

The hydrosphere

Properties of water.

Water is essential to the support of all life. Life, after all began in the oceans about 2600Myr ago. Many plants and animals can live only in water. Human bodies contain about 70% water. It is essential in the transfer of chemicals to and from living cells.

Both the freezing point and boiling point (100⁰C) of water are out of line compared with the rest of the periodic table. Both are unexpectedly high as can be seen from the data below. Moreover the range of temperatures in which liquid water exists is large. All this is due to extensive *hydrogen bonding* – an effect responsible for many of the unusual properties of water

Compound	Molecular Weight	Melting point (⁰ C)	Boiling point (⁰ C)	Range (⁰ C)
H ₂ O	18	0	100	100
H ₂ S	34	-85	-60	25
H ₂ Se	81	-66	-41	25
H ₂ Te	129.6	-49	-2	47
H ₂ Po	212	decomposes	decomposes	-

Even so, this range defines an ‘inhabitable ring’ in the solar system where water-based life can exist. Venus and Mercury are too hot; Jupiter, Saturn and so on are too cold.

The density of water is at a maximum at 4⁰C. Ice I (there are at least ten phases of ice) is an open structure, held together by hydrogen bonds, and is less dense than liquid water. This is useful since the oceans freeze from the top down, not the bottom up but there are minor disadvantages (burst pipes for example).

The *latent heat of fusion* (i.e. the heat required to convert 1kg of ice to water without changing the temperature) is 0.334kJ/kg. The *latent heat of vaporisation* (i.e. the heat required to convert water to vapour without a change of temperature) is 2300kJ/kg. For *dry air*, C_p is about 1000JK⁻¹kg⁻¹. Note that the effect of the latent heat is equivalent to a rise in temperature of 2300K.

The hydrosphere

The total volume of water on the earth is about 310 million cubic miles (1284 million cubic kilometres). 97% of this is in the oceans. If it were spread evenly over the earth, the planet would be covered to a depth of 2.8km. 2.25% is locked up in the polar ice-caps and in glaciers. About 0.75% is in soil, lakes and rivers. 0.035% is in the atmosphere. To give some idea of what this amount is; if all the water vapour in the atmosphere were instantly converted to rain, the total rainfall (averaged over the earth’s surface) would be about 3cm. Yet the annual average rainfall here is 90-100cm. There is a *hydrologic cycle*.

The hydrologic cycle

Water is cycled between the oceans and the atmosphere. As always, the cycle is driven by the sun. Most of the water vapour in the atmosphere (84%) comes from the oceans. Transpiration from plant leaves accounts for most of the rest. The sun heats the water in the oceans (and on the land surface), giving evaporation. The warm, moist air rises, expands (under reduced pressure higher in the atmosphere) and cools. The water vapour condenses to form clouds. The winds then carry the clouds across the earth’s surface until the water is released as precipitation (rain, hail or snow) to fall on the earth for further recycling. Most of the precipitation falls into the oceans (75% of the surface of the planet being ocean). We rely on the rest. The rate of circulation of water within the hydrologic cycle is very rapid. Since the total mass of water in the atmosphere is constant, precipitation is balanced by evaporation. Thus, comparing throughputs shows that the average residence time of water molecules in the atmosphere is about *10 days*.

Water in the atmosphere

Water greatly affects the behaviour of the atmosphere. The main areas are

1. Thermodynamics (through condensation and evaporation)
2. Cloud formation (and thus the planetary albedo as well as precipitation effects)
3. Cleansing of the atmosphere by rainout (e.g. removal of substances within clouds such as hygroscopic [water-absorbing] aerosols), *washout* (removal of aerosols and dissolution of soluble atmospheric gases through capture by falling raindrops)
4. Chemistry of the atmosphere (as a solvent or participant in reactions)
5. Absorption of radiation; water is a major greenhouse gas.

