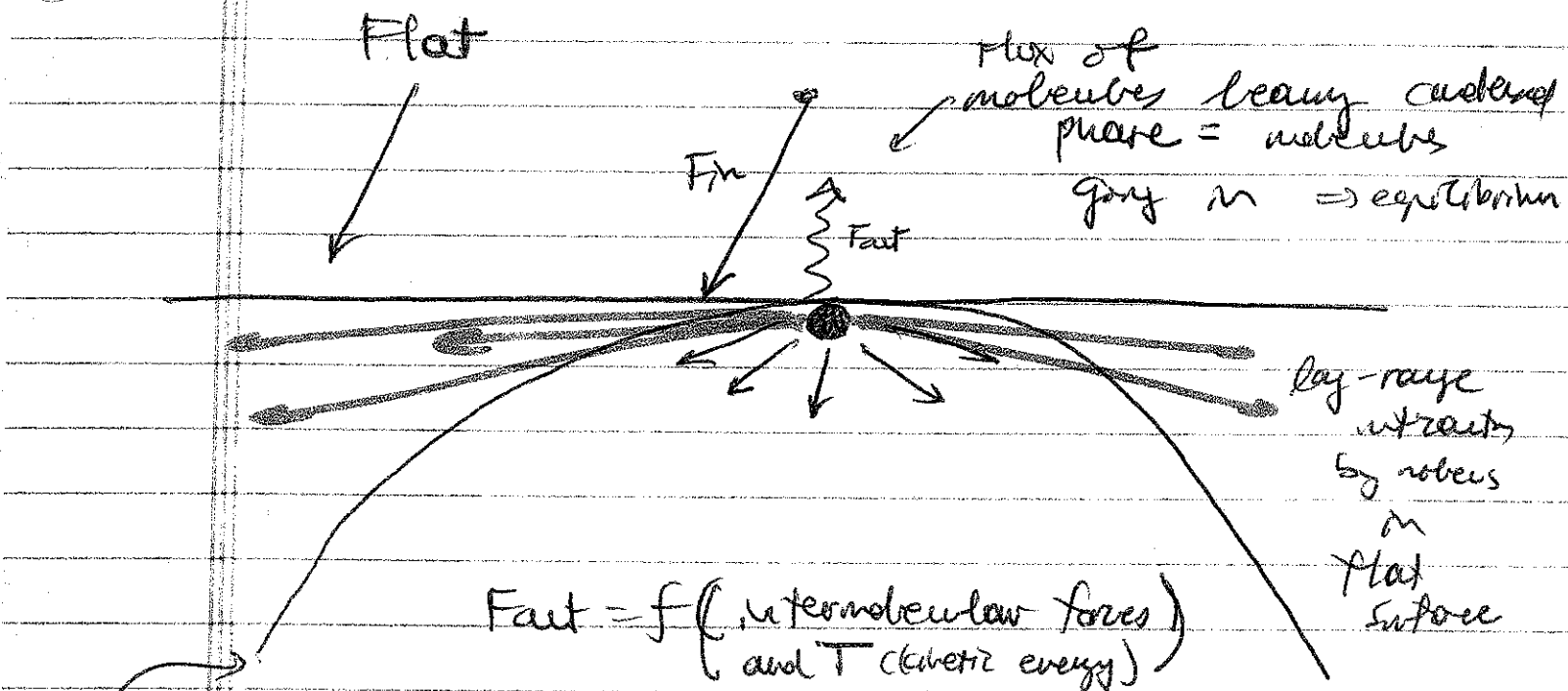
This is referred to as "saturation ratio", S

$S > 1$ is often called supersaturation, S^*



Kelvin equation says that $P \uparrow$ when $R_p \downarrow$. Why does that happen physically?

