Lecture Ch. 5a

- Surface tension (Kelvin effect)
  - Hygroscopic growth (subsaturated humidity)
  - Saturation
- Chemical potential (Raoult effect)
  - Chemical Potential (partly from 4.5.1)

Chapter 5

p 158, problem 7d

$w_l = \frac{\rho_s}{\rho_w}\frac{4}{3}\pi\int_0^\infty r^3 n(r)\,dr$

Curry and Webster, Ch. 5 (skip 5.6, 5.7); also 4.5.1 if not review.
Optional: Pruppacher and Klett, Ch. 6.
Homework Problem 3 and 7 (Ch. 5) {7d misprint given in Errata!}.

Condensed (Liquid) Water

- **Ch. 4: Will H_2O condense?**
  - Clausius-Clapeyron describes $e_{sat}(T)$
- **Ch. 5: What will H_2O condense on?**
  - Kohler describes droplet formation
- **Ch. 6: How much H_2O will condense?**
  - Dew point temperature provides metric
- **Ch. 7: How does condensed H_2O affect stability?**
  - Conditional stability is affected by moist adiabats
- **Ch. 8: What happens to condensed H_2O?**
  - Precipitation processes

Surface Thermodynamics

- Surfaces require energy (work) to form
- Smaller particles have
  - higher surface-to-volume ratios
  - higher curvature
- Higher curvature requires more energy per mass

$dW_{st} = \sigma\,dA$

Extrinsic for fixed

[1] Strictly speaking, since the surface tension is a change in work potential, it is defined in terms of the Helmholtz function. However, the interpretation of $\sigma = dG/dA$ is generally accepted but it cannot be demonstrated in a thermodynamically rigorous manner.

Kelvin Effect

- Work to form surface:

$$dW_{st} = \sigma\,dA \qquad (5.1)$$

- Expansion against pressure difference

expansion against a difference in pressure

$$\sigma_{lv}\,dA = \Delta p\,dV \qquad (5.4)$$

$$\Delta p = \frac{2\sigma_{lv}}{r} \qquad (5.6)$$

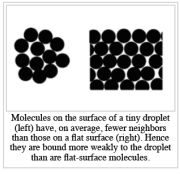
P/P_0 for water drops of different radii at STP[14]

Droplet radius (nm)	1000	100	10	1
P/P_0	1.001	1.011	1.114	2.95

Surface Tension

- By definition $\sigma = dG/dA$
- By 1st Law (modified for surface area change)

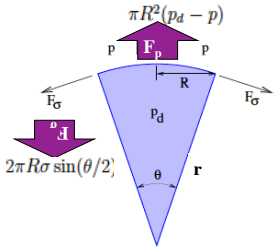
$$dG = -\eta dT + V dp + \sigma dA$$



Molecules on the surface of a tiny droplet (left) have, on average, fewer neighbors than those on a flat surface (right). Hence they are bound more weakly to the droplet than are flat-surface molecules.

Kelvin Effect

- Force Balance: $F_p = F_\sigma$
  - Area of spherical cap:
    - $2\pi R\sin(\theta/2)$
  - Approximate for small θ:
    - $\sin(\theta/2) \sim R/r$
  - So area of surface force:
    - $2\pi R(R/r) = \pi R^2(2/r)$
- Result: $p_d - p = 2\sigma/r$
  - Or: $\Delta p = 2\sigma/r$



Nucleation (Pure Water)

- Using Gibbs for open system and surface:

$$dG = -\eta dT + V dp + \sigma_{lv} dA + \mu_l dn_l + \mu_v dn_v \qquad (5.8)$$

- At constant T and p, and dn_l=-dn_v:

$$dG = \sigma_{lv} 8\pi r\, dr + (\mu_l - \mu_v)\, dn_l \qquad (5.9)$$

- For phase equilibrium (flat surface):

$$\mu_l - \mu_v = R^* T \ln\left(\frac{e_s}{e}\right) \qquad (5.10)$$

- For spherical droplet:

$$dn_v = \frac{1}{M_v} dm_v = \frac{\rho_l}{M_v} 4\pi r^2\, dr \qquad (5.11)$$

Chemical Potential

$$\mu = \frac{\partial G}{\partial n}$$

?