The amount of water vapour in the atmosphere is limited by the *saturation vapour pressure*. This is the *partial pressure of water vapour* in equilibrium with the condensed phase (i.e. the attempt to add any more vapour will cause condensation). Note that this is the partial pressure of the water; the total pressure of the atmosphere is irrelevant. This quantity can be obtained from the *Clausius-Clapeyron equation*, a standard result of equilibrium thermodynamics. This states that, for a vapour in equilibrium with its condensed phase, the partial pressure, p , is given by

$$\frac{d \ln p}{dT} = \frac{L}{RT^2} \quad (1)$$

where L is the latent heat of evaporation (in kJ/mole). This is often given in J/kg, i.e.

$L_S = 1000L / M_v$ where L_S is the latent heat in J/kg and M_v is the molecular weight (in grams). We can define a specific gas constant for water, $R_S(\text{H}_2\text{O}) = 1000R / M_v$. In the case of water, the partial pressure p is conventionally represented by the symbol e , and the saturated partial pressure by e_s . Setting $p = e_s$, we can easily integrate (1), to give

$$e_s = e_s^0 \exp\left(-\frac{L}{R}\left[\frac{1}{T} - \frac{1}{T_0}\right]\right) = e_s^0 \exp\left(-\frac{L_S}{R_S(\text{H}_2\text{O})}\left[\frac{1}{T} - \frac{1}{T_0}\right]\right) \quad (2)$$

where e_s^0 is a constant (usually the saturated vapour pressure at S.T.P. [298.15K and one atmosphere pressure]) and T is the absolute temperature. Note that this equation shows that e_s is strongly dependent on temperature; warm air can contain much more water vapour than cold air. For example, in the tropics (air temperature 25°C) the partial pressure of water vapour is 32mb; in the polar vortex (temperature -20°C) the partial pressure is 1.2mb.

There are two other ways of expressing the amount of water vapour in the atmosphere. The *specific humidity*, q , is defined as

$$q = \frac{\text{Mass of water in the air parcel}}{\text{Total mass of the air parcel}} = \frac{m_v}{m} = \frac{\rho_v}{\rho} \quad (3)$$

The final equality follows from the fact that the volume is the case in both cases. We can use the standard equation of state for the water vapour and the air to give expressions for ρ_v and ρ . This gives $\rho_v = e / R_S(\text{H}_2\text{O})T$ and $\rho = P / R_S T$. Hence we have

$$q = \frac{\rho_v}{\rho} = \frac{eM_v}{PM} \quad (4)$$

It is usually possible to ignore the effect of the water vapour on \overline{M} and so we can use the value of 28.96 used before. Obviously, we can define saturated specific humidity, $q_s = e_s M_v / \overline{PM}$. Note that although the saturated vapour pressure *does not* depend on the atmospheric pressure, the saturated specific humidity *does*.

The other measure is the *relative humidity*, RH . This is the ratio of the partial pressure of water in the atmosphere to the saturated vapour pressure at that temperature, expressed as a percentage i.e.

$$RH = 100e(T) / e_s(T) \quad (5)$$

Measuring the amount of water vapour in the atmosphere.

There are two standard measurements; the *wet-bulb thermometer* and the *dew-point meter*. A wet-bulb thermometer consists of a thermometer surrounded by a wick that is kept saturated with water. Water vapour both condenses onto the wick and evaporates from it. The excess of evaporation over condensation cools the thermometer and the temperature is measured. We will consider an idealised version of this. The *wet-bulb temperature*, T_w , is defined as the lowest temperature to which an air parcel can be cooled by evaporating water into it adiabatically and at constant pressure. If the initial temperature of the bulb is T , the net amount of water evaporated is Δm_v and the total mass of the air parcel is m then we have

$$\begin{aligned} L_S \Delta m_v &= C_p m (T - T_w) \\ \Delta m_v / m &= C_p (T - T_w) / L_S \end{aligned} \quad (6)$$

ignoring the effect of the water on the heat capacity term. We can also write

$$\frac{\Delta m_v}{m} = \frac{m_v(\text{final})}{m} - \frac{m_v(\text{initial})}{m} = q(\text{final}) - q(\text{initial}) = q_s(T_w) - q(T) \quad (7)$$

The final equality comes from the fact that the air parcel at the wet-bulb temperature must be saturated. Thus we have

$$q(T) = q_s(T_w) - C_p (T - T_w) / L_S \quad (8)$$

$q_s(T_w)$ can be found from the Clausius-Clapeyron equation (or in practice looked up in tables) so we can obtain $q(T)$. A properly set-up wet-bulb thermometer gives a reasonable approximation to T_w .