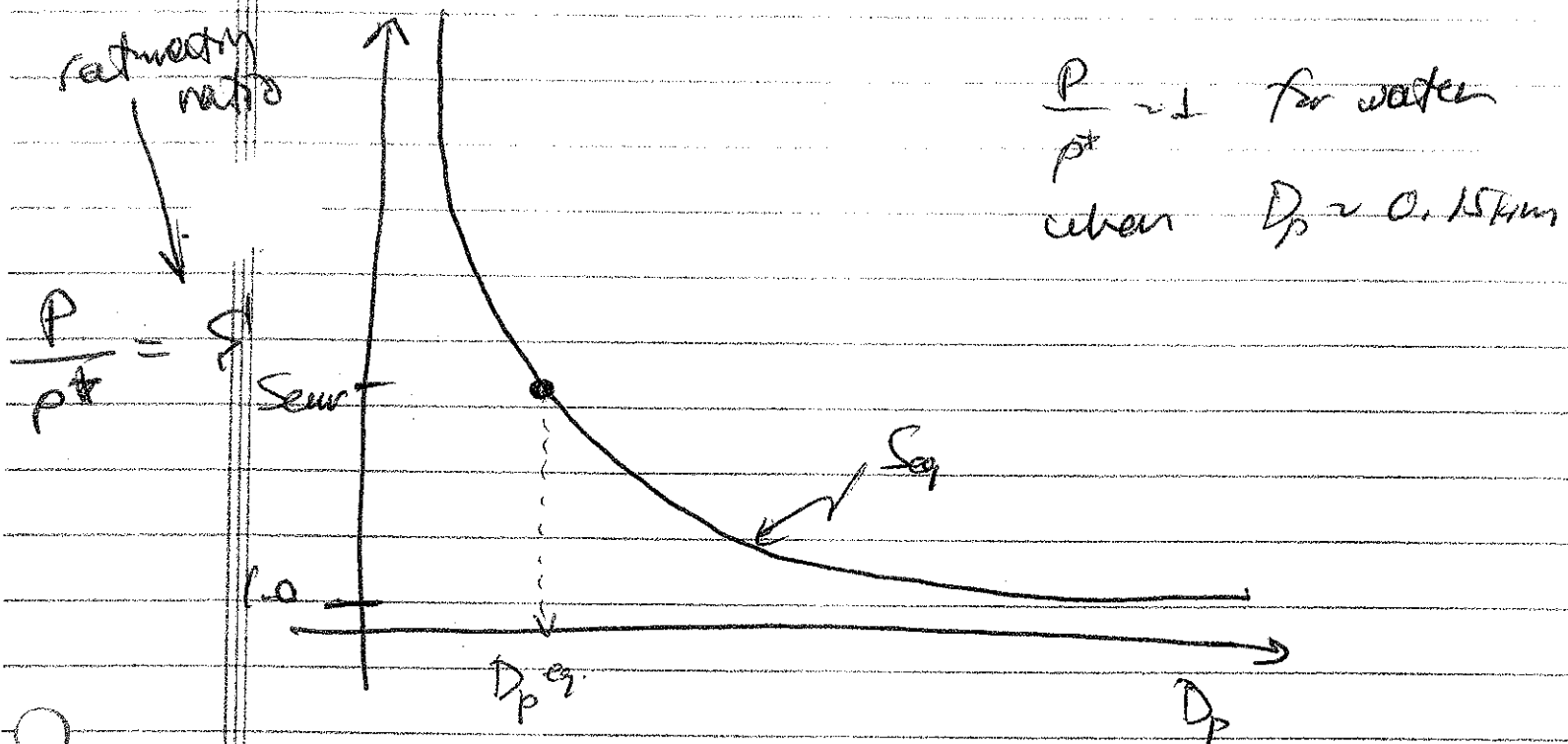
○



○ Curved

$R_p \downarrow$, Ray-ray interactions \downarrow , $F_{act} \uparrow$
vapor pressure \uparrow

Implication of The Kelvin Equation



Stability of a drop with respect to its environment

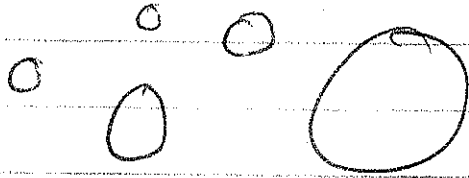
→ Take drop in equilibrium with its environment.

$$\frac{dm}{dt} = h_m (S_{env} - S_{eq})$$

stability analysis.

→ Pure water droplets are always unstable!

Take a population of water droplets



generated by, say, an atomizer.

→ Is this droplet population in equilibrium ever?

→ what will happen?

→ Is this in agreement with A & in physical systems?

→ Phenomenon called Ostwald Ripening
(known since the 1800's).

Curiously subtle effects - Köhler Egn

→ Pure water drops don't exist in the atmosphere, unless they are very large.

→ This created a lot of controversy in the 1860's and 1900's about how droplets are generated

- sea spray?
- how about high-level clouds?

→ Köhler figured it out, with the observation of Atten that there are a lot of carbon-sulfur nuclei (pre-existing particles). This is known as Köhler Theory.

