DEN5406: Mass Transfer and Separations Processes I

Week 10: Drying, Advanced Adsorption and Exchange, and Separation Method Selection

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Separations and Syllabus Goals

Obtain Quantitative Understanding of the following processes:

✔ **Filtration - ✔ we started and continue!** **We'll also cover this week:**

Aggregation

✔ **Centrifugation**

Crystallization (controlled freezing) separation

Adsorption ✔

✔ **Leaching (extracting metals from ores, making coffee, dry cleaning)**

✔ **Osmosis**

- **Forward Osmosis**
- **Reverse Osmosis**

✔ **Ion-exchange membranes**

Drying ✔

✔ **Distillation (controlled evaporation and condensation)**
and the many kinds of distillation

Applications: Surviving in Space, on a desert island without fresh water

Recommended Reading

Available on Knovel – in the library:
De Haan & Bosch, Industrial Separation Processes, 2013, de Gruyter (Berlin)

Distillation Fundamentals and Principles, Gorak & Sorensen, eds., 2014, Elsevier

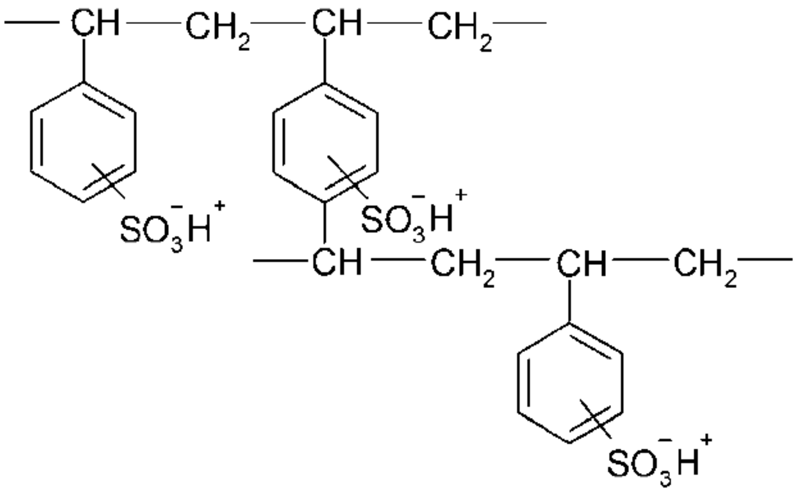
Reactive & Membrane-Assisted Separations, Lutze & Gorak, eds., 2016, de Gruyter

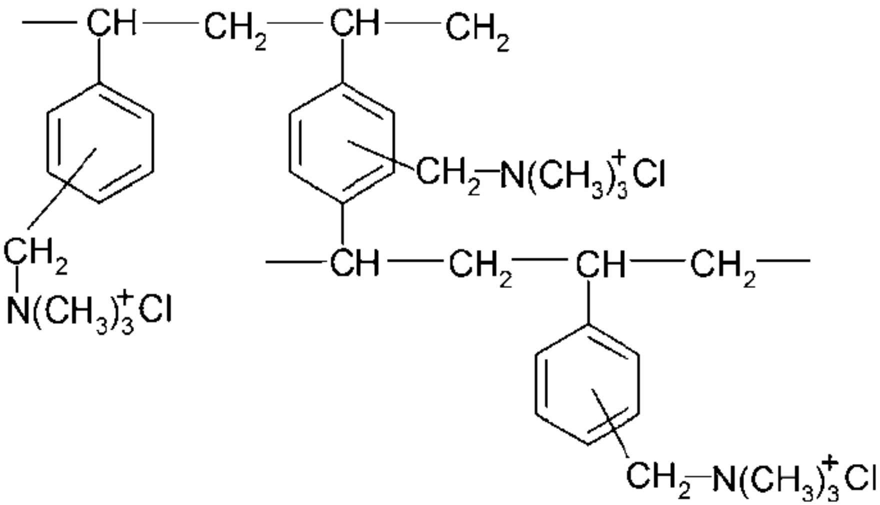
Also from
Seader, Henley, & Roper, Separations Process Principles, 2011, Wiley

Pre-assigned class reading -> will have a chance to discuss problems in class

Drying of Solids:
Ch. 7 in
De Haan & Bosch, Industrial Separation Processes, 2013, de Gruyter (Berlin)

Types of Exchange Resins





Sulfonated side groups for Cation exchange

Aminated side groups for Anion exchange (Cl^- or OH^- form)

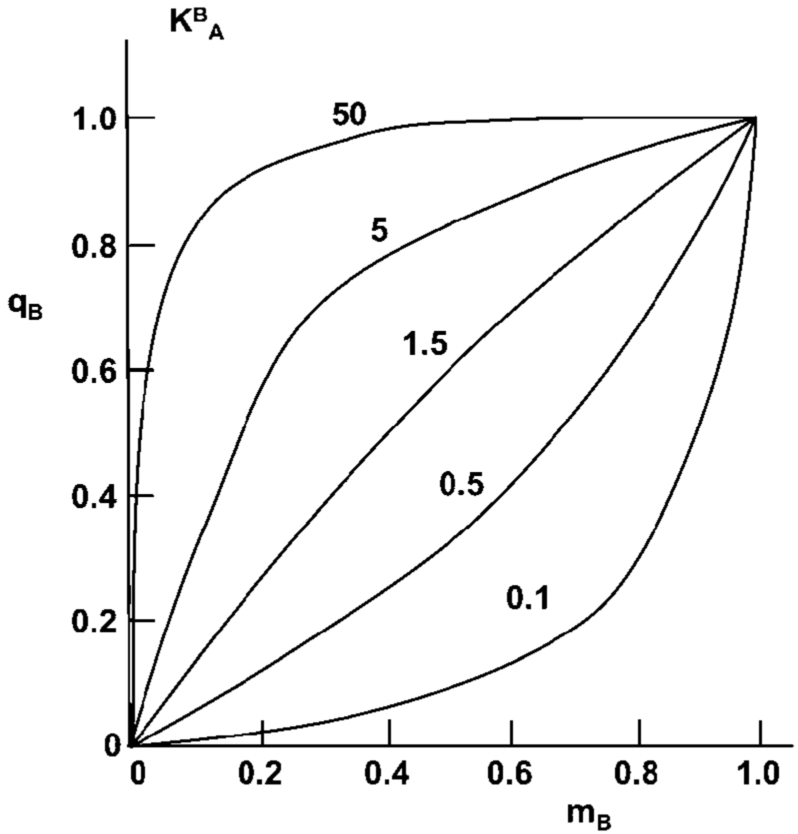
De-ionization of water makes use of both types of resins.
Cationic resins are placed first to avoid precipitaiton of metal hydroxides
Mixed bed systems give better results than sequential columns.

Styrene-divinyl benzene based exchange resins

Ion-Exchange Capacity and Rate

For Cations B+ from solution in exchange for A+ on the resin:

$$\textbf{resin-SO}_3^{\,-}\textbf{A}^+ + \textbf{B}^+ \Leftrightarrow \textbf{resin-SO}_3^{\,-}\textbf{B}^+ + \textbf{A}^+$$



Univalent ion-exchange plot

$$K_A^B = \frac{q_{B,resin}\, m_{A,liquid}}{q_{A,resin}\, m_{B,liquid}}$$

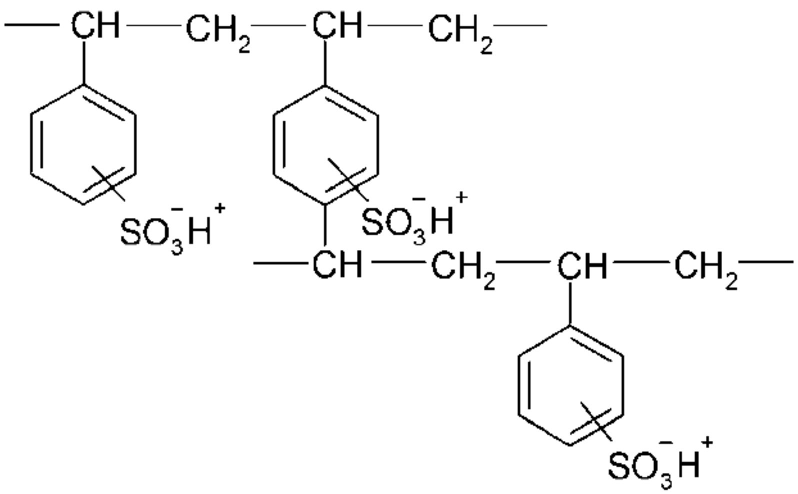
Equilibrium constant determining selectivity of a resin for B over A

q = capacity (conc.) ions in resin [mol/kg]

m = concentrations of the ions in the solution [mol/L] or [mol/kg]

B is preferred if $K_A^B > 1$

Problem Solving



Sulfonated side groups for Cation exchange

Problem 7. A commercial ion-exchange resin is made of 88 wt% styrene (MW = 0.104 kg/mol) and 12 wt% divinyl benzene (MW = 0.1302 kg/mol). Estimate the maximum ion-exchange capacity in equivalents/kg resin when an sulfonic acid group (MW = 0.0811 kg/mol) has been attached to each benzene ring.

How do we go about solving this?

Hints: What is ion-exchange capacity?
What are the units of capacity?

Drying of Solids
Please read – Ch. 7from De Haan & Bosch, Industrial Separation Processes, 2013, de Gruyter (Berlin) (on Knovel)

You'll learn about drying fruit, and bread, and vapor in pores

Drying – Slowly at Low Vapor Pressures

For low drying rates, and
low vapor concentrations c,
drying rate Φ_{vap} is proportional
to the driving force ($c_{sat(Ts)} - c_f$)

$$\textit{Drying rate } \Phi_{vap} \qquad = k_g\,(c_{sat(Ts)} - c_f\,)$$

units [mol s^{-1} m^{-2}]

where

T_f = temperature of heated air (with concentration c_f)
T_s = temperature of wet surface [K]
c_{sat} = saturation vapor (water) concentration at T_s [mol m^{-3}]
c_f = vapor (water) concentration in *feed* gas (air) [mol m^{-3}]
k_g = mass transfer coefficient [m s^{-1}]

Drying – Terminology and Learning Goals

By the end of this lecture you'll be able to: **drying.** (how prosaic!) Yet, in a quantitative way in which none of your friends outside this class would be able to.

Say what are **wet-bulb temperature, absolute humidity, relative humidity, How to make bread rusk, .** Other vocabulary: **Chilton-Colburn transfer numbers for heat and mass,**

We'll identify **Drying Mechanisms** and

Derive **simplified rate equations** to **estimate drying times**

Discuss **Drying Methods** and **Drying Equipment**

Applications in: Foods, building materials, powders, papers, fabrics

Discuss Efficiency and cost –
Drying vs. unnecessary transportation of products containing water

Bread Rusk and Hair Drying

Need to strike an optimum balance between Temperature and Drying Rate

Drying – Wet Bulb Temperature

When the amount of air >> amount of evaporated moisture
The dynamic equilibrium (non-equilibrium steady state)
Temperature of a wet surface is called T_{wb}, the **wet-bulb temperature**

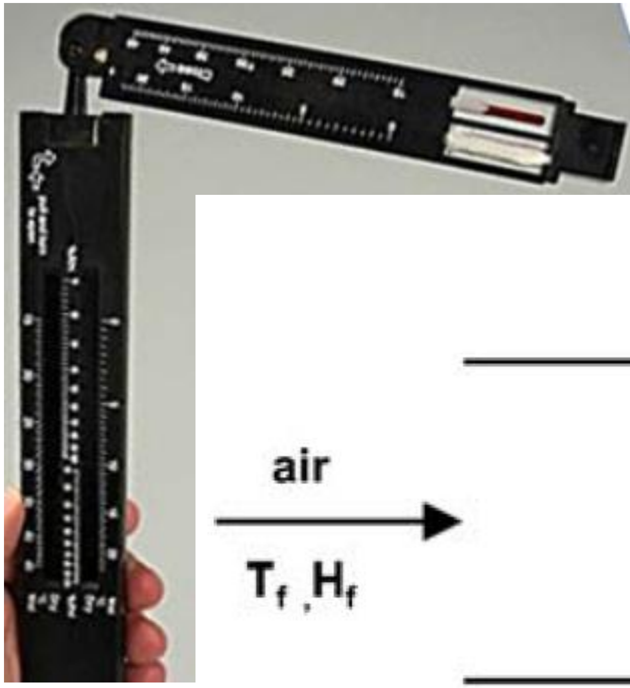
$$\Phi_{vap} \cdot \Delta H_{vap} = h\,(T_f - T_{wb}) \qquad \text{units } [\mathrm{J\ s^{-1}\ m^{-2}}]$$