A *dew-point meter* has of a cooled surface. The air in contact with this is cooled at constant pressure until it saturates and begins to deposit dew. This is the *dew point*, T_d . Since the amount of vapour in the air has not changed until the dew point is reached and also the pressure has remained constant, the partial pressure of water must also be constant during the cooling process. Hence $e(T) = e_s(T_d)$. This gives the relative humidity directly; $RH = 100e_s(T_d) / e_s(T)$. Note that the dew-point depression is much greater (about twice) the wet-bulb depression; the dew-point experiment involves only condensation; the wet-bulb involves both evaporation and condensation and the effects of these processes act against each other.

We must consider three major processes in the atmosphere:

- cooling (or warming) at constant pressure – in most cases this implies constant height.
- expansion / compression (i.e. the effect of moving parcels of air up or down)
- mixing of hot and cold air at different pressures (again moving parcels of air up or down)

Thermodynamics of air and clouds (Adiabatic expansion with condensation)

We return to the thermodynamics of air parcels. When we considered the *dry adiabatic lapse rate*, we derived the equation

$$\delta Q = C_p dT - (1/\rho) dP \quad (9)$$

where we consider a unit mass of air and so replace the volume V by $(1/\rho)$. This ignores the possibility that water vapour in the air can evaporate (or condense). This releases (requires) the latent heat. The effect of this (for detailed – and non-examinable – proof see below) is that the lapse rate in wet air is much less than in dry air. The temperature does not fall so fast with height because the latent heat released as the water vapour condenses out warms the air up. The temperature/height curve changes shape as it passes through a cloud. The regions where the temperature is nearly constant as the height rises are due to the heating effect of the condensation of water vapour in the cloud

To prove this, we must reconsider the enthalpy balance (9) including the latent heat effects where water evaporates or condenses. This can occur only when the air is saturated with water vapour. This gives

$$dH = C_p dT + L_S dm_v + (1/\rho) dP \quad (10)$$

m_v is the mass of water vapour present in a unit mass of air (and is therefore the ratio of the density of water vapour to the density of air, (ρ_v/ρ)). We can use the equation of state for a gas, $P = R_S \rho T$ and set $m_v = eM_v / P\bar{M}$ using the definition of specific humidity, but remembering that everything is referred to unit mass of air. Hence, at constant pressure,

$$dm_v = \frac{M_v}{M} \left(\frac{de}{P} - \frac{e}{P^2} dP \right) \quad (11)$$

If the air is saturated, we can set $e = e_s$ and use the Clausius-Clapeyron equation

$$\frac{de_s}{dT} = \frac{L_S e_s}{R_S (\text{H}_2\text{O}) T^2} \quad (12)$$

and so, substituting this into the equation above,

$$dm_v = \frac{M_v e_s}{MP} \left(\frac{L_S}{R_S (\text{H}_2\text{O}) T^2} dT - \frac{dP}{P} \right) \quad (13)$$

which can be substituted into the enthalpy equation to give a relationship entirely in terms of the atmospheric variables (T, P). If we consider the system to be adiabatic as before, we have the amended heat equation

$$\delta Q = C_p dT - (1/\rho) dP + L_S dm_v = 0 \quad (14)$$

Again, we use the simple gas law $P = R_S \rho T$ to substitute for the density,

$$C_p (dT/T) - R_S (dP/P) + (L_S/T) dm_v = 0 \quad (15)$$

Using equation (13) to substitute for dm_v gives (after some manipulation)

$$\left(C_p + \frac{L_S^2 q_s}{R_S (\text{H}_2\text{O}) T^2} \right) d \ln T - \left(R_S + \frac{L_S q_s}{T} \right) d \ln P = 0 \quad (16)$$

The extra terms increase dP/dT since $L_S / R_S (\text{H}_2\text{O}) T > 1$. But we know that the lapse rate $dT/dz = dP/dz (dT/dP)$. dP/dz , the pressure variation with height, is not much affected by water vapour. So an increase in dP/dT will decrease the lapse rate dT/dz .