→ Assume we have a crystalline particle of known dry size, d . The particle is completely deliquescent, i.e. it changes into an aqueous solution at some characteristic $f_l < 1$ (i.e. $f^* < 1$).

When that happens, the particle is an aqueous solution surrounded by water vapor.

So, let's first assume particle is in equilibrium, neglecting curvature effects:

$$\textcircled{1} \quad \mu_{\text{H}_2\text{O (g)}}(T, P) = \mu_{\text{H}_2\text{O (l)}}(T, P)$$
 ← partial pressure of H_2O in gas phase (ideal gas).
 equality of chem. potential between liq + gas for H_2O

we know that b/c of the solute, $\mu_{\text{H}_2\text{O (l)}}$ drops, being equal to:

$$\textcircled{2} \quad \mu_{\text{H}_2\text{O (l)}} = \mu_{\text{H}_2\text{O (pure), l}}^* + RT \ln X_{\text{H}_2\text{O}}$$
 ← standard reference chemical potential at pressure P temperature T

we also know that when the gas is at an equilibrium P which is different from 1 atm, $\mu_{\text{H}_2\text{O (g)}}$ is given by:

$$\textcircled{3} \quad \mu_{\text{H}_2\text{O (g)}}(P, T) = \mu_{\text{H}_2\text{O (pure), g}}^{\Delta}(T) + RT \ln y P$$
 ← ideal,
 ← standard ref. chem. potential at $P = 1 \text{ atm}$ and T
 ← total pressure
 ← not free of H_2O in gas phase

$$= \mu_{\text{H}_2\text{O (pure), g}}^{\Delta}(T) + RT \ln P$$
 ← partial pressure of H_2O

Combining 1, 2, 3:

$$\mu_{\text{H}_2\text{O (pure), l}}^* + RT \ln X_{\text{H}_2\text{O}} = \mu_{\text{H}_2\text{O (pure), g}}^{\Delta}(T) + RT \ln P$$

From which

$$\frac{P}{X_{\text{H}_2\text{O}}} = \exp \left\{ \frac{\mu_{\text{H}_2\text{O (pure), g}}^{\Delta}(T) - \mu_{\text{H}_2\text{O (pure), l}}^*}{RT} \right\} \quad \textcircled{4}$$

() (4) is just a "typical" equilibrium reaction relationship.

Analysis of it however gives some very nice insight:

$$\frac{P}{x_w x_w} = \exp \left\{ \frac{\mu_{H_2O}^*(T) - \mu_{H_2O, \text{pure}}^A(T)}{RT} \right\} \quad (4)$$

\uparrow
 $= f(x, T)$
 or $f(P, T)$
 (b/c P, x are not independent)

$= f(T) \text{ only}$

○ Because of the equality, both sides have to have the same functionality, i.e. $P/x_w = f(T)$ only.

Then we consider what happens as $x_w \rightarrow 1$ by definition $f_w \rightarrow 1$ so that

$$\lim_{x_w \rightarrow 1} \frac{P}{x_w} (T) = P^{\text{sat}}(T) \quad (5)$$

\uparrow
 saturation vapor pressure of H_2O over pure H_2O

○ Given that both sides of (4) do not depend on x , that means the R.H.S. of (4) is always equal to 5.

That means $\exp\left\{\frac{\mu_{HX(g)}^*(T) - \mu_{HX(l)}^*(T)}{RT}\right\} = P_{\text{sat}}$, so:

$$P = f_w X_w P_{\text{sat}} \quad (5) \quad \text{Raoult's Law}$$

i.e. Raoult's law is a natural consequence of chemical equilibrium!

If you consider curvature effects.

P is actually affected by the diameter

$$P = P_{\text{flat}} \exp\left(\frac{2\sigma V}{RT R}\right) \quad (5)$$

Curved

$$P = f_w X_w P_{\text{sat}} \exp\left(\frac{2\sigma V}{RT R}\right) \Rightarrow$$

$$\Rightarrow \frac{P}{P_{\text{sat}}} = f_w X_w \exp\left(\frac{2\sigma V}{RT R}\right)$$

Most general form of Köhler equation

Simplifications to Köhler equation.

$$\frac{p}{p_{\text{sat}}} = f^* = \gamma_w x_w \exp\left(\frac{2\sigma V}{RT R_p}\right) \quad (6)$$