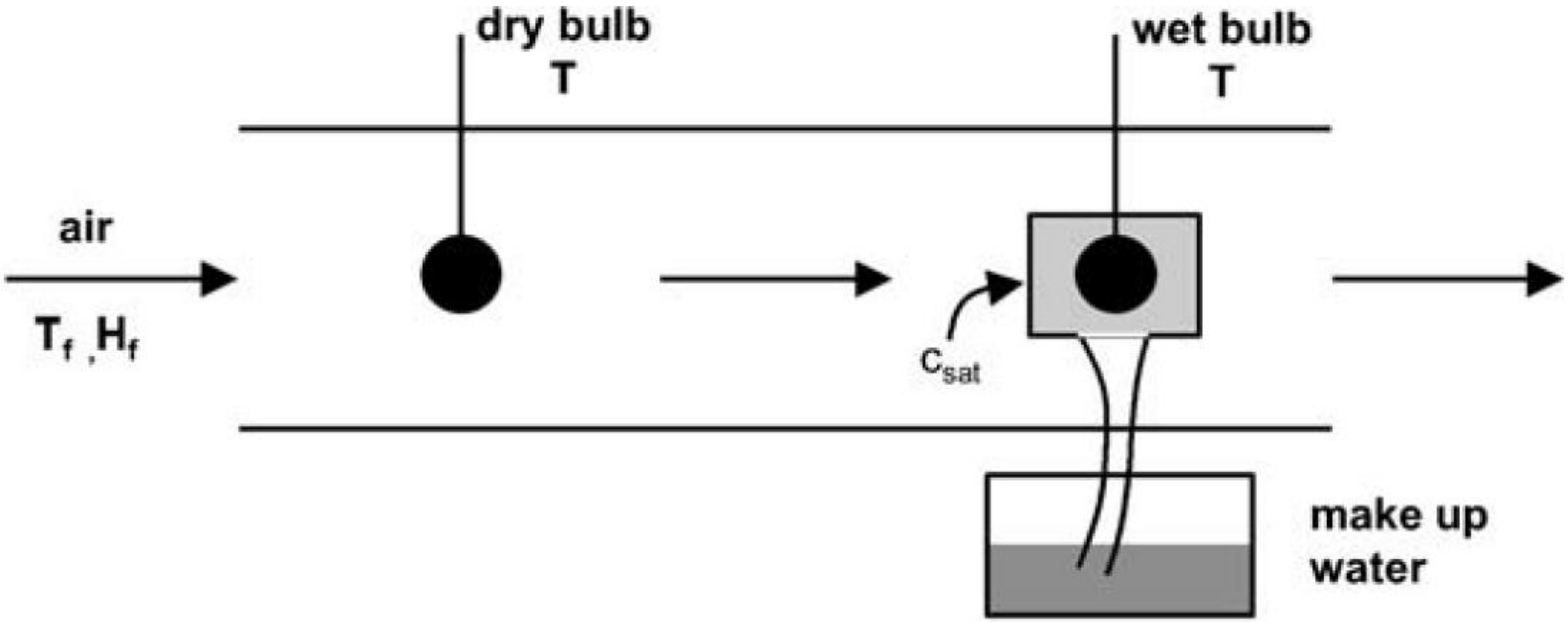
Drying rate Energy — *Energy transfer from the surface*

where
h = heat transfer coefficient (convection) [$\mathrm{W\ m^{-2}\ K^{-1}}$]
ΔH_{vap} = molar heat of evaporation [K]

Examples – Passive cooling in non-glazed pottery
T_{wb} indicates max amount of vapor that can be carried the dry gas

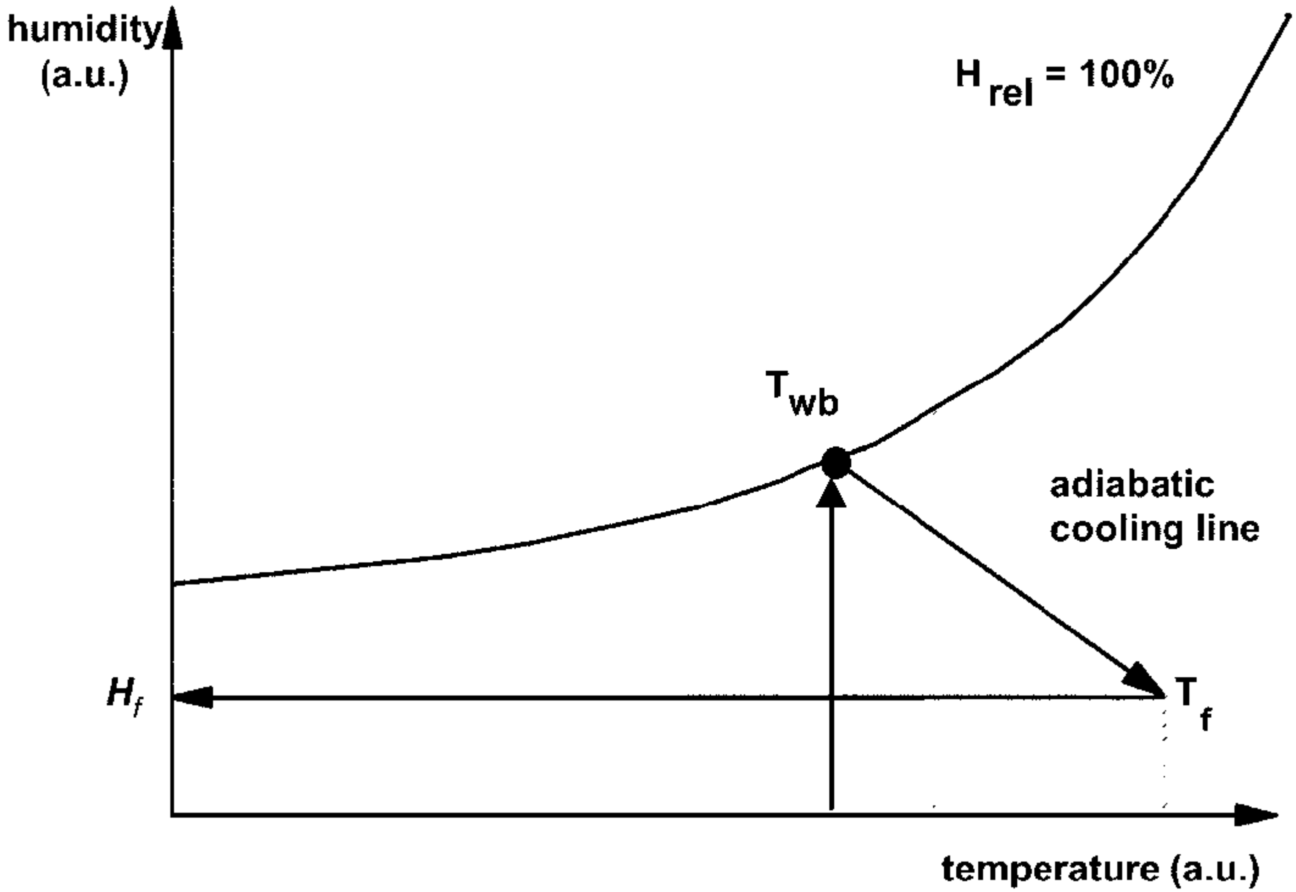
Air Humidity – From Wet-Bulb Temp.





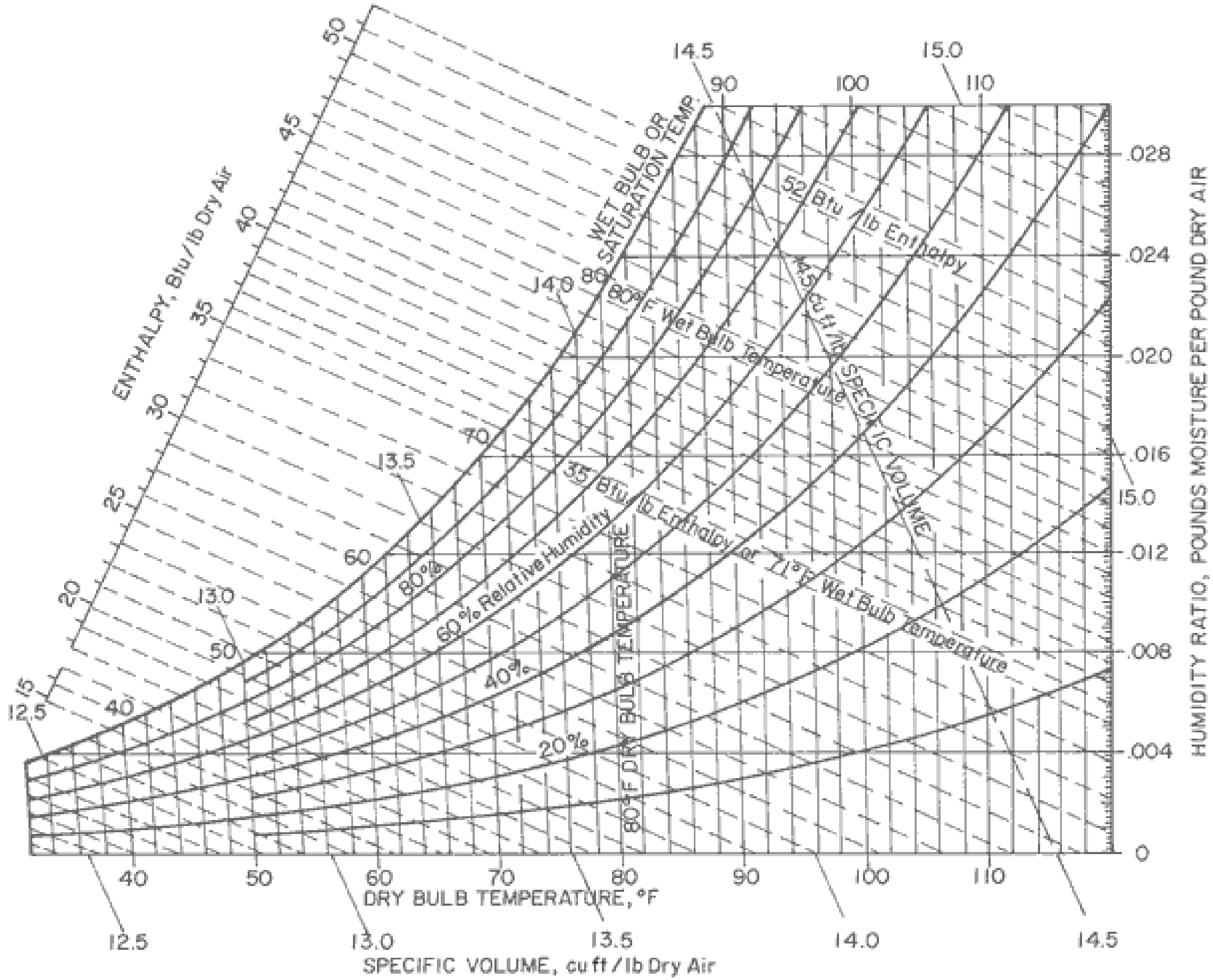
Psychrometer – measures directly the wet-bulb temperature

Air Humidity – From Wet-Bulb Temp.