Cooling in the atmosphere

Dew and frost form as a result of condensation or sublimation of water vapour on solid surfaces (in particular the ground). These radiate heat during the night, cooling themselves (and the air immediately above them) to temperatures below the saturation vapour pressure. Cooling occurs at constant partial pressure of water vapour until the point where the saturation vapour pressure is reached. There are two important cases. First, the air will become saturated with respect to ice and this temperature is the *frost point* (T_f). Freezing may not occur; this process requires appropriate surfaces for ice to form. Cooling may continue until the air becomes saturated with respect to water. This temperature is the *dew point* (T_d).

Condensation occurs as microscopic droplets formed on condensation nuclei (for example on aerosols in the atmosphere). This results in *fog*. As droplets form, they themselves can radiate heat (they act as black bodies). However, the air is heated up by the latent heat of fusion being produced. The effect is that the cooling rate below the dew-point is slower than above the dew-point.

The argument is essentially the same as the argument for lapse rates above. The heat that must be lost by the atmosphere below the dew-point is

$$\delta Q = \left(C_P + \frac{L_S^2 q_s}{R_S (\text{H}_2\text{O}) T^2} \right) dT \quad (17)$$

since the pressure is constant. This is greater than before the dew-point and, even with the extra mechanisms of heat loss now present, cannot be removed as fast as before.

Mixing in the air

- *Horizontal mixing*. If two adjacent air masses of low humidity mix the process occurs at constant pressure. If no condensation occurs, the result is air with a temperature which is the average of that of the two air masses. If condensation occurs (as it will if one of the masses is hot and humid and the other one is cold) then supersaturation and condensation will occur giving a *mixing fog*. An example of this is the tail of a jet aircraft; hot, humid air emerges from the combustion chamber into the cold, dry, air outside.
- *Vertical mixing*. In unstable regions of the atmosphere, convection may ensure vertical motion. This will give a thorough mixing of a whole layer. If condensation occurs, the process of cloud formation can begin

Clouds

There is a general classification of clouds summarised in the list below. Terms can either be nouns (the -us form) or qualifiers (the -o form).

- Cirrus (cirro) A cloud containing ice-crystals - therefore high altitude
- Stratus (strato) A layer cloud. This may be continuous or show structure
- (alto) A middle-height cloud
- Cumulus (cumulo) indicates vertical circulation within the cloud, this gives the 'fluffy' shape and is quite different from the stratus form
- Nimbus (nimbo) Cloud producing precipitation (rain., snow, hail)

Not all the possible combinations can occur even in principle, but many do. For example a cumulonimbus cloud is a cloud with large vertical movement of air producing (usually a lot of) rain – it is a thunderstorm cloud.

Let us consider an average cumulus cloud. The shape is (crudely) cylindrical – this is good enough for a rough estimate. A typical cloud will be about 2km in diameter and 2km in depth. Hence the volume is about $\pi d^2 H / 4 = 6.28 \times 10^9 \text{ m}^3$. A cloud contains of the order of 50-500 million water droplets per cubic metre. Each of these droplets is about 10 microns in radius. Thus the volume of a single droplet is $4\pi r^3 / 3$ i.e.

$4.2 \times 10^{-15} \text{ m}^3$. Given the density of water, 1000 kg/m^3 , the mass of the droplet is about

$4.2 \times 10^{-12} \text{ kg}$. Thus the mass of the cloud (at the lowest reasonable density of droplets) is about $1.3 \times 10^6 \text{ kg}$ – about 1300 tonnes.

This seems a lot, but if all the water in this cloud fell at once, the depth of water would be (Volume of water)/(area of cloud base); which for the figures we gave above is $4.2 \times 10^{-4} \text{ m} = 0.42 \text{ mm}$ which is not a lot. During a storm therefore, lots of 'clouds' must pass over you.