Two is of the droplet, i.e. the molar volume of solute-water solution

simplification of K. term:

- $v \approx v_l \leftarrow$ "dilute approximation", i.e. most of the solution is H₂O
- $\sigma \approx \sigma_w \leftarrow$ surface tension of water. Very good approximation for salts, may not be as good for organics
- $R_p > 0.1 \mu\text{m} \Rightarrow$ Kelvin effect is "small", which means $\exp(-) = \mathcal{O}(1)$, i.e. of order unity
The argument in exponential is small

$$\text{hence } \exp\left(\frac{2\sigma V}{RT R_p}\right) \approx 1 + \frac{2\sigma V}{RT R_p} \approx$$

Taylor expansion.

$$\approx 1 + \frac{2\sigma_w v_w}{RT R_p}$$

expanding out v_w and expressing R_p as $D_p = 2R_p$

$$\exp\left(\frac{2\sigma V}{RT R_p}\right) \approx 1 + \frac{4\sigma_w M_w}{RT \rho_w D_p} \quad (7)$$

$$x_w \times w$$

- $x_w \approx 1$ ← b/c of dilute approximation, most of solution is water, hence behaves ideally.

and fraction of "salt" ions in solution

$$x_w = 1 - x_s \leftarrow (\text{from } x_w + x_s = 1)$$

$$= 1 - \frac{n_s}{n_s + n_w}$$

number of moles of ions in particle (after dissociation).

- if $n_s \ll n_w$ (dilute approximation) $\Rightarrow n_s + n_w \approx n_w$

$$x_w \approx 1 - \frac{n_s}{n_w}$$

but $n_s = \frac{\left(\frac{\pi}{6} d^3\right) \rho_s}{V_s}$ ← volume of salt in particle

← van't Hoff factor

V_s ← molar volume of salt

$$= \frac{\pi}{6} d^3 \frac{\rho_s}{M_s}$$

and $n_w = \frac{V_{\text{droplet}} - V_{\text{dry particle}}}{V_w}$ ← negligible if particle is very small

$$\approx \frac{\pi}{6} D_p^3 \frac{\rho_w}{M_w}$$

$$\text{So } x_w \approx 1 - \frac{\rho_s}{\rho_w} \frac{M_w}{M_s} \frac{d^3 \rho_s}{D_p^3} \quad (8)$$

Substituting (6) & (7) into equation (5), we get

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$$Q \cdot S^+ = \left(1 - \underbrace{\left(\frac{\rho_s}{\rho_w} \frac{M_w}{M_s} \frac{dV_s}{D_p^3} \right)}_B \right) \left(1 + \underbrace{\left(\frac{4\sigma_w M_w}{RT\rho_w D_p} \right)}_A \right) =$$

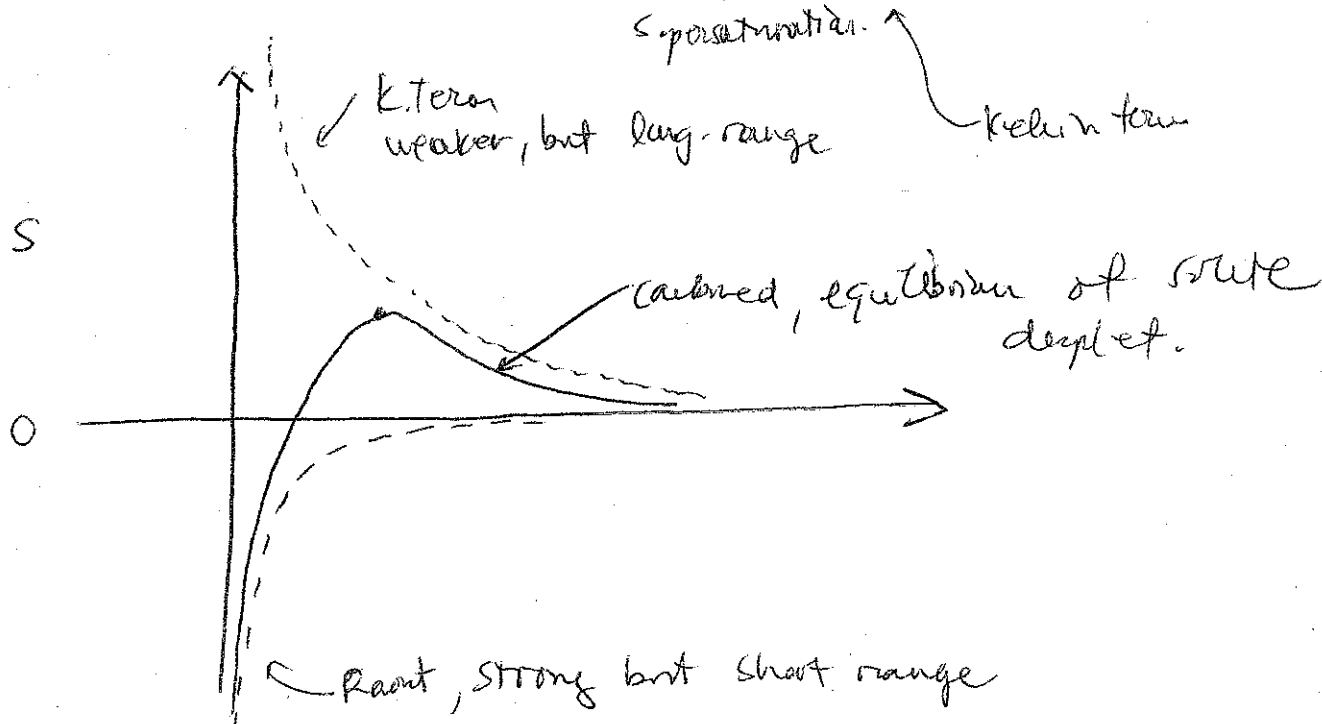
$$= \left(1 - B/D_p^3 \right) \left(1 + \frac{A}{D_p} \right) = 1 + \frac{A}{D_p} - \frac{B}{D_p^3} - \frac{AB}{D_p^4} \Rightarrow$$