Relating Wet and Dry-bulb temperatures – via adiabatic cooling lines

Psychrometric Charts



A **grain of water** is approximately one drop, and there are 7,000**grains of water** to one **pound** of **water**

Psychrometric Chart

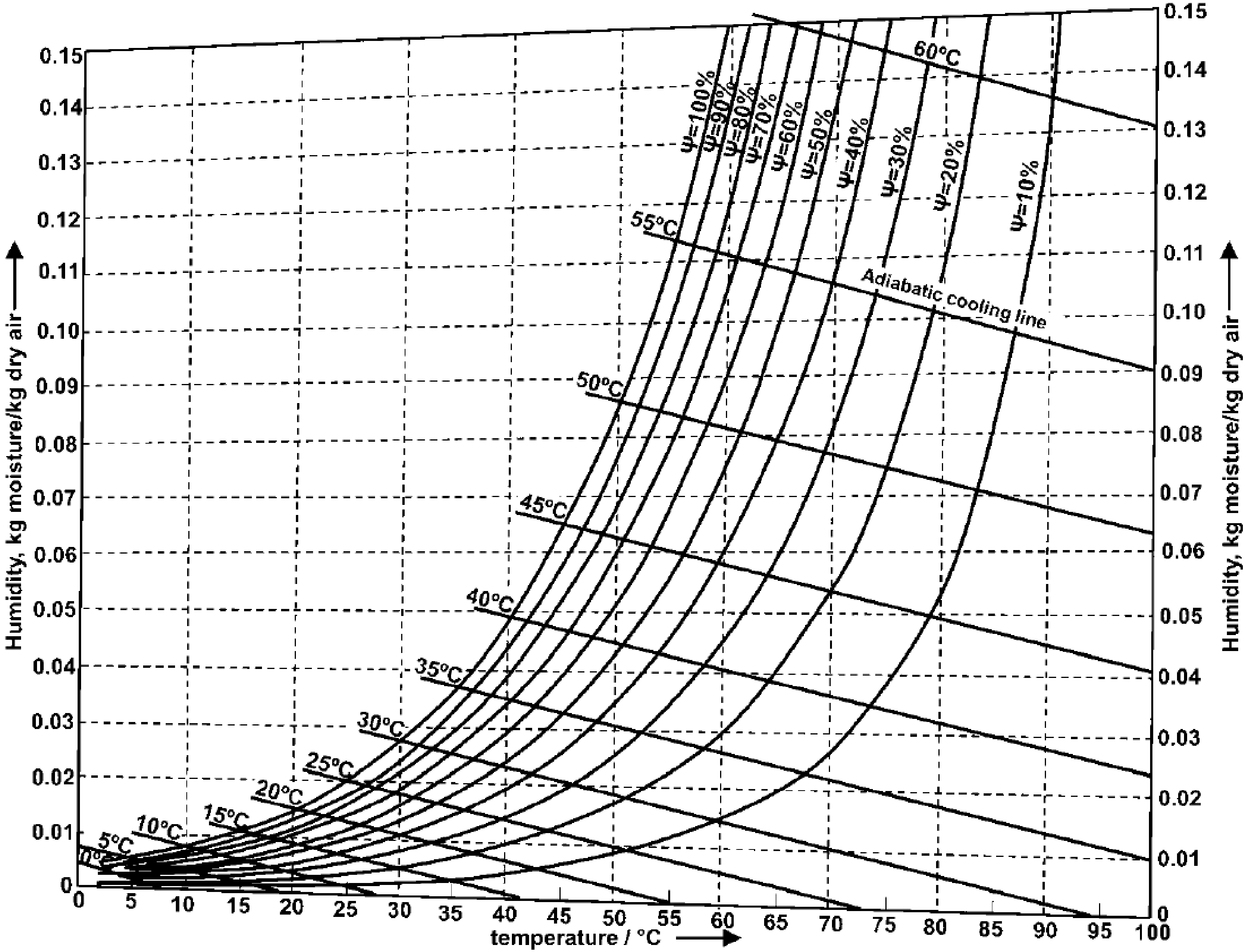
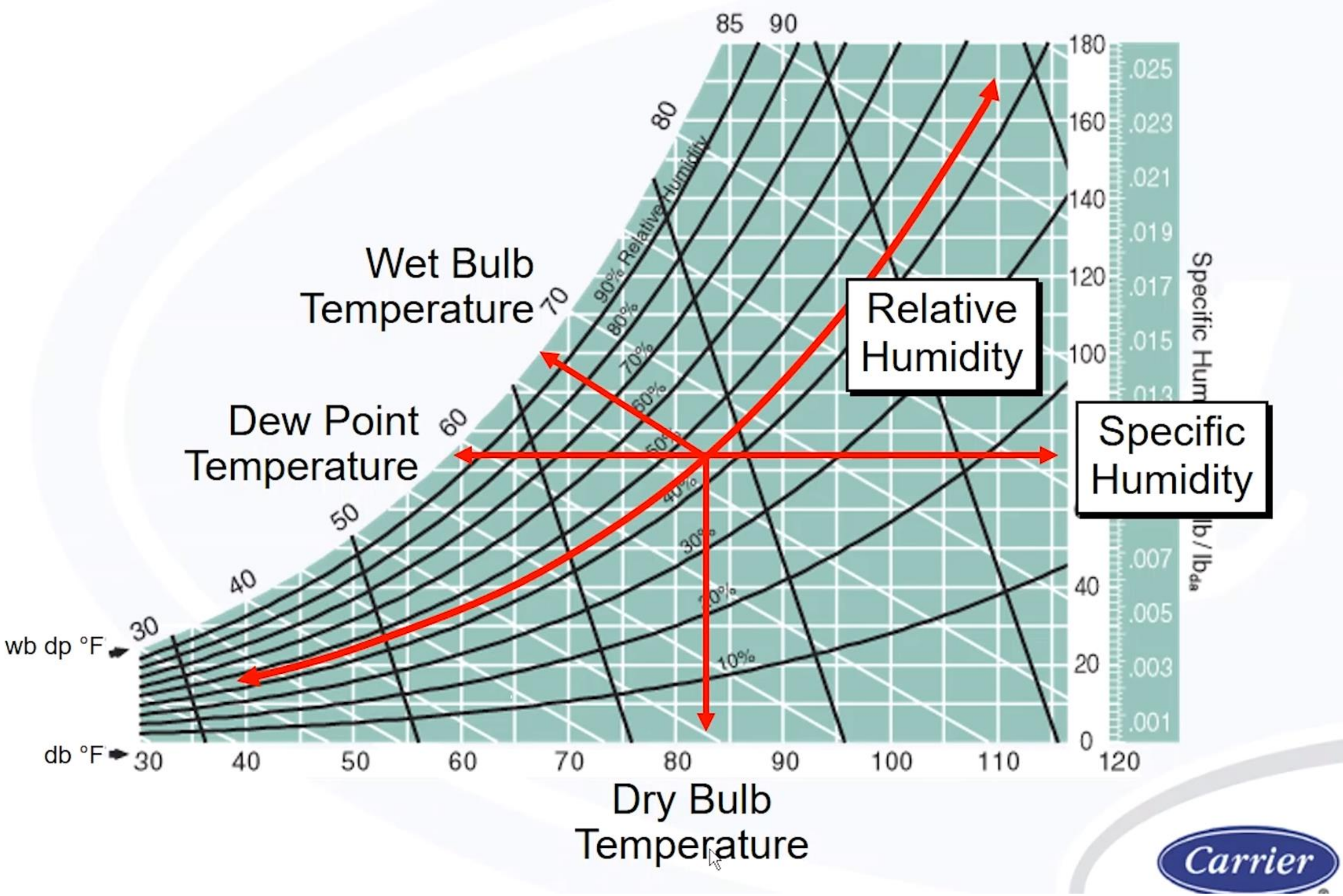
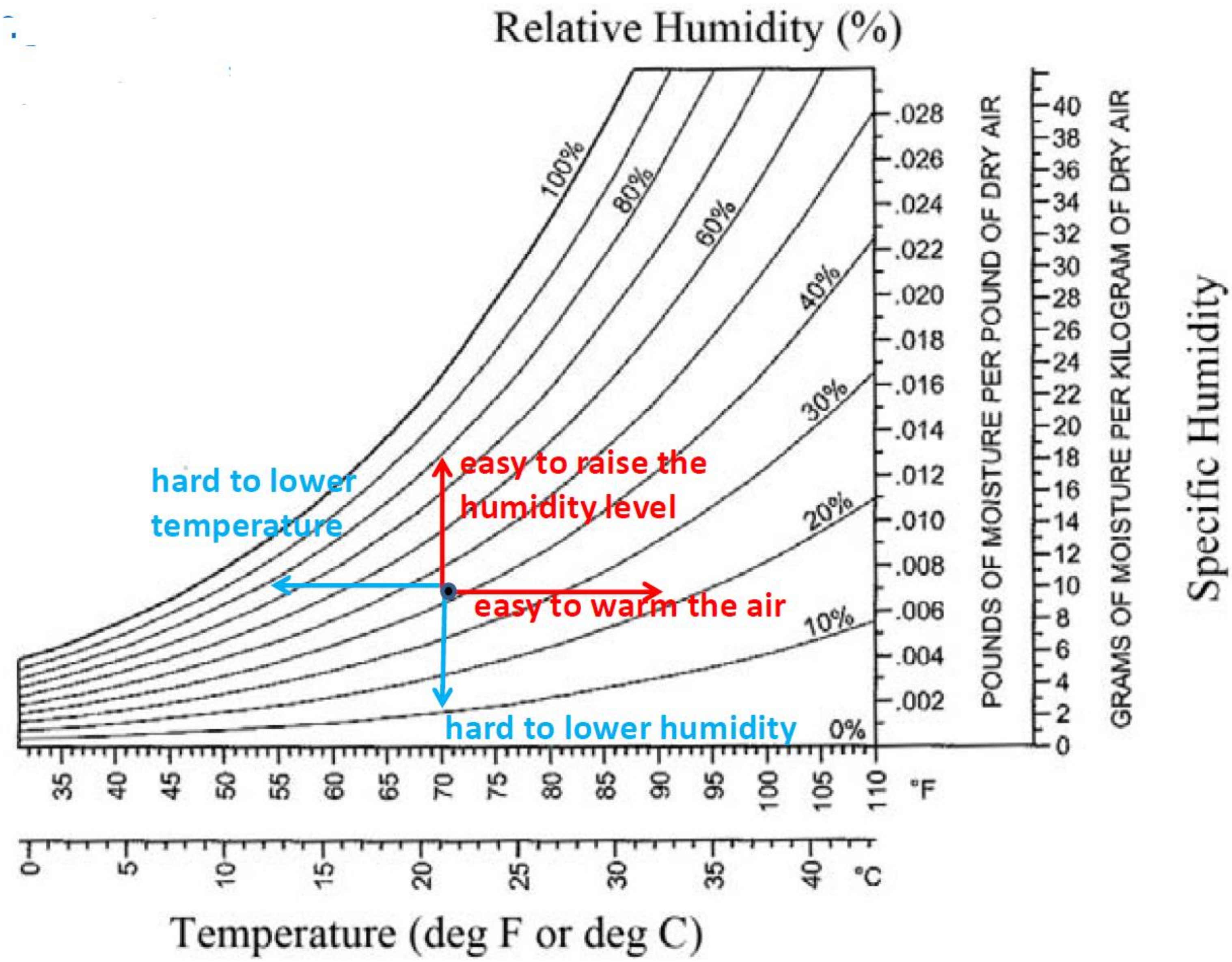


Fig. 7.3 Psychrometric chart of air-water at 1 bar total pressure (adapted from [56]).