Cloud formation. Clouds are formed as hot humid air rises and cools by adiabatic expansion. When air reaches saturation, excess water vapour condenses onto small particles called *cloud condensation nuclei*. The partial vapour pressure required to produce condensation is *higher* than the thermodynamic vapour pressure because the surface of a drop is curved. On the other hand, the effect of dissolving material into the drop *decreases* the vapour pressure. Both effects depend on the drop radius, r but act in the opposite relation as shown below (for a proof see the appendix)

$$\frac{p(\text{droplet})}{p(\text{flat, pure})} = 1 + \frac{A}{rT} - \frac{mB}{r^3} \quad (18)$$

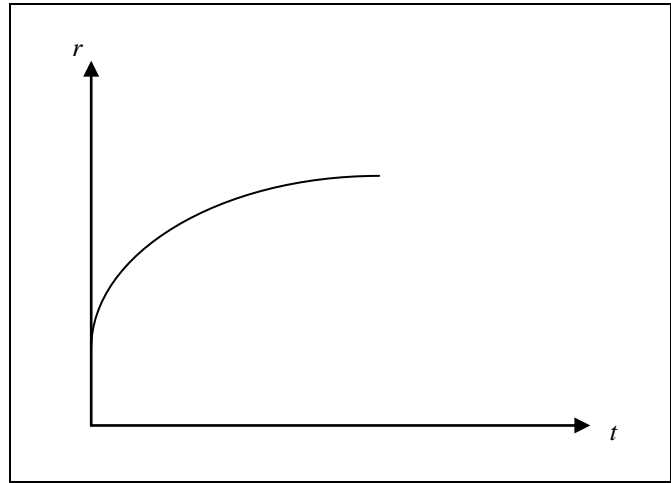
where A and B are constants and m is the mass of dissolved solute. The solute nuclei come from natural sources such as dust from wind erosion, sea salt etc. (see the list of aerosol sources given earlier). They can also arise from industrial products (sulphate particles, coal dust). About 100 such particles per cm^3 are needed to form a cloud. Since there are 10^3 particles / cm^3 over the sea, 10^4 particles / cm^3 over land and 10^5 particles / cm^3 over cities, forming clouds should not, on the face of it, be a problem. However, matters are not quite so simple.

Growing droplets in clouds

Growth by condensation: Consider a water drop at rest. Water vapour condenses onto the surface of the droplet, releasing latent heat. The temperature of the droplet rises, altering the vapour pressure, e . Eventually a steady state is reached. There is a gradient of the partial pressure of the water vapour driving a flux of water vapour towards the drop. Also the rate of heat loss is equal to the heat gained by the drop from the latent heat of the water. This gives an equation of the form for the growth rate of the radius r of the drop

$$r \frac{dr}{dt} = C \text{ where } C \text{ is a constant. This integrates to give } r^2 = r_0^2 + 2Ct$$

where r_0 is the initial droplet size. The diagram above shows the behaviour expected. The problem is that detailed calculation shows that it would take 1-4 hours for a drop to grow from 2 to 30 microns. Yet in a typical cloud there are many droplets larger than 10 microns although the lifetime of a cloud can be as short as ten minutes.. One final problem, as the cloud rises, the temperature falls and so the saturated vapour pressure falls. Thus the *supersaturation* in the cloud must rise. This means that more and more nuclei are capable of acting as condensation nuclei for water droplets. More of the water vapour is removed and eventually an equilibrium is reached again. How then does the cloud grow? Clearly condensation is not enough to explain cloud growth



Another possible growth mechanism is *coalescence* - two droplets collide to make a larger droplet. The probability of coalescence depends on (i) the size of the droplets (i.e. their cross-section) and their relative velocity. The velocity of droplets depends on a balance between gravity and frictional forces. For reasonably small particles (less than 30 microns in diameter), the terminal velocity is given by Stokes Law;

$$F_v = 6\pi\eta r v \tag{18}$$

where F_v is the *drag force* i.e. the force exerted by the viscous forces on the particle that act against the force pushing the particle through the medium (in this case gravity). η is the viscosity of the medium (air in this case) and r is the radius of the particle.