$$\mu_v = \mu_v^0 + R^* T \ln\frac{e}{e_0}$$

Key Combined 1st+2nd Law Results

- 1st Law: du=dq+dw; u is exact — Eq. 2.8
  - $du=dq_{rev}$-pdv (expansion only) — p. 56
- Define Enthalpy: H=U+PV — Eq. 2.12
  - dh=du+pdv+vdp
- 2nd Law: $[dq_{rev}/T]_{int.cycle}=0$ — Eq. 2.27
- Define Entropy: $d\eta=dq_{rev}/T$ — Eq. 2.25a
  - $Td\eta=dq_{rev}$
  - $du=Td\eta$-pdv
- Define Gibbs: G=H-Tη — Eq. 2.33
  - $dg=dh-Td\eta-\eta dT=(du+pdv+vdp)-Td\eta-\eta dT$
  - $dg=du-(Td\eta-pdv)+vdp-\eta dT=vdp-\eta dT$ p. 58
- $(\delta p/\delta t)_g=\eta/v$ — Eq. 2.40

Chemical Potential

$dG = -\eta dT + Vdp$ — **1st Law p. 58**

$dG = Vdp$ — **Constant T**

$$G(p_2) - G(p_1) = \int_{p_1}^{p_2} V\, dp = \int_{p_1}^{p_2} \frac{nRT}{p} dp = nRT \int_{p_1}^{p_2} \frac{dp}{p}$$

Ideal gas
Constant n [moles]

$$\frac{G(p_2)}{n} - \frac{G(p_1)}{n} = \mu_2 - \mu_1 = RT \ln\left(\frac{p_2}{p_1}\right)$$

$$\mu_v = \mu_v^0 + RT \ln\left(\frac{e}{e_0}\right)$$

For water vapor

N.B. This is R (book: R*) not R_d or R_v.

Chemical Potential

- By definition $\mu_v = \mu_v^0 + R^* T \ln\frac{e}{e_0}$
  - With respect to reference state "0"
  - Increase is proportional to concentration
- At saturation $\mu_{vs} = \mu_v^0 + R^* T \ln\frac{e_s}{e_0}$
- But at saturation vapor(sat'd)=liquid $\mu_l = \mu_{vs}$
- So we get

$$\mu_l - \mu_v = R^* T \ln\left(\frac{e_s}{e}\right)$$

Nucleation (Pure Water) Part 2

- Differential:

$$dG = \left(-R_v T \ln\frac{e}{e_s} \rho_l 4\pi r^2 + \sigma_{lv} 8\pi r\right) dr \qquad (5.12)$$

- Integrated:

$$\Delta G = 4\pi r^2 \sigma_{lv} - \frac{4}{3}\pi r^3 \rho_l R_v T \ln S \qquad (5.13)$$

- Find maxima:

$$\left[\frac{d(\Delta G)}{dr}\right]_{T,S} = \sigma_{lv} 8\pi r^* - 4\pi r^{*2} \rho_l R_v T \ln S = 0$$

- Solve for $S= e_s(r)/e_s$

$$e_s(r) = e_s \exp\left(\frac{2\sigma_{lv}}{\rho_l R_v T r^*}\right) = e_s \exp(a/r) \qquad (5.14c)$$

$a = 2\sigma_{lv}/(\rho_l R_v T)$

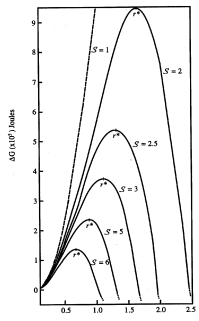


Figure 5.2 ΔG vs. r for several values of S at constant temperature. Each curve represents an energy barrier to embryo growth for a particular supersaturation. For radii less than the critical radius (i.e., $r < r^*$), growth occurs only by increasing S. However, if a drop can reach the critical radius, a slight addition of molecules will push the drop over the barrier into the region where $r > r^*$. In this region, the drop can grow spontaneously, since an increase in r is accompanied by a decrease in the Gibbs energy. Note that higher values of S correspond to lower Gibbs energy peaks, as expected. (From Byers, 1965.)

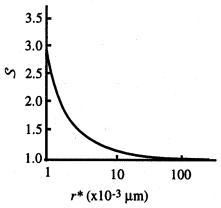


Figure 5.3 Equilibrium saturation ratio for pure water drops as a function of radius. Values are calculated from the Kelvin equation (5.14). The curve represents an unstable equilibrium. A drop above the equilibrium curve will grow, while a drop below the equilibrium curve will evaporate.

Lecture Ch. 5b

- Combining Surface and Solute Effects
  - Köhler Curves
- Nucleation
  - Competition between surface and chemical effects
  - Köhler curves
- Aerosol-cloud interactions

Chapter 5

p 158, problem 7d

$$w_l = \frac{\rho_l}{\rho_a}\frac{4}{3}\pi\int_0^\infty r^3 n(r)\,dr$$

Curry and Webster, Ch. 5 (skip 5.6, 5.7).
Also might need 4.5.1 if not review.