Properties of Air - Psychrometric Chart



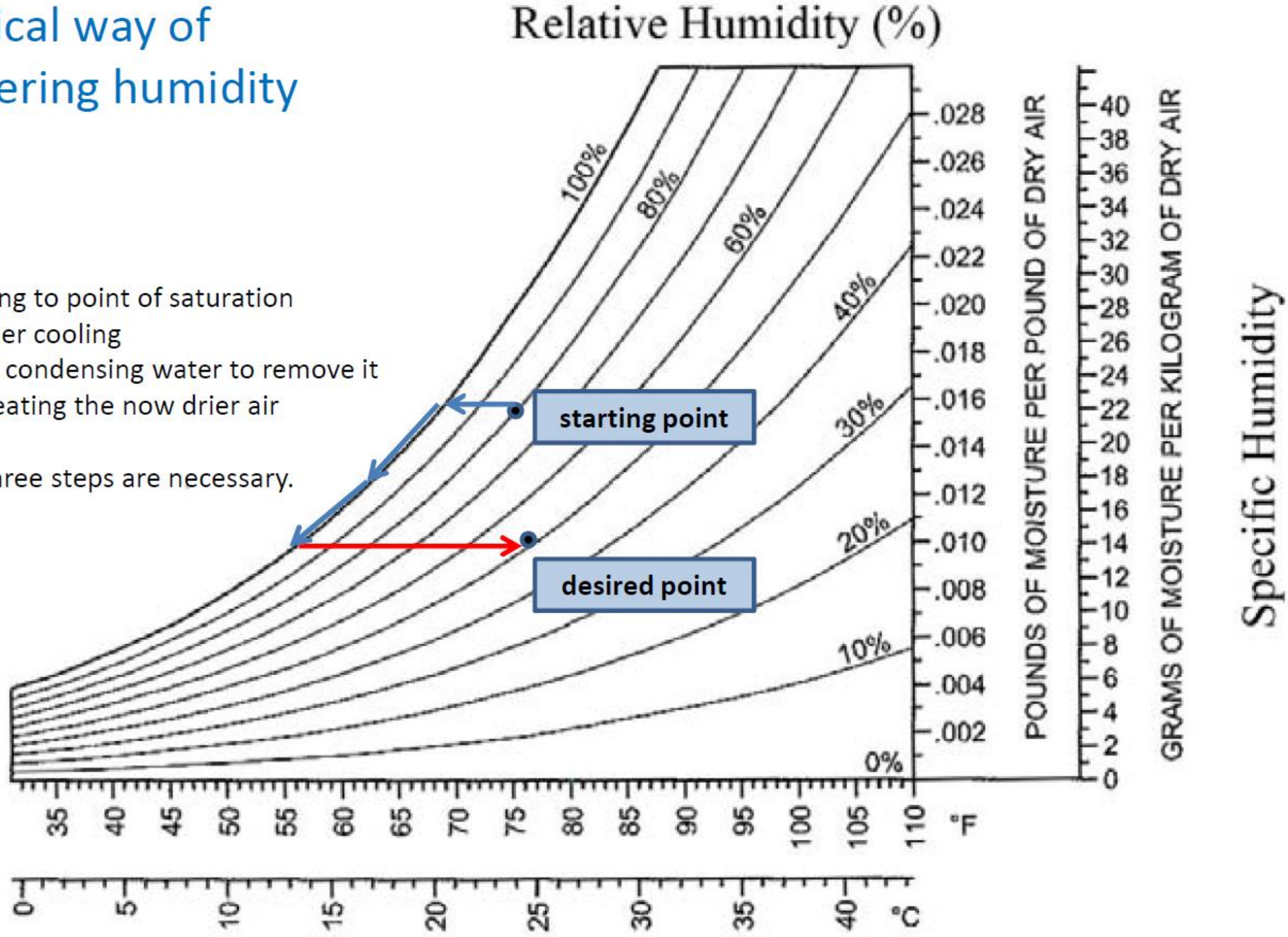
Psychrometric Chart - Practice



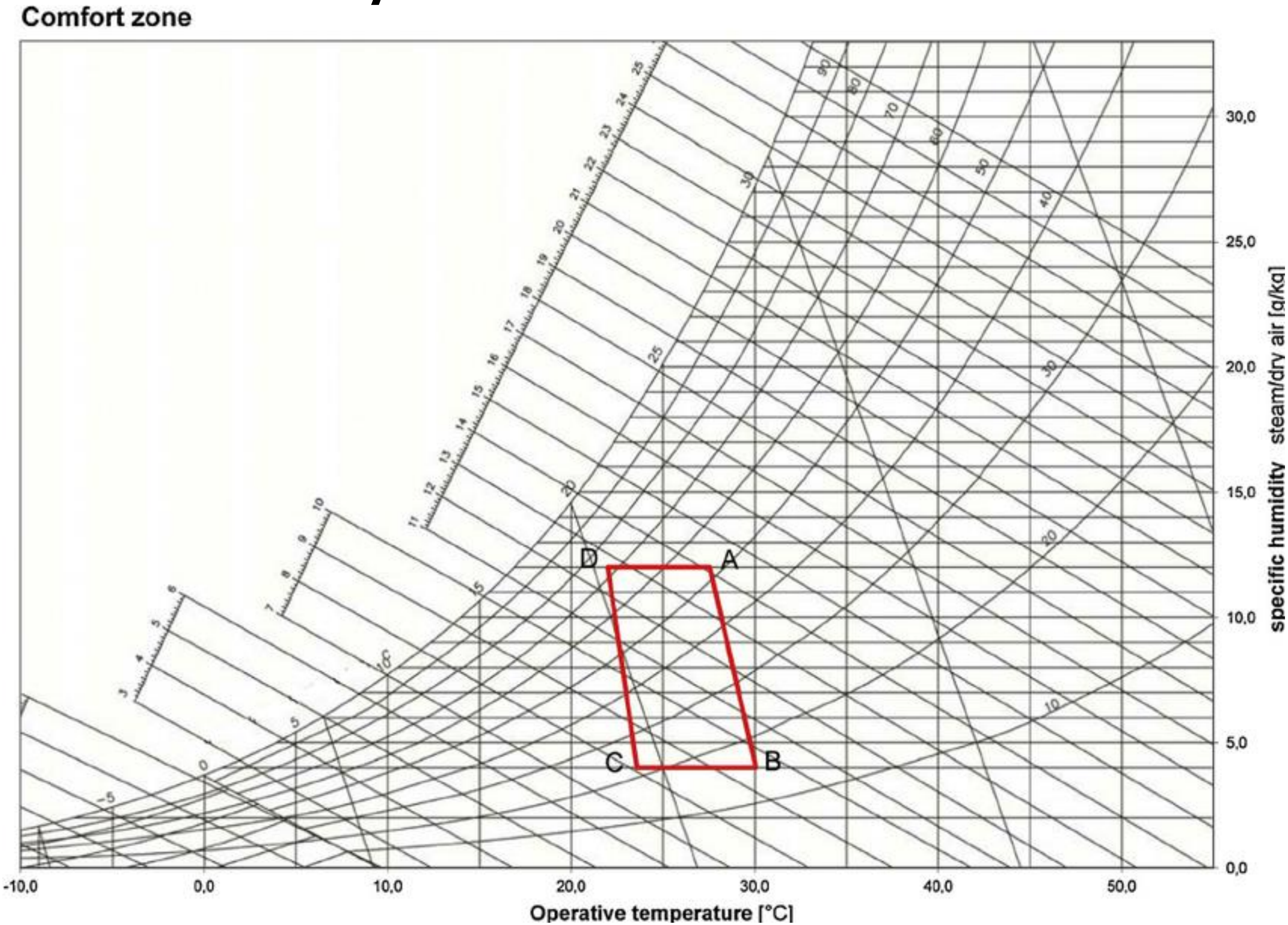
Typical way of lowering humidity

1. Cooling to point of saturation
2. Further cooling
   while condensing water to remove it
3. Re-heating the now drier air

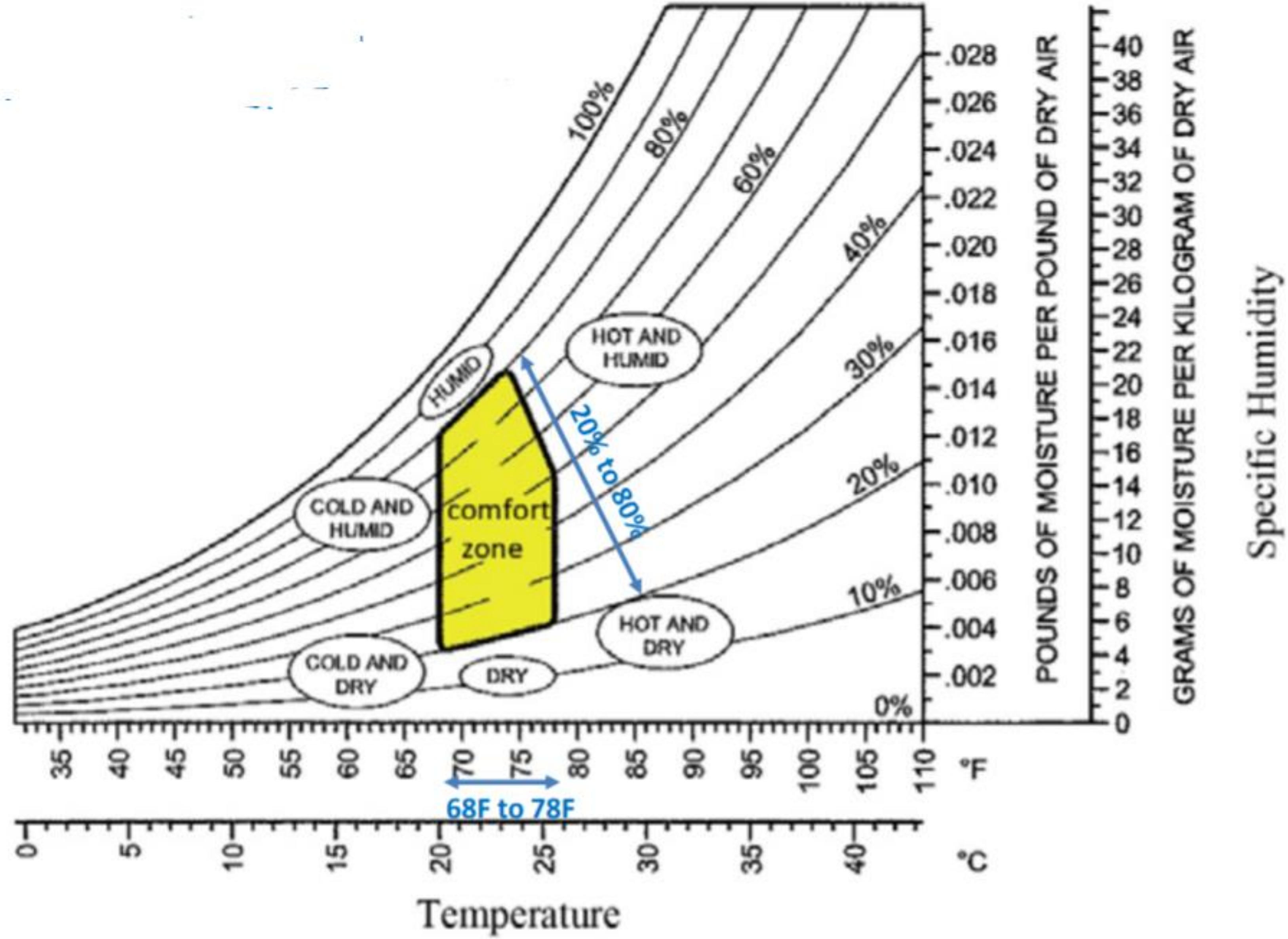
Thus, three steps are necessary.



Psychrometric Chart



Psychrometric Chart



Comfort Zone

◉ **California Energy Code Comfort Model, 2013 (DEFAULT)**

For the purpose of sizing residential heating and cooling systems the indoor Dry Bulb Design Conditions should be between 68°F (20°C) to 75°F (23.9°C). No Humidity limits are specified in the Code, so 80% Relative Humidity and 66°F (18.9°C) Wet Bulb is used for the upper limit and 27°F (-2.8°C) Dew Point is used for the lower limit (but these can be changed on the Criteria screen).

○ **ASHRAE Standard 55 and Current Handbook of Fundamentals Model**

Thermal comfort is based on dry bulb temperature, clothing level (clo), metabolic activity (met), air velocity, humidity, and mean radiant temperature. Indoors it is assumed that mean radiant temperature is close to dry bulb temperature. The zone in which most people are comfortable is calculated using the PMV (Predicted Mean Vote) model. In residential settings people adapt clothing to match the season and feel comfortable in higher air velocities and so have wider comfort range than in buildings with centralized HVAC systems.

http://www.energy-design-tools.aud.ucla.edu/climate-consultant/request-climate-consultant.php

