

# Fundamentals of Atmospheric Physics

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### **CLOUD FORMATION**

The Gibbs free energy G = U - TS + pV

 $\delta G = \delta U - T \delta S - S \delta T + p \delta V + V \delta p$ 

Using

$$dU = dQ + dW,$$

 $\delta G = -S \,\delta T + V \,\delta p$ 

Consider a water droplet immersed in water vapour, at partial pressure e and temperature T (the remaining 'dry air' plays no role and can be ignored). Suppose that the liquid and vapour are not in equilibrium,

so that 
$$e \neq e_{\rm s}(T)$$

Suppose that the Gibbs free energy per unit mass of the vapour is

 $G_{\rm v}(T, e)$ 

 $G_{I}(T, e)$ and that of the liquid is

Now let the partial pressure be varied slightly from

e to e + de,

while the temperature is held constant  $\delta \overline{G} = -S \overline{\delta T} + V \overline{\delta p}$ 

$$\delta G_{v} = V_{v} \delta e$$

 $\delta G_1 = V_1 \delta e$ 

where  $V_{\nu}$  and  $V_{l}$  are the specific volumes of the vapour and liquid, respectively.

 $|V_{\rm v}| >> V_1$ 

$$\delta(G_v - G_l) = (V_v - V_l) \ \delta e \approx V_v \ \delta e$$

The vapour satisfies the ideal gas law

 $V_v = R_v T/e$ 

$$\delta(G_v - G_l) = R_v T \, \delta e/e = R_v T \, \delta(\ln e)$$

Integrating at fixed T gives

$$G_{v}(T,e) - G_{l}(T,e) = R_{v}T \ln e + F(T)$$

where F(T) is a function of integration

However, at equilibrium, on the vapour pressure curve where

$$e = e_s(T) \implies G_v = G_l$$

(This result is used in the standard derivation of the Clausius-Clapeyron equation.) Using this condition to fix F(T),

 $0 = R_v T \ln e_s + F(T)$ 

$$G_{v}(T,e)-G_{l}(T,e)=R_{v}T\ln(\frac{e}{e_{s}(T)})$$

Now suppose that at some initial time we have a

mass of water vapour,	m
partial pressure	e
temperature	Т
with no droplet present	

<mark>at</mark> and The total Gibbs free energy at this time is

$$G_0 = G_v(T, e) m_0 \quad *$$

A droplet then starts to condense, at fixed temperature and pressure; suppose that at some later instant its radius is a, so that its surface area is

$$A = 4 \ \pi \ a^2$$

and its mass is

$$m_l = 4 \pi a^3 \rho_l / 3$$

(where  $\rho_1$  is the density of the liquid) and the mass of the surrounding vapour is  $m_v$ 

The total Gibbs free energy of the system is now the sum of the Gibbs free energies of the liquid and vapour, plus a contribution due to surface tension:

# $G = G_{v}(T, e) m_{v} + G_{l}(T, e) m_{l} + \gamma A$ \*\*

where  $\gamma$  is the surface tension (or the surface energy per unit area)

By conservation of mass  $m_v = m_0 - m_l$ 

using equations \* and \*\*, we get

 $G - G_0 = (G_l - G_v)m_l + \gamma A$ 



using 
$$G_v(T,e) - G_l(T,e) = R_v T \ln(\frac{e}{e_s(T)})$$

$$G - G_0 = -\frac{4}{3}\pi a^3 \rho_l R_v T \ln(\frac{e}{e_s(T)}) + 4\pi a^2 \gamma$$

The variation with radius a of the total Gibbs free energy of the system therefore takes the form

 $G(a) = G_0 - \beta a^3 + \alpha a^2$ 



Figure plots this function for two values of the relative humidity  $e/e_s$ 

Several useful facts can be learned from this figure

#### Note first that, if

### $e \leq e_s(T)$

(indicating subsaturated or exactly saturated conditions), then the logarithm in equation is negative or zero, so that and the curve of G(r) has no turning point other than a = 0.  $\beta \leq 0$ 

If  $e > e_s(T)$  (indicating supersaturated conditions), then the logarithm is positive,  $\beta > 0$ , and there is a maximum of G at a radius a given by

$$a = 2\alpha/3\beta = \frac{2\gamma}{\rho_l R_v T \ln(\frac{e}{e_s(T)})}$$



Subsaturated conditions ( $e < e_{s}$ )

$$\Delta G = \underbrace{-4/3\pi a^3 \rho_l R_{\gamma} T \ln(e/e_s(T))}_{>0} + \underbrace{4\pi a^2 \gamma}_{>0}$$

Formation of droplets is not favored Random collisions of water molecules do occur, forming very small embryonic droplets (that evaporate) These droplets never grow large enough to become visible



If droplet grows (a increases), then  $\Delta G>0$ , this won't happen spontaneously

Supersaturated conditions  $(e > e_s)$ 

$$\Delta G = \underbrace{-4/3\pi a^3 \rho_l R_{\gamma} T \ln(e/e_s(T))}_{<0} + \underbrace{4\pi a^2 \gamma}_{>0}$$

 $\Delta G$  initially increases with increasing a

 $\Delta G$  is a maximum where radius = a

 $\Delta G$  decreases with increasing Radius beyond  $\boldsymbol{a}$ 



If droplet grows (R increases), then  $\Delta G$  can be positive or negative

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## Supersaturated conditions ( $e > e_s$ )

Embryonic droplets with R < a tend to evaporate

Droplets which grow by chance (collisions) with R > a will continue to grow spontaneously by condensation

They will cause a decrease in the Gibbs free energy (total energy) of the system



This is known as Kelvin's formula; it may also be written in the form

 $e = e_s(T) \exp \frac{A}{a}$ 

 $A = \frac{2\gamma}{\rho_l R_v T}$ 



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Kelvin's formula  

$$e_s(a) = e_s(\infty) \exp \frac{2\gamma}{\rho_l R_v Ta}$$

Vapour pressure over curved interface always larger than of the same substance over a flat surface.