● $S^+ \approx 1 + \frac{A}{D_p} - \frac{B}{D_p^3}$ "classical" Köhler equation

Assume very small compared to $\frac{B}{D_p^3}$

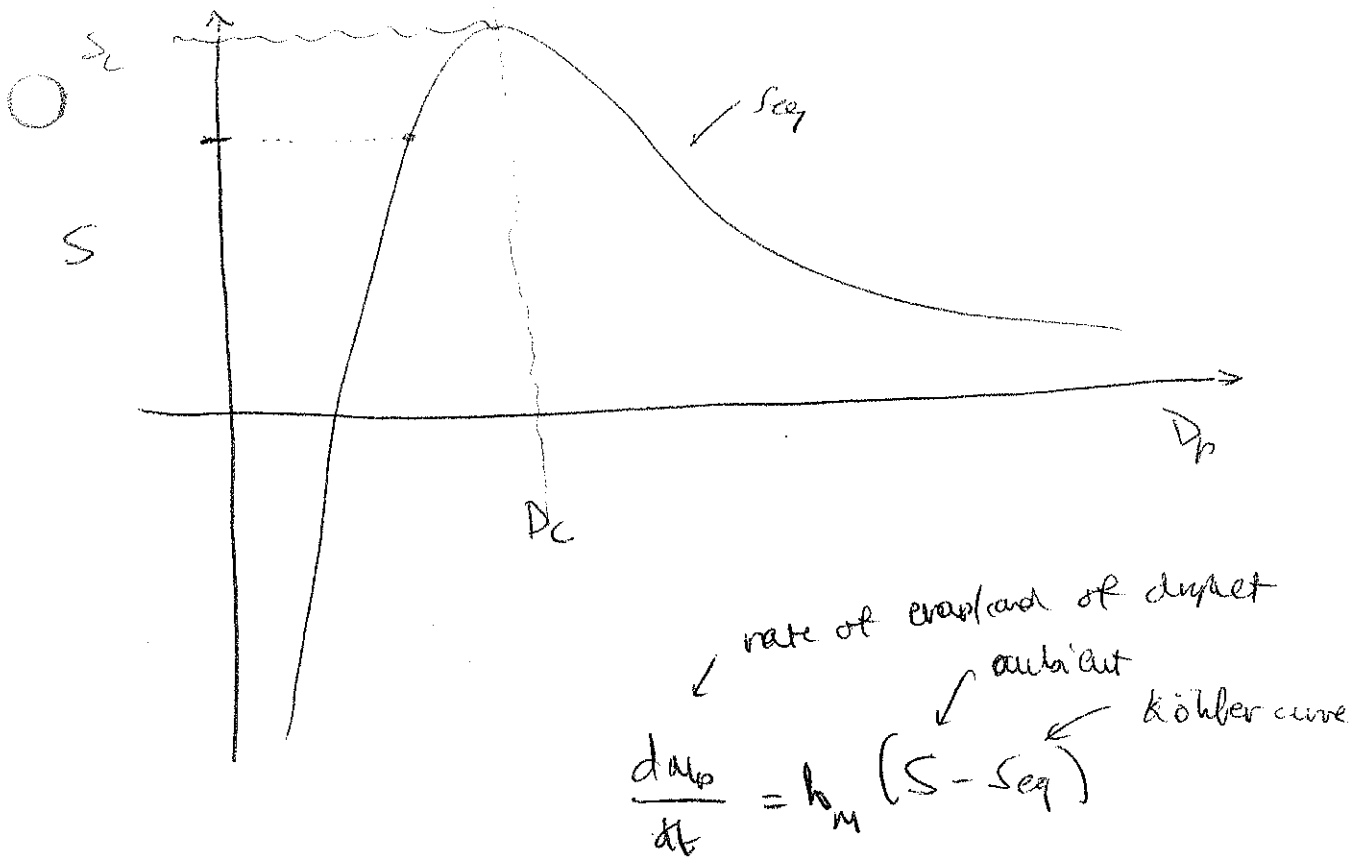
otherwise written as $S - 1 = s = \frac{A}{D_p} - \frac{B}{D_p^3}$