And http://www.energy-design-tools.aud.ucla.edu/

Climate Consultant App

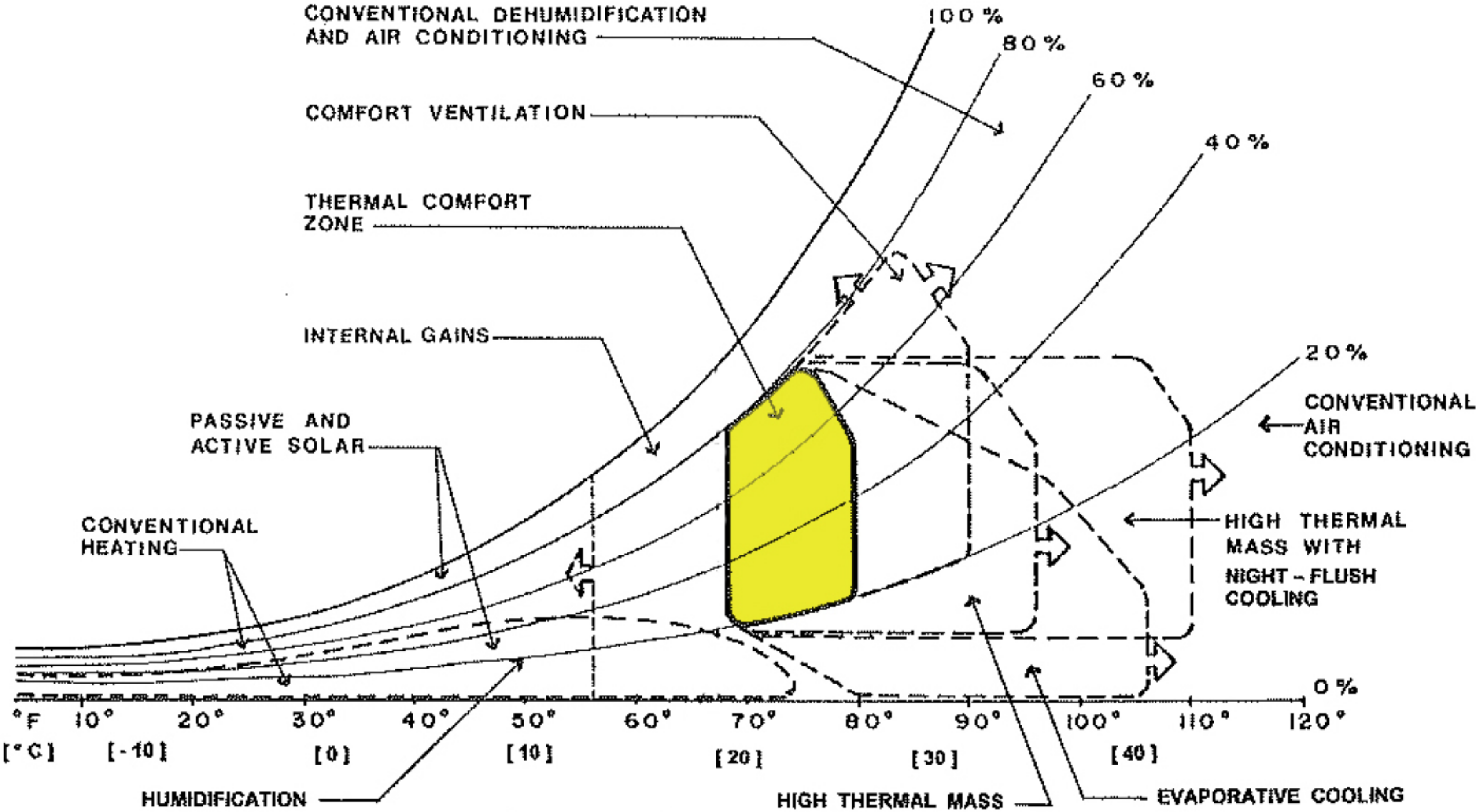
WEATHER DATA SUMMARY

LOCATION: LONDON/GATWICK, -, GBR
Latitude/Longitude: 51.15° North, 0.18° West, **Time Zone from Greenwich** 0
Data Source: IWEC Data 037760 WMO Station Number, **Elevation** 62 m

MONTHLY MEANS	JAN	FEB	MAR	APR	MAY	JUN	JUL	AUG	SEP	OCT	NOV	DEC	
Global Horiz Radiation (Avg Hourly)	87	125	181	267	318	301	317	303	237	167	111	70	Wh/sq.m
Direct Normal Radiation (Avg Hourly)	126	129	113	205	221	167	197	223	183	170	106	67	Wh/sq.m
Diffuse Radiation (Avg Hourly)	56	81	127	145	174	181	182	163	139	97	79	54	Wh/sq.m
Global Horiz Radiation (Max Hourly)	285	447	644	803	884	893	869	811	689	559	351	223	Wh/sq.m
Direct Normal Radiation (Max Hourly)	693	790	846	881	858	854	833	837	800	789	680	466	Wh/sq.m
Diffuse Radiation (Max Hourly)	157	224	348	420	434	459	472	427	386	262	193	133	Wh/sq.m
Global Horiz Radiation (Avg Daily Total)	709	1194	2116	3636	4910	4906	5019	4351	2973	1747	969	548	Wh/sq.m
Direct Normal Radiation (Avg Daily Total)	1024	1222	1309	2784	3441	2729	3117	3203	2306	1775	928	527	Wh/sq.m
Diffuse Radiation (Avg Daily Total)	461	779	1492	1983	2680	2953	2885	2336	1732	1011	691	422	Wh/sq.m
Global Horiz Illumination (Avg Hourly)	9464	13705	19994	29208	34964	33516	35144	33463	26111	18298	12092	7719	lux
Direct Normal Illumination (Avg Hourly)	9816	11252	10630	19924	21383	16366	18845	21293	17287	15267	8703	5091	lux
Dry Bulb Temperature (Avg Monthly)	4	3	6	8	12	15	17	16	13	10	7	5	degrees C
Dew Point Temperature (Avg Monthly)	1	1	3	3	7	9	12	11	9	8	5	3	degrees C
Relative Humidity (Avg Monthly)	81	84	78	75	73	70	75	75	75	86	87	88	percent
Wind Direction (Monthly Mode)	200	80	280	70	210	20	200	210	10	70	180	220	degrees
Wind Speed (Avg Monthly)	3	2	4	3	3	3	2	2	3	2	2	3	m/s
Ground Temperature (Avg Monthly of 3 Depths)	5	6	7	8	11	13	14	14	12	10	7	6	degrees C

http://www.energy-design-tools.aud.ucla.edu/climate-consultant/request-climate-consultant.php
And weather data from
https://energyplus.net/weather-location/europe_wmo_region_6/GBR//GBR_London.Gatwick.037760_IWEC

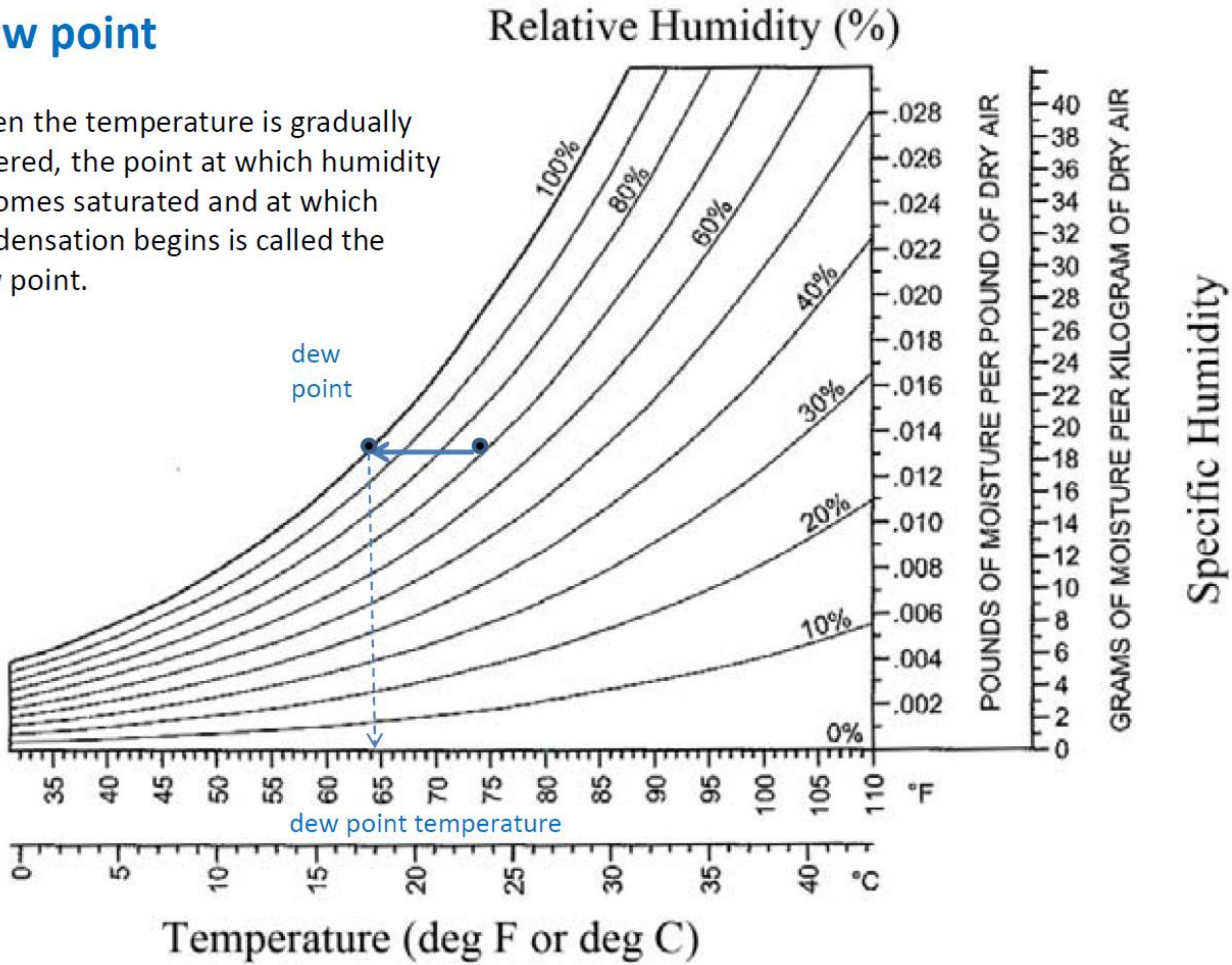
Various technologies
to bring indoor air conditions into the comfort zone



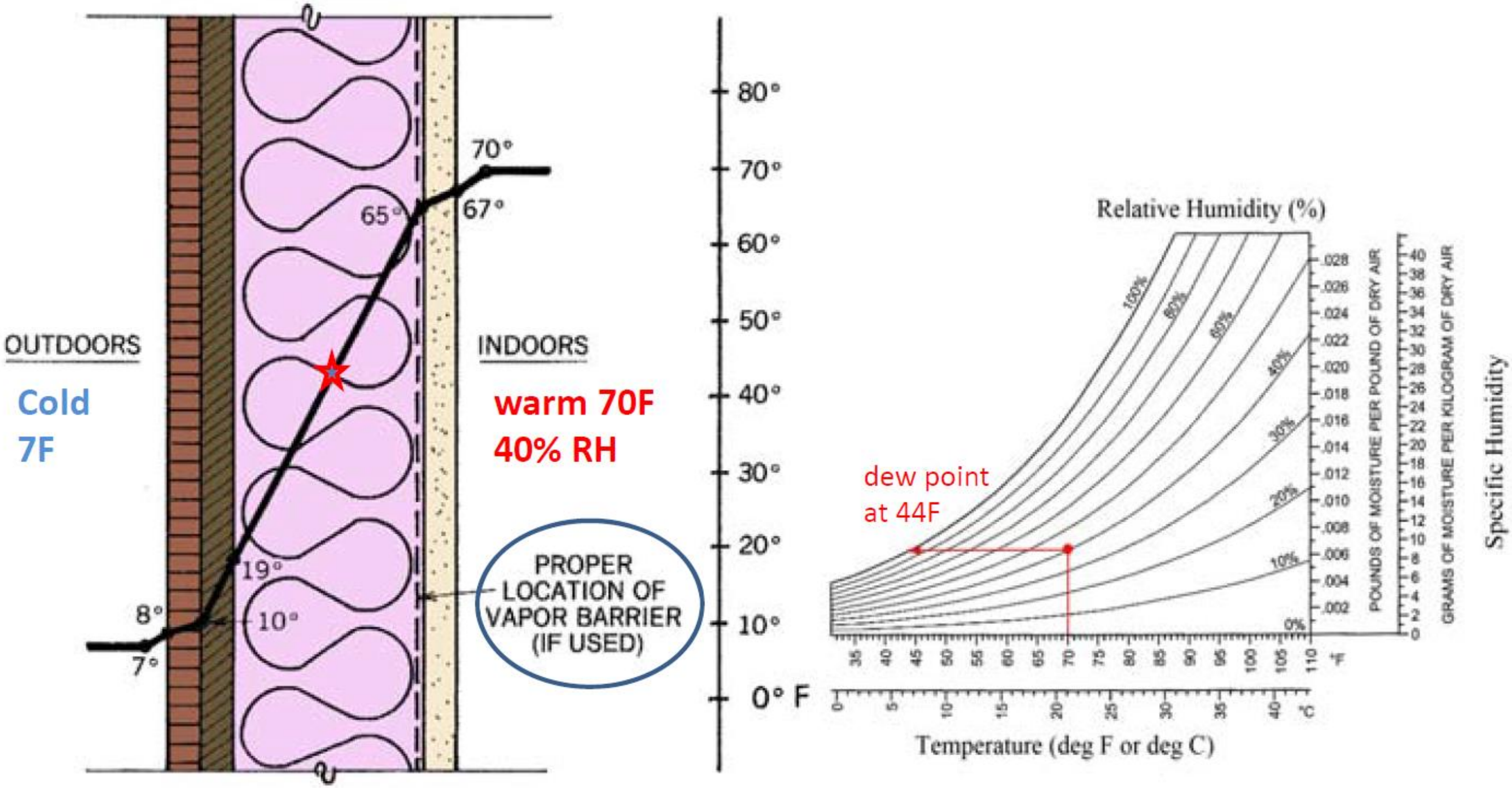
(From *Psychrometric-Bioclimatic Chart*, copyright by Baruch Givoni and Murray Milne.)