Vapour pressure determined by energy required to separate molecules from attractive forces of neighbors (surface tension).

Curvature reduces the number of neighboring molecules, and therefore also attractive forces.

Molecules can escape easier in vapour phase, i.e. higher vapour pressure.

### Raoult's law

The above theory must be modified significantly if solutes are present in the cloud droplet.

Raoult's law states that, over a droplet containing

N moles solute

N<sub>0</sub> moles pure water,

The vapour pressure must be modified by the factor



if N << No. Consider a spherical droplet of radius a and volume

$$V_a = 4\pi a^3/3$$

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#### containing

mass m of solute of molar mass M

 $N = i_{\rm d} m/M,$ 

Where  $\mathbf{i}_{\mathrm{d}}$  is the number of ions produced by the dissociation of one solute molecule

For example  $i_d = 2$  for NaCl,

Which dissociates completely into Na<sup>+</sup> and Cl<sup>-</sup> ions

$$N_0 = \rho_{\rm l} V_a/M_{\rm w}$$

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Where

### $\rho_1$ density of the pure water

M<sub>w</sub> molar mass of pure water

(This approximation ignores the small mass m of solute within the droplet and the fact that the density of the solution is slightly different from  $\rho_{\rm l}$ .)

We therefore obtain

$$\phi = 1 - \frac{B}{a^3} \qquad B = \frac{3i_{\rm d}mM_{\rm w}}{4\pi\rho_{\rm l}M};$$

$$e = e_s(T) \exp\frac{A}{a} \qquad A = \frac{2\gamma}{\rho_{\rm l}R_{\rm v}T}$$

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#### We obtain the relative humidity RH, given by

99.0

0.01



Kelvin factor exp(A/a) which decreases with increasing a,

> Raoult factor which increases with increasing a

Fig. gives an example of this function of radius a: Köhler curve.

0.10 a

Radius / µm

1.00

10.00

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The relative humidity has a maximum at  $a=a_c$ 

In this example  $a_c \approx 0.2 \ \mu m$ , at which value RH=RH<sub>c</sub>  $\approx 100.4\%$ 

Consider such a droplet in air with an ambient relative humidity less than this value of  $RH_c$ , as given say by the thick dashed horizontal line

For this ambient RH there are two equilibrium values of a, on either side of  $a_c$ .

The smaller value (point A) corresponds to stable equilibrium, for if the RH over the drop falls slightly below the ambient value, corresponding to a slight decrease in the drop's radius, condensation will occur and the radius will increase again to the equilibrium value.



Conversely, a slight increase in radius will cause some evaporation, leading to a decrease in radius to the equilibrium value. A stable droplet of this kind is called a haze droplet.

However, the other equilibrium point ,B, will correspond to instability:

for example, as light increase in radius will lead to condensation and hence to a further in crease in radius.

The droplet is then said to be activated



# Fick's law

The analysis given above considers only the water vapour in the immediate neighbourhood of the droplet.

However, if the droplet is to grow, there must be a continual supply of water vapour to its surface.

This can happen by diffusion if there is a vapour density gradient in the region surrounding the droplet, with the vapour density increasing with distance.

A simple representation of this diffusion is in terms of Fick's law

$$f = -D \nabla \rho_v$$

vapour density, vapour-flux vector diffusion coefficient, assume dconstant

ρ<sub>v</sub> f

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Assuming that at some instant the radius of the droplet is a and that the distribution of the vapour density is spherically symmetric,

 $\rho_v = \rho_v(r),$ 

the total inward flux of mass of vapour through a sphere  $\mathsf{S}_r$  of radius r > a is

$$-\int_{\mathbf{S}_r} \boldsymbol{f} \cdot \boldsymbol{n} \, dS = 4\pi r^2 \, \frac{d\rho_{\mathbf{v}}}{dr} \, D,$$

Where n is the outward normal to  $S_r$ 



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However, water vapour is lost only by condensation at r = a,

so for

#### r > a

this flux must be independent of  $\mathbf{r}$  and equal to the rate of increase of mass of the droplet,

 $dM_l/dt$ 

$$\frac{d\rho_{\rm v}}{dr} = \frac{dM_{\rm l}/dt}{4\pi D} \,\frac{1}{r^2},$$

Which can be integrated from r = a to  $r = \infty$  to give

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$$\rho_{\rm v}(a) = \rho_{\rm v}(\infty) - \frac{1}{4\pi Da} \frac{dM_{\rm l}}{dt}$$

using the ideal gas law

$$\rho_v = e/(R_v T)$$

for the vapour,

$$\frac{dM_{\rm l}}{dt} = 4\pi Da \left[\rho_{\rm v}(\infty) - \rho_{\rm v}(a)\right] = \frac{4\pi Da}{R_{\rm v}} \left[\frac{e(\infty)}{T(\infty)} - \frac{e(a)}{T(a)}\right]$$

 $e(\infty)$  $T(\infty)$  vapour pressure temperature

far from the droplet

e(a) and  $\overline{T}(a)$  at its surface

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$$\boldsymbol{f} = -D\nabla\rho_{\rm v},$$



$$-\int_{\mathbf{s}_r} \boldsymbol{f} \cdot \boldsymbol{n} \, dS = 4\pi \, r^2 \, \frac{d\rho_{\mathbf{v}}}{dr} \, D,$$

$$\frac{d\rho_{\rm v}}{dr} = \frac{dM_{\rm l}/dt}{4\pi D} \frac{1}{r^2},$$

$$r = a$$
 to  $r = \infty$ 

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