saturation



Stability analysis of droplet with solute

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● If you are to the left of D_c (i.e. $R < D_c$) then a slight fluctuation of S above S_c will give a driving force that will eventually lead to an equilibrium (as long as you do not exceed S_c !)

● If you are to the right of D_c , you can either have unstable growth, or "shrink" to an equilibrium size with $S < S_c$... There are unstable drops, or drops that are much smaller and are in eq. with their environment

So if $S > S_c \Rightarrow$ particle is unstable and forms a drop.

Hence S_c is a very important property and is called "critical supersaturation". D_c is called "critical wet diameter".

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Calculation of S_c : $\frac{\partial S_{eq}}{\partial D_p} = 0$

$$\frac{\partial}{\partial D_p} \left(\frac{A}{D_p} - \frac{B}{D_p^3} \right) = -\frac{A}{D_p^2} + \frac{3B}{D_p^4} = \frac{1}{D_p^2} \left[\frac{3B}{D_p^2} - A \right]$$

So $\frac{\partial S_{eq}}{\partial D_p} = 0 \Rightarrow$

$$\frac{3B}{D_p^2} - A = 0 \Rightarrow D_p = \left(\frac{3B}{A} \right)^{1/2} = D_c$$

↑ wet diameter at maximum, i.e. it's D_c .

$$S_c = \frac{A}{D_c} - \frac{B}{D_c^3} = \frac{A}{\left(\frac{3B}{A} \right)^{1/2}} - \frac{B}{\left(\frac{3B}{A} \right)^{3/2}} = \left(\frac{A}{3B} \right)^{1/2} \left[A - \left(\frac{A}{3B} \right) B \right]$$

$$= \left(\frac{A}{3B} \right)^{1/2} \left[A - \frac{A}{3} \right] = \frac{2A}{3} \left(\frac{A}{3B} \right)^{1/2} = \left(\frac{4A^3}{27B} \right)^{1/2}$$

So $S_c = \left(\frac{4A^3}{27B} \right)^{1/2}$, $D_c = \left(\frac{3B}{A} \right)^{1/2}$

S_0 , to summarize:

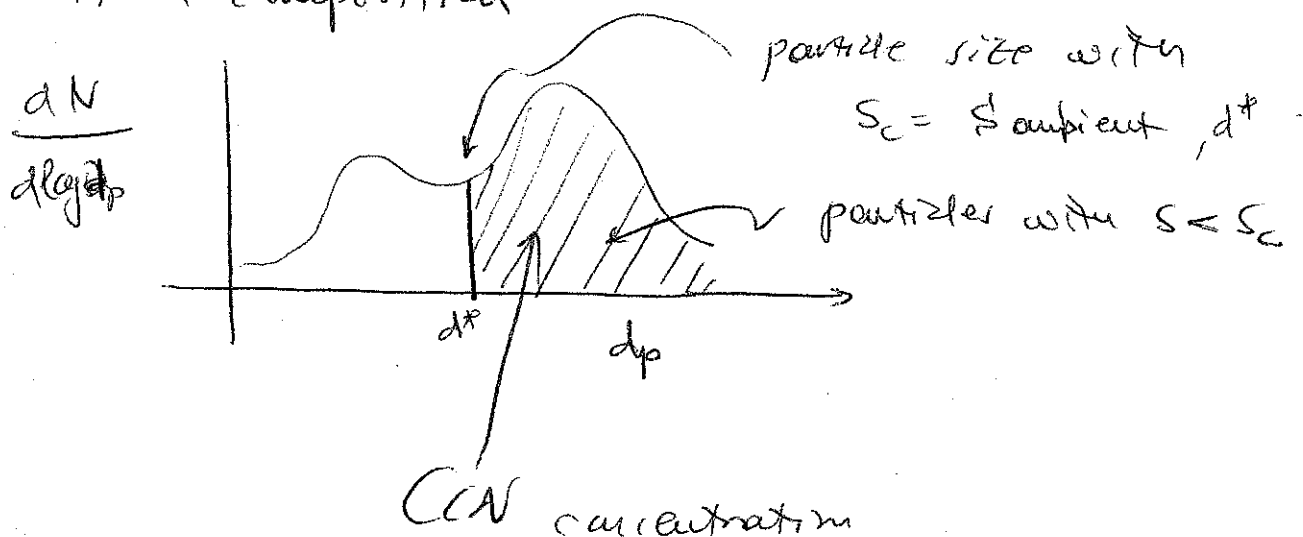
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- if ambient $S > S_c$, particles become unstable and grow without stopping.
- if ambient $S < S_c$, particles shrink and attain equilibrium with $S \Rightarrow$ interstitial

\Rightarrow Hence, if we know S and particle composition + size distribution, we can calculate the number of droplets that would form (assuming we allow particles enough time exposed to S).

\rightarrow This is how we calculate CCN concentrations.

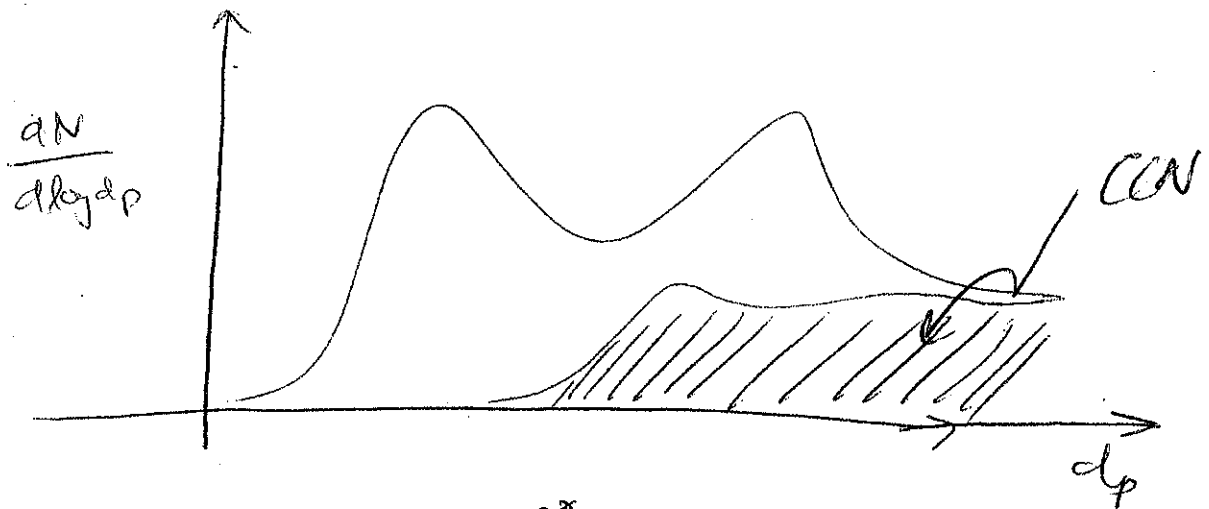
- (a) Simplest possible case: particles are of uniform composition



- $$[CCN] = \int_{d_p^*}^{\infty} \left(\frac{dN}{d \log d_p} \right) d \log d_p$$

~ particles do not have uniform composition with size

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$$[CCN] = \int_0^{\infty} \underbrace{f_s(d_p, S)}_{\uparrow} \left(\frac{dN}{d \log d_p} \right) d D_p$$

Fraction of activation of
particles of diameter d_p @ supersaturation S .