Dew point

When the temperature is gradually lowered, the point at which humidity becomes saturated and at which condensation begins is called the dew point.



Danger – Reaching Dew Point in a Wall



Vapour barriers – needed to prevent mould

Psychrometric Chart

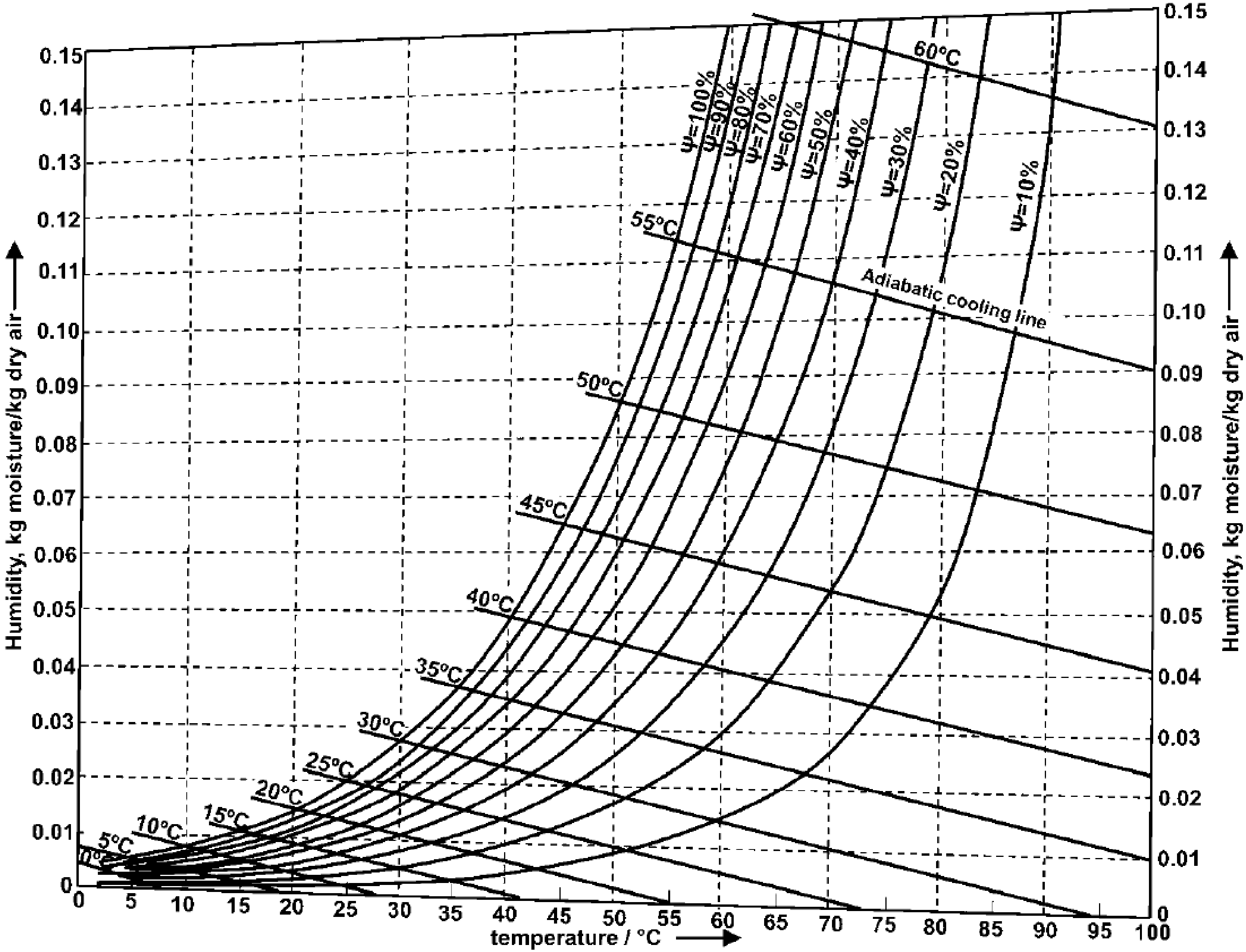


Fig. 7.3 Psychrometric chart of air-water at 1 bar total pressure (adapted from [56]).

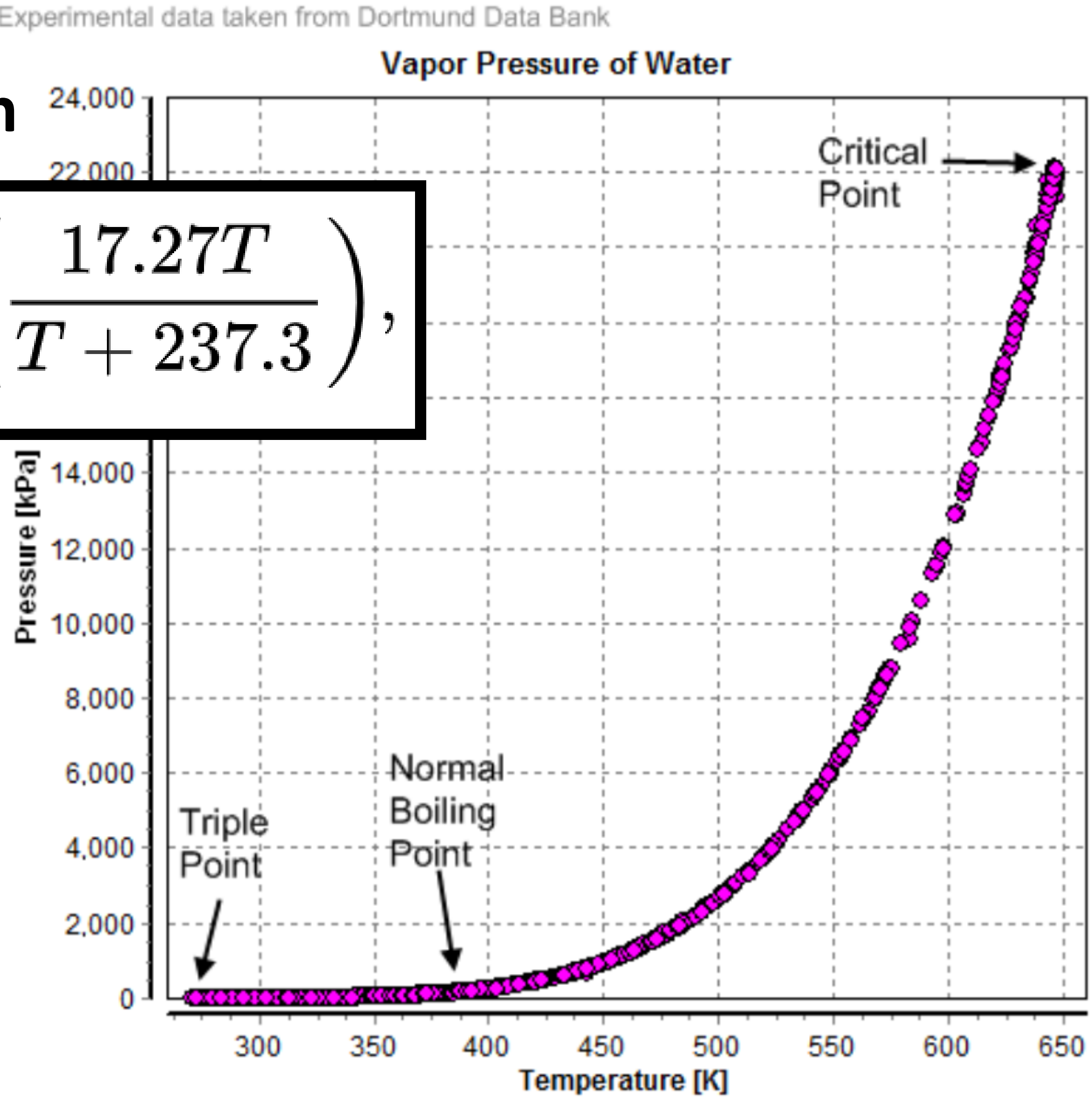
Saturation Vapor Pressure of Water

The Tetens equation

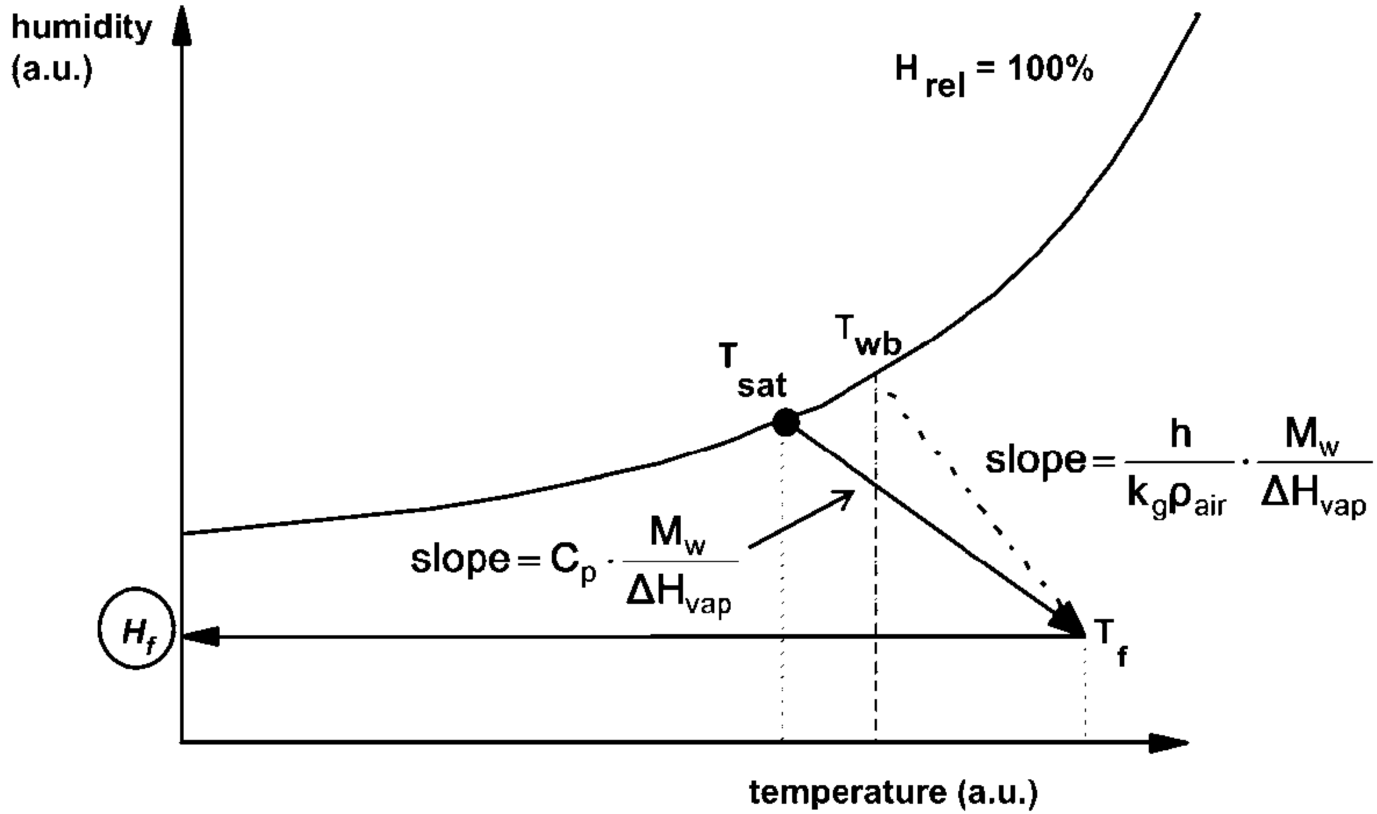
$$P = 0.61078 \exp\left(\frac{17.27T}{T + 237.3}\right),$$

where
T = temperature in °C
and *P* = pressure in kPa

Above form valid for
T > 0 °C



Air Humidity – From Wet-Bulb Temp.



Longer contact with cool water leads to temp. T_{sat} less than T_{wb} (not an adiabatic process anymore)

When stream of air Φ_{air} at T_f is mixed thoroughly and **adiabatically**, with liquid at T_{sat}, it leaves completely saturated with vapors (@Tsat)

In **Adiabatic** cooling dry bulb temperature is lowered without altering the amount of heat in the air. Latent Heat is the heat in the gas absorbed by the moisture as it changes from liquid to vapor during **evaporation**.