Chemical Effects

- Gibbs for an open system (this allows number of moles to change), from Ch. 4:

$$dG = -\eta\,dT + V\,dp + \sum_i\sum_j \frac{\partial G}{\partial n_{ij}}\,dn_{ij} \qquad (4.5)$$

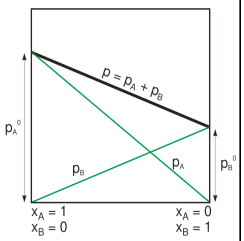
$$dG = -\eta\,dT + V\,dp + \sum_i\sum_j \mu_{ij}\,dn_{ij} \qquad (4.7)$$

Raoult's Law

- True for "ideal" solutions and $X_i \sim 1$: $p_A = X_A p_A^\circ$

$$\frac{p_{soln}}{e_s} = \frac{X_{H_2O}\,e_s + X_{solt}\,p^\circ_{solt}}{e_s}$$

- For dilute solution with $n_{solt} \ll n_{H2O}$:
  - use expansion of $(1/(1+x)) \sim 1-x$ +H.O.T. for small x:



$$\frac{p_{soln}}{e_s} \approx X_{H_2O} = \frac{n_{H_2O}}{n_{H_2O} + n_{solt}} = 1 - \frac{n_{solt}}{n_{H_2O}} \qquad (4.45)$$

Van't Hoff Factor

$$\frac{p_{soln}}{e_s} \approx X_{H_2O} = \frac{n_{H_2O}}{n_{H_2O} + n_{solt}} = 1 - \frac{n_{solt}}{n_{H_2O}} \qquad (4.45)$$

$$n^{eff}_{solt} = i\,n_{solt} \qquad (4.47)$$

$$\frac{p_{soln}}{e_s} = 1 - \frac{i\,n_{solt}}{n_{H_2O}} \qquad (4.48)$$

$$\frac{e_s(n_{solt})}{e_s} = 1 - \frac{3i\,m_{solt}\,M_v}{4\pi M_{solt}\,\rho_l\,r^3} = 1 - \frac{b}{r^3} \qquad (5.16a)$$

$$b = 3i\,M_v\frac{m_{solt}}{4\pi M_{solt}\,\rho_l}$$

Now, combining surface+solute

- Substitute e_s(solt) for "plain" e_s
  - e(r,solt)= e(solt)*exp(a/r)
    $= e_s*(1-\frac{b}{r^3})*(\exp(a/r))$
- Expand for exp(x) for small x=a/r
  $= e_s*(1-b/r^3)*(1+a/r+\ldots)$
- Could also go back to $dg_{r,solt}=dg_r+dg_{solt}$
  - $dg_r=\sigma dA=fcn(a)$
  - $dg_{solt}=fcn(b)$ (i.e. dg for Raoult Effect)

$a = 2\sigma_{lv}/(\rho_l R_v T)$

$b = 3i M_v \frac{m_{solt}}{4\pi M_{solt}\rho_l}$

Chemical and Surface Effects

$$\frac{e_s(r,m_{solt})}{e_s} = \left(1-\frac{b}{r^3}\right)\exp\left(a/r\right) \qquad (5.17)$$

Both effects | **Raoult effect** | **Kelvin effect**

$a = 2\sigma_{lv}/(\rho_l R_v T)$.

$b = 3i M_v \frac{m_{solt}}{4\pi M_{solt}\rho_l}$

If r is not too small, (5.17) can be written as

$$\frac{e_s(r,n_{solt})}{e_s} = 1+\frac{a}{r}-\frac{b}{r^3} \qquad (5.18)$$

*What this means is that, for small x, use expansion exp(x)=1+x+H.O.T., then drop terms with $1/r^4$ and smaller.

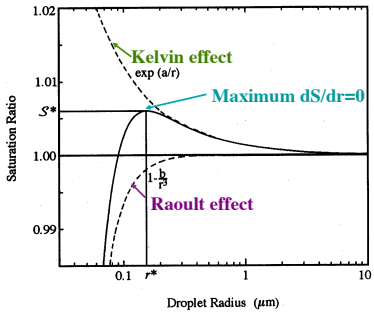


Figure 5.5 Equilibrium saturation ratio for a solution drop as a function of drop radius. The solution effect ($1-b/r^3$) dominates when the radius is small. For values of $r < r^*$, drop growth occurs only in response to an increase in the relative humidity. If the relative humidity at the critical radius slightly exceeds the critical saturation ratio, then the drop can grow spontaneously, and will continue to grow as long as the ambient saturation ratio remains higher than the equilibrium saturation ratio of the drop.