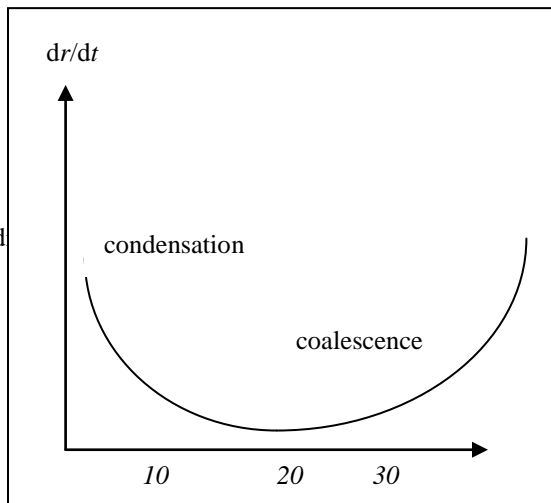
Droplet diameter (mm)	Terminal velocity (m/sec)
0.01	0.003
0.1	0.025
1.0	4.03
5.0	9.09

When these forces are in equilibrium the droplet reaches terminal velocity. This obviously depends on the droplet size. Typical values are given in the table above.

The expression controlling the rate of growth takes the form

$$\frac{dr}{dt} = \frac{EwV}{4\rho} \tag{19}$$

where E is the collection efficiency taking account of the fact that the drop is not a sphere, w is the volume swept out by the falling droplet, V is the density of water. Combining the two modes of growth we get an overall growth rate curve of the form shown on the right. It is clear that there is a 'barrier' to growth at the 20 micron size where neither process is efficient. The



mechanism that overcomes this barrier is still not understood. Possibilities include increasing the efficiency of collisions by including the effect of turbulence, invoking droplet-droplet interactions by electrical forces. When the droplet reaches a diameter of 2-3mm they are broken apart by collisions rather than built up. Above 6mm the droplet becomes unstable anyway; the surface tension cannot hold it together.

Once the drops grow to a size beyond the ability of the updrafts in the cloud to maintain them, they begin to fall. Below the cloud, they are in unsaturated air and begin to evaporate again. Rain falling from a cloud need not reach the ground This can sometimes be seen as a tapering veil beneath a cloud; the *virga*. Only the larger drops; those that have swept up their neighbours by coalescence, can reach the ground as rain. In the case of colder clouds, the precipitation often begins as ice or hail which melts on the way down. Sometimes, of course, it doesn't

Thunderstorms.

One of the most dramatic events in the weather; pictures of thunderstorms have been found in cave paintings. Thunderstorms occur when moist, warm air near the ground becomes buoyant and rises to form small cumulus clouds. These clouds grow and surge upwards to combine and form cumulonimbus; anvil-shaped clouds. These main extend half a mile into the stratosphere. Within these clouds there is vigorous movement; updrafts and downdrafts at tens of metres per second. Such movements lead to a separation of electrical charges within the cloud; Positive charge gets carried to the top and negative charge to the bottom. The charge carriers are electrons, molecules, aerosol dust, hailstones and snowflakes. The process of charging is unclear but may include frictional contact, freezing, melting, and break-up of water droplets. Once charge separation has occurred, an electric field is established. The air may then become ionised. Thus a small region of the atmosphere is changed from being a good insulator to a highly conducting path. Thus there can be (and is) an electrical discharge. This is lightning – which is simply a high-voltage spark. The average lightning discharge involves the flow of ten coulombs of charge across a potential difference of about 100 million volts. Thus the energy is about 10^9 J (about 280Kwatt-hours). This is enough to run an air conditioner for two weeks.

The main types of lightning are

1. *Ground discharges* [thunderbolts, forked lightning]. These occur between the cloud and the ground. They consist of a 'leader stroke' establishing an ionised path to the ground up which a 'return stroke' passes.
2. *Cloud lightning* [sheet lightning, heat lightning] occurs within the cloud. It gives a diffuse illumination without a distinct channel being seen. If there are distant thunderstorms on the horizon, the sheet lightning is what will be seen
3. *Air discharges* [streak lightning] passes from cloud to cloud or cloud to air but does not reach the ground (i.e. no return stroke).
4. *Ball lightning* Unusual and still not fully explained. Usually small balls (but reported diameters up to 1m) of electrical discharge. Move slowly in the air or along the ground; usually disappear with a violent explosion.