Drying – Slowly at Low Vapor Pressures

For low drying rates, and low vapor concentrations c, drying rate Φ_{vap} is proportional to the driving force $(c_{sat(Ts)} - c_f)$

Drying rate Φ_{vap} $= k_g\,(c_{sat(Ts)} - c_f)$

units [mol s^{-1} m^{-2}]

where

T_f = temperature of heated air (with concentration c_f)

T_s = temperature of wet surface [K]

c_{sat} = saturation vapor (water) concentration at T_s [mol m^{-3}]

c_f = vapor (water) concentration in *feed* gas (air) [mol m^{-3}]

k_g = mass transfer coefficient [m s^{-1}]

Drying – Wet Bulb Temperature

When the amount of air >> amount of evaporated moisture
The dynamic equilibrium (non-equilibrium steady state)
Temperature of a wet surface is called T_{wb}, the **wet-bulb temperature**

$$\Phi_{vap} \cdot \Delta H_{vap} \quad = \quad h\,(T_f - T_{wb}) \qquad \text{units [J s}^{-1}\text{ m}^{-2}]$$

Drying rate — *Energy transfer*
Energy — *from the surface*

where
h = heat transfer coefficient (convection) [W m^{-2} K^{-1}]
ΔH_{vap} = molar heat of evaporation [K]

Examples – Passive cooling in non-glazed pottery
T_{wb} indicates max amount of vapor that can be carried the dry gas

Air Humidity – Measurement & Units

When Humidity is measured as

Moisture content H_f per unit dry air

it is easy to find the mix's heat capacity

$C_p = C_{p,\ dry\ air} + H_f \cdot C_{p,\ vapor}$ [J/K.kg]

Then combining Drying rate

$\Phi_{vap} = k_g\,(c_{sat(Ts)} - c_f)$ [mol s^{-1} m^{-2}] and

Energy Transfer rate:

$\Phi_{vap} \cdot \Delta H_{vap} = h\,(T_f - T_{wb})$ units [J s^{-1} m^{-2}]

we get:

$$c_{sat(Twb)} - c_f = \frac{h\,(T_f - T_{wb})}{\Delta H_{vap} \cdot k_g}$$ [mol s^{-1} m^{-2}]

Heat Transfer vs. Mass Transfer

Entity	Diffusivity	Diffusive flux	Transport coefficient	Dimensionless group
Heat	α	$q_z = -\alpha \frac{\mathrm{d}(\rho c_p T)}{\mathrm{d}z}$	$h:\ q_z = h\Delta T$	$\mathrm{Nu} := \frac{hL}{\lambda}$
Mass	D	$J_z = -D_{AB}\frac{\mathrm{d}C_A}{\mathrm{d}z}$	$k:\ J_{Az} = k\Delta C_A$	$\mathrm{Sh} := \frac{kL}{D_{AB}}$
Momentum	ν	$\tau_{zx} = -\nu \frac{\mathrm{d}(\rho \mathrm{v}_x)}{\mathrm{d}z}$	$\frac{f}{2}:\ \tau_{zx} = -\frac{f}{2}\rho \mathrm{v}_{x,\infty}^2$	$\frac{f}{2} = \frac{\mu}{\rho \mathrm{v}_{x,\infty}^2}\frac{\mathrm{d}\mathrm{v}_x}{\mathrm{d}z}\Big\vert_{y=0}$

Reynolds analogy – ok for ideal gases

$$\frac{f}{2} = \frac{k}{\mathrm{v}} = \frac{h}{\rho c_p \mathrm{v}}$$

f = Fanning's friction factor
Sc = Schmidt number
Pr = Prandtl number

Chilton–Colburn J-factor analogy – also for liquids

$$J_M = \frac{f}{2} = J_H = \frac{h}{c_p\, G} Pr^{\frac{2}{3}} = J_D = \frac{k_c'}{\bar{v}} \cdot Sc^{\frac{2}{3}}$$

Chilton-Colburn analogy of transfer numbers: https://www.youtube.com/watch?v=7YlQ_4jL_gs
In Part 2 of KETF40 Mass Transfer & Unit Operations Course, ChemE, Lund University
https://www.youtube.com/watch?v=bVzYzOCVGd8&list=PLvpgTFzUKO49qlw61JRGCeezUpcqxnhK8

Chilton-Colburn J-factor analogy

Chilton–Colburn analogy – heat & mass transfer

$$J_M = \frac{f}{2} = \frac{Sh}{Re\,Sc^{\frac{1}{3}}} = J_H = \frac{f}{2} = \frac{Nu}{Re\,Pr^{\frac{1}{3}}}$$

If one type of transfer number is known, we can use it to find the value of the others. E.g.,

From the Nusselt number, for heat transfer, we can find the Sherwood number for mass transfer!

Chilton-Colburn analogy of transfer numbers: https://www.youtube.com/watch?v=7YlQ_4jL_gs
In Part 2 of KETF40 Mass Transfer & Unit Operations Course, ChemE, Lund University
https://www.youtube.com/watch?v=bVzYzOCVGd8&list=PLvpgTFzUKO49qlw61JRGCeezUpcqxnhK8

Air Humidity – Adiabatic Saturation

Using the Chilton-Colburn analogy, one can derive:

$$\frac{Nu}{Sh} = \frac{hD_g}{k_g \lambda} = \frac{h}{k_g}\frac{1}{\rho_{air} C_p}\frac{Pr}{Sc} = \left(\frac{Pr}{Sc}\right)^{-1/3} \Rightarrow \frac{h}{k_g} = \rho_{air} C_p \left(\frac{Sc}{Pr}\right)^{2/3}$$

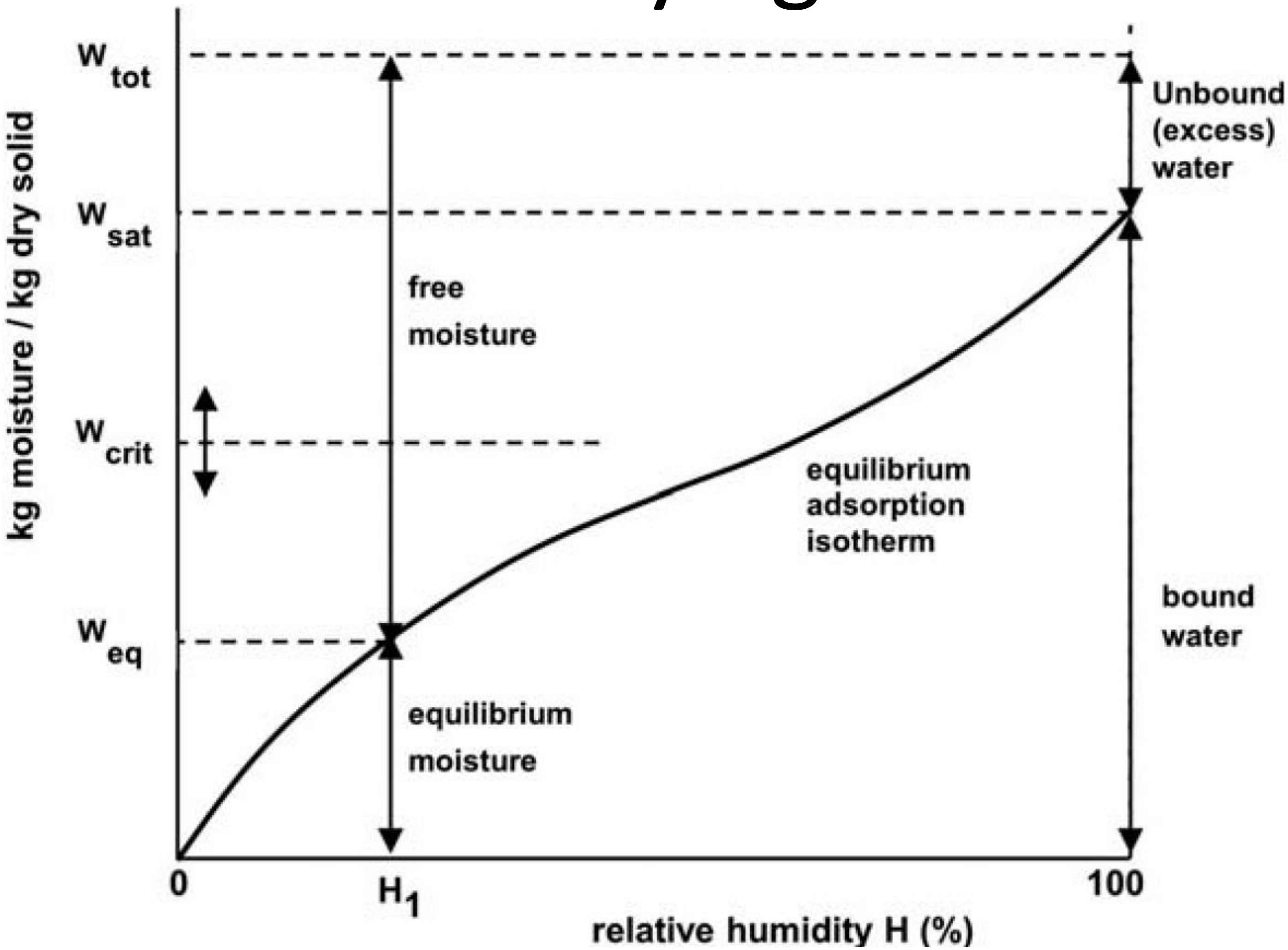
And since *Prandtl & Schmidt #s (Pr, Sc) for air are almost equal,*

$$\frac{h}{\rho_{air} \cdot k_g} \approx Cp$$

therefore, **saturation humidity *H_{sat}*** as a function of Adiabatic **saturation temperature *T_{sat}*** = T_{wb} is:

$$H_{sat} - H_f = C_p \frac{M_w}{\Delta H_{vap}} (T_f - T_{sat})$$

Drying Solids



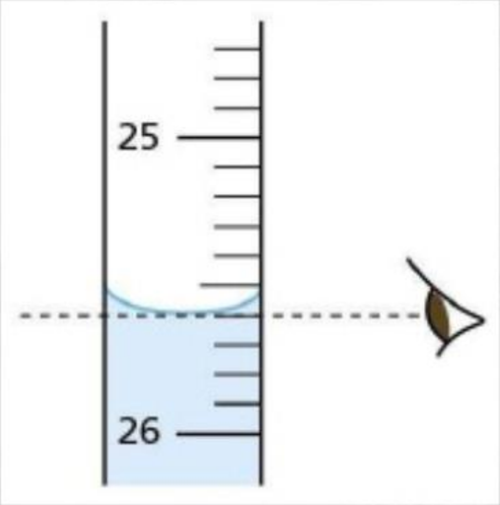
Unbound vs. Free Moisture

Bound/Unbound Water and *Structure of the solid* – lead to different drying regimes and mechanisms

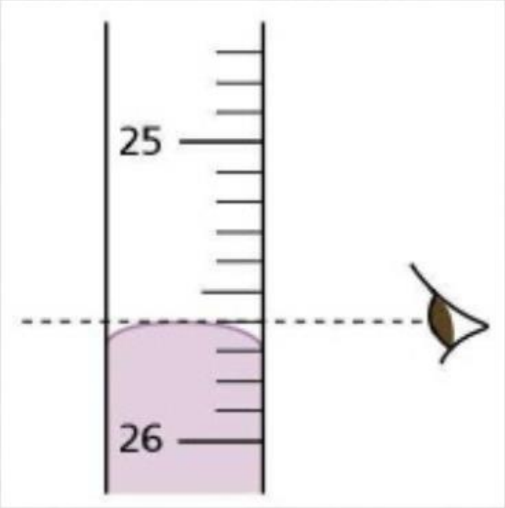
Measuring Volume of Liquids

- Solution when placed in a glass container will form a curved surface called a meniscus.

- If the meniscus is concave, read off the scale at the bottom of the meniscus. If the meniscus is convex, read off the scale at the tope of the meniscus instead.

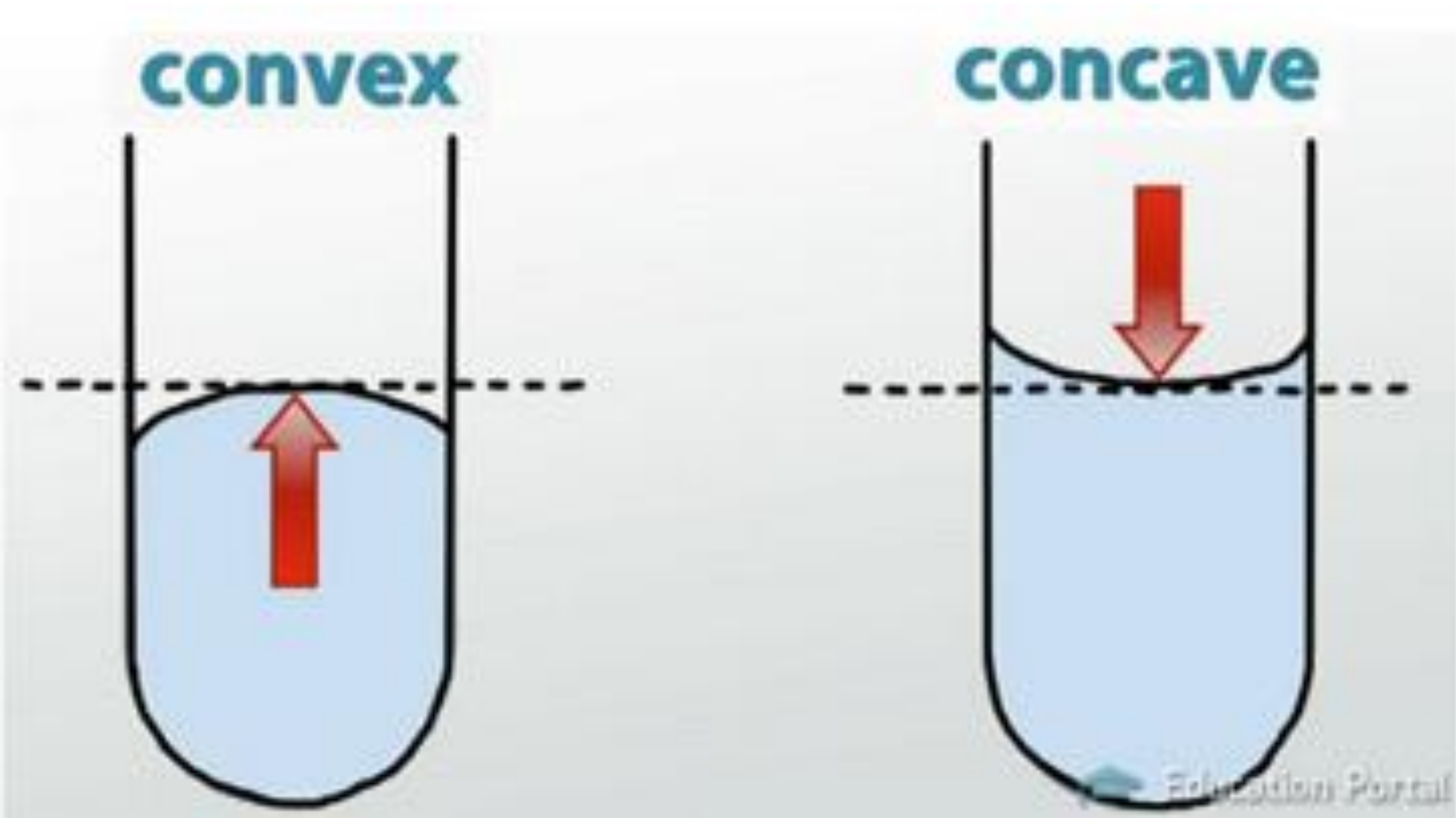


Concave meniscus



Convex meniscus

Drying Solids – Hydrophilicity and Pores



Hydrophobic walls　　　　Hydrophilic walls

The curvature of the menisci in pores determines the pressure of water in the pores.

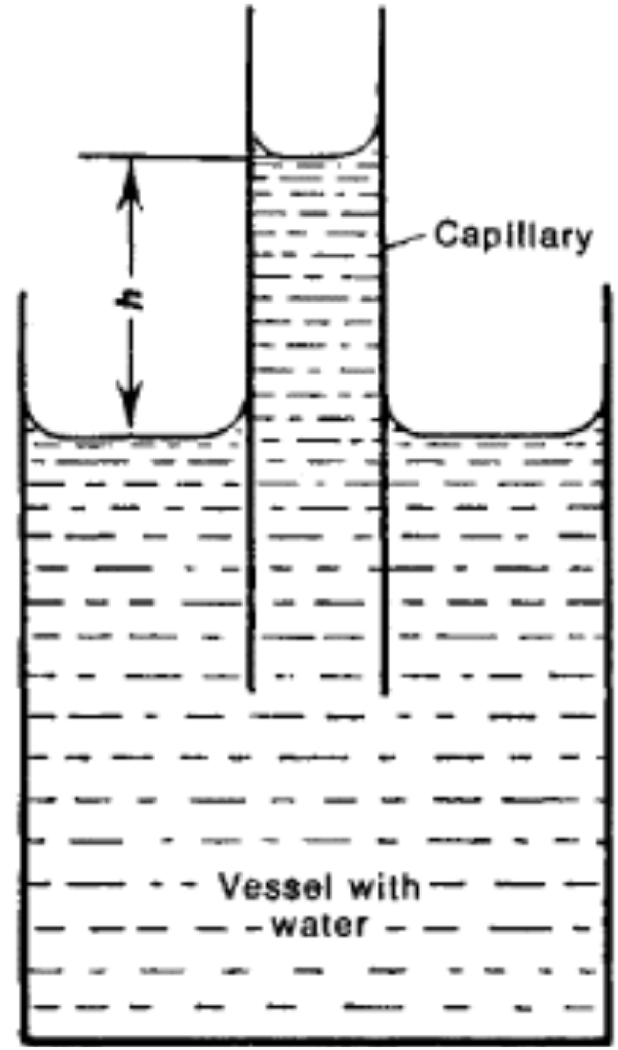
Drying Solids – Water in Pores

$$p_{sat} = p_{sat}^{\infty} \exp \frac{V_{liq}(P_{liq} - P)}{RT}$$

where V_{liq} = molar volume of liquid.

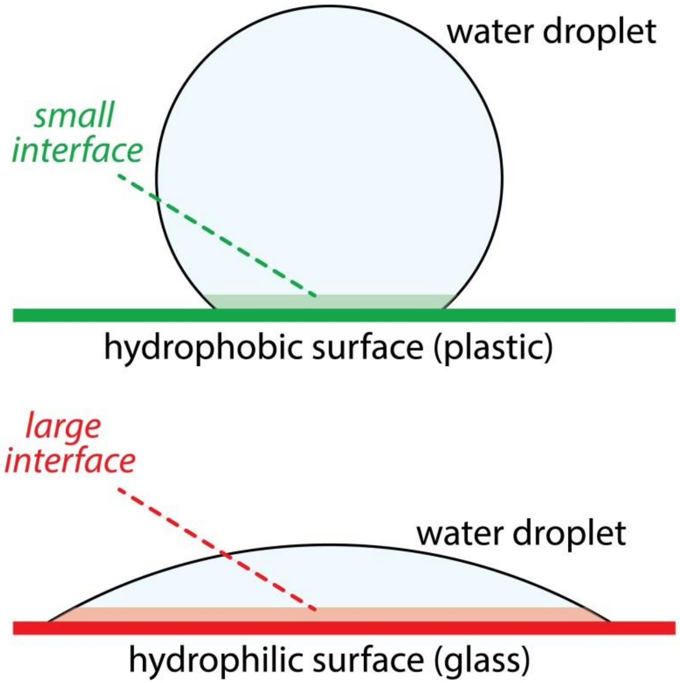
Pressure in the liquid can affect pressure above it

$$P_{liq} - P = \gamma \left(\frac{1}{r_1} + \frac{1}{r_2} \right)$$

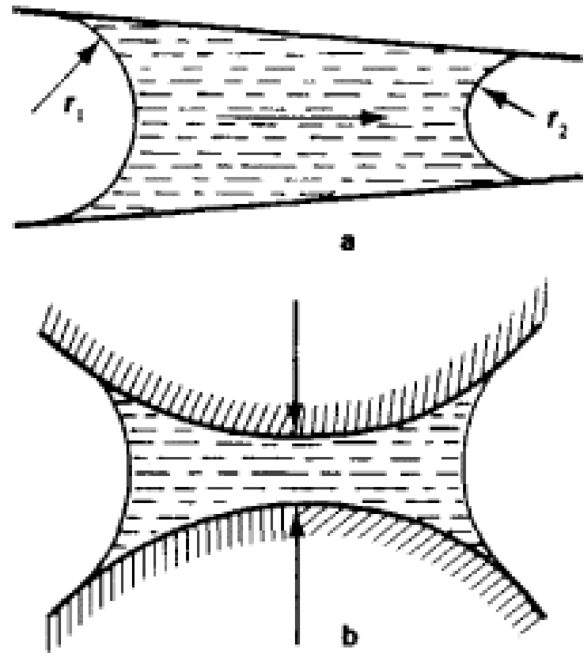


Pressure in curved geometries – from Laplace Eqn.

Pressure in Droplets vs Bubbles



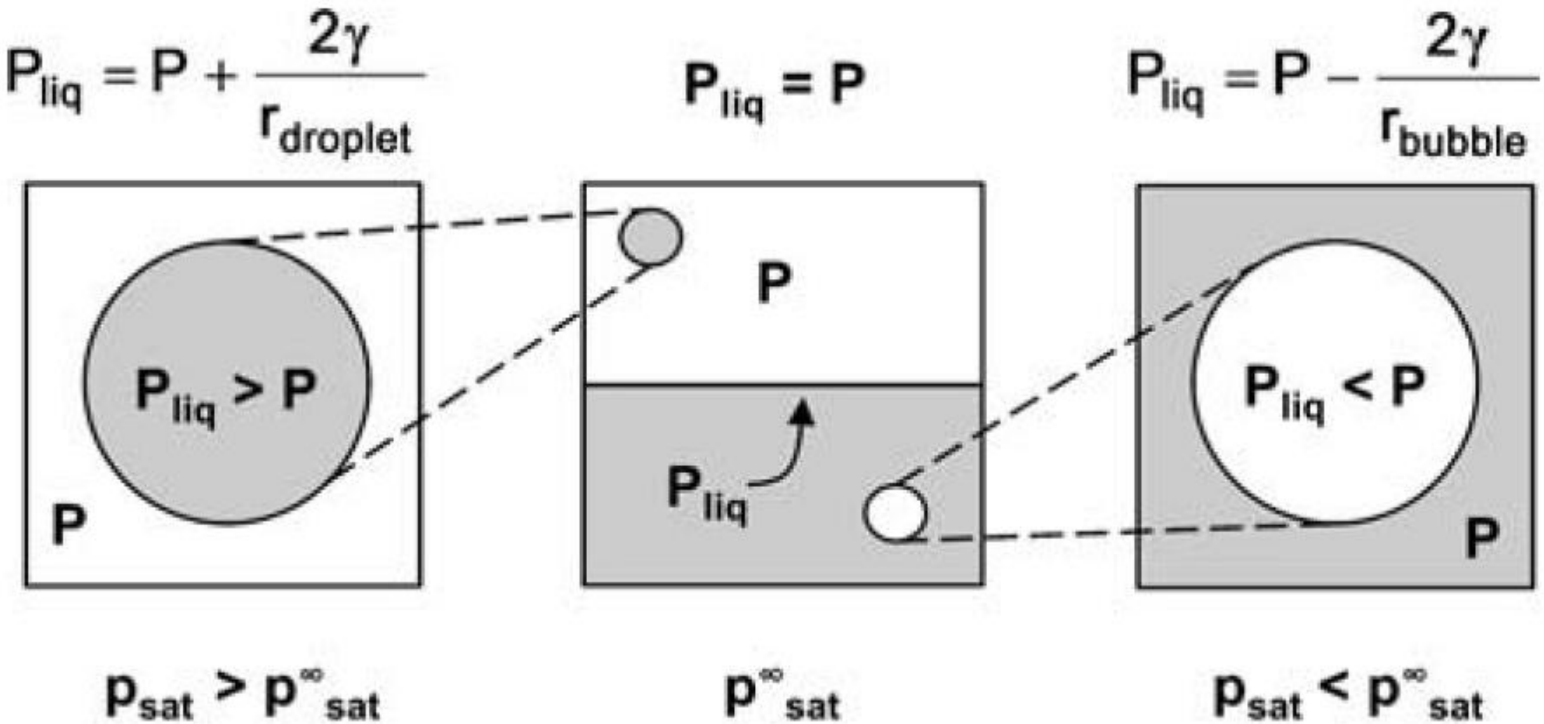
$$\Delta P = \gamma\left(\frac{1}{r_1} + \frac{1}{r_2}\right)$$



Pressure in curved geometries – from Laplace Eqn.