THE NUCLEUS IN AND THE GROWTH OF HYGROSCOPIC DROPLETS.

By Hilding Köhler (*Uppsala*).

Received 6th April, 1936.

The nature of the nuclei of which a cloud is really formed can best be investigated through the droplets of which the cloud is composed. Such an investigation generally presents great difficulty. After long microscopic investigations I proved that the ice which, in fog, is deposited on mountains as frost is formed through the undercooling of water droplets. The difficulties have thus been reduced to an analysis of such masses of ice.

Since the investigations of Melander and Lüdeling it has been sup-

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A Continuous-Flow Streamwise Thermal-Gradient CCN Chamber for Atmospheric Measurements

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Atmospheric Environment Vol. 8, pp. 1251–1256. Pergamon Press 1974. Printed in Great Britain.

POLLUTION AND THE PLANETARY ALBEDO

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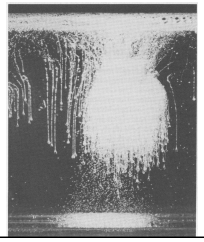
(*First received* 27 *February* 1974 *and in final form* 17 *May* 1974)

Abstract—Addition of cloud nuclei by pollution can lead to an increase in the solar radiation reflected by clouds. The reflection of solar energy by clouds already may have been increased by the addition of man-made cloud nuclei. The albedo of a cloud is proportional to optical thickness for thin clouds, but changes more slowly with increasing thickness. The optical thickness is increased when the number of cloud nuclei is increased. Although the changes are small, the long-term effect on climate can be profound.

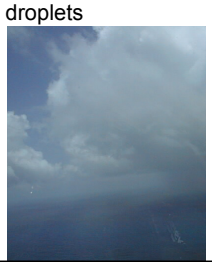
Bubbles

- Liquid (H_2O/EtOH) supersaturated with vapor (CO_2) nucleates on salt to form bubbles

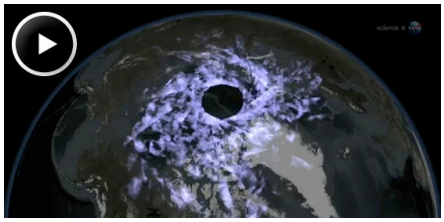


Clouds

- Vapor (air) supersaturated with liquid (H_2O) nucleates on particles to form droplets



Noctilucent Clouds: Another Type of Nucleation



- Meteor dust nucleates noctilucent clouds
  - http://science.nasa.gov/science-news/science-at-nasa/2012/07aug_meteorsmoke/

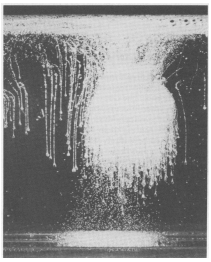
Midterm Wed. Nov. 19

- Chapters 1-4, excluding ocean-specific sections
  - Composition, Structure, State
  - First and Second Laws of Thermodynamics
  - Transfer Processes plus Simple Thermo Model
  - Thermodynamics of Water
- In class 80 min (12:30-1:50 pm, NTV 330)
- Closed book
- Constants provided

Curry and Webster, Ch. 1-4

Micro-Thermodynamics

- Saturation has the most possible dissolved species
- Equilibrium means two phases are balanced
- Supersaturated states are not stable
- Nucleation initiates a change of "phase" (from particle to droplet)



Bohren, 1987

Macro-Thermodynamics

- Hot air rises
- Rising air cools
- Cooled moist air saturates
- (Sub & Super)-saturated water vapor condenses
- Condensation liberates heat

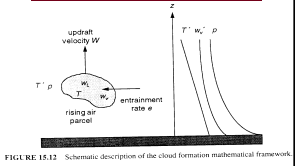


FIGURE 15.12 Schematic description of the cloud formation mathematical framework.

What did we learn in Ch. 5?

- Kohler equation: **What will H_2O condense <u>on</u>?**
  - Kelvin effect describes the dependence of surface energy on particle/droplet size
  - Raoult effect describes the increased energy of dissolved components in mixtures
- Nucleation (a.k.a. activation)
  - Formation of a new phase
  - Role of particles as "triggers" but not "drivers"
- History and recent advances
  - Development of theory (Kohler, 1936)
  - Measurement of particle nucleation (Nenes and Roberts, 2005)
  - Implications for albedo (Twomey, 1974)