Although lightning is the most spectacular effect of a thunderstorm, it is only a small part of the total energy budget of the storm

Thunder is the sound wave produced by a lightning stroke. The sudden rise in pressure in the lightning channel produces an intense sound wave as in an explosion. Sound travels at 310-340m/sec so the sound follows behind the lightning flash. Hence counting the interval between the flash and the thunder gives a rough estimate of the distance of a storm (about 1km for every three seconds but there may be echoes which confuse matters).

Appendix: Initial problems of condensation, Thomson relations and Raoult's Law

It is harder to make water condense onto a curved surface than onto a planar surface because there is a pressure difference ΔP across a curved surface. This is because work has to be done against the surface tension to increase the area. Try to expand a bubble (or a droplet) by a volume dV , causing a change in area dA . Then we have

$$\Delta P \cdot dV = \gamma dA \quad (\text{A1})$$

where γ is the surface tension. Then, for a sphere,

$$\Delta P \cdot 4\pi r^2 dr = \gamma [4\pi(r + dr)^2 - 4\pi r^2] = 8\pi r \gamma dr \quad (\text{A2})$$

giving $\Delta P = 2\gamma / r$. Note that since the work is done *against* the surface tension, this must be provided by the pressure difference – the pressure difference gets less as the bubble or droplet expands.

For a molecule in a gas outside the surface, but in equilibrium with that surface, the change in energy due to curvature is $\Omega \Delta P$ where Ω is the molar volume of the gas. This is the change in the chemical potential of the gas (with reference to a flat surface) i.e.

$$\mu(\text{curved}) - \mu(\text{flat}) = 2\gamma\Omega / r = RT \ln \left(\frac{p(\text{curved})}{p(\text{flat})} \right) = RT \ln \left(\frac{\rho(\text{curved})}{\rho(\text{flat})} \right) \quad (\text{A3})$$

applying the perfect gas law to both cases. Hence, rewriting and expanding the resulting exponential

$$\rho(\text{curved}) = \rho(\text{flat}) \exp(2\gamma\Omega / rRT) \approx \rho(\text{flat}) \left(1 + \frac{2\gamma\Omega}{rRT} \right) \quad (\text{A4})$$

A second effect on the pressure of the water vapour outside the droplet comes from *Raoult's Law* which states that the partial vapour pressure of a component of a solution is proportional to the mole fraction present in the solution $p_i = p_i^0 x_i$. If we put solute into a solvent, giving a mole fraction x_c of solute, then the vapour pressure of the *solvent* is given by $p_i = p_i^0 (1 - x_c)$. If a water droplet, mass m_v has a mass m of solute dissolved in it, then the number of moles of solvent is given by $N_v = \frac{4}{3}\pi r^3 \rho_w (1000 / M_w)$ where ρ_w is the density of water. The number of moles of solute is $N_s = m(1000 / M_s)$ and so the mole fraction of solvent is

$$x_v = N_v / (N_v + N_s) \approx 1 - N_s / N_v = 1 - \frac{m}{r^3} \left(\frac{M_w}{\frac{4}{3}\pi \rho_w M_s} \right) \quad (\text{A5})$$

Since the effects of curvature and Raoult's law are independent to first order, and since $p_i = \rho_i R_s T$, we can combine (A4) and (A5) to obtain

$$\frac{\rho(\text{droplet})}{\rho(\text{flat, pure})} = \frac{p(\text{droplet})}{p(\text{flat, pure})} = \left(1 + \frac{A}{rT} - \frac{Bm}{r^3} \right) \quad (\text{A6})$$

where the constants A and B are obtained from the equations above. This shows that vapour pressure required to condense water droplets has two terms. For very small droplets, the second (Raoult law) term will dominate. In that case, it will be *easier* to condense water onto a droplet than onto a flat surface. As the droplet grows, the Thomson term will dominate (as the droplet grows, A / rT gets smaller much more slowly than $Bm / r^3 T$). It will be come *harder* to condense water onto a droplet than onto a flat surface. At $r^2 = 3BmT / A$, the unfavorable effect is at a maximum (for drops of a few microns diameter). Thereafter, it becomes easier to condense water onto the drop as the drop grows larger, and the drop can grow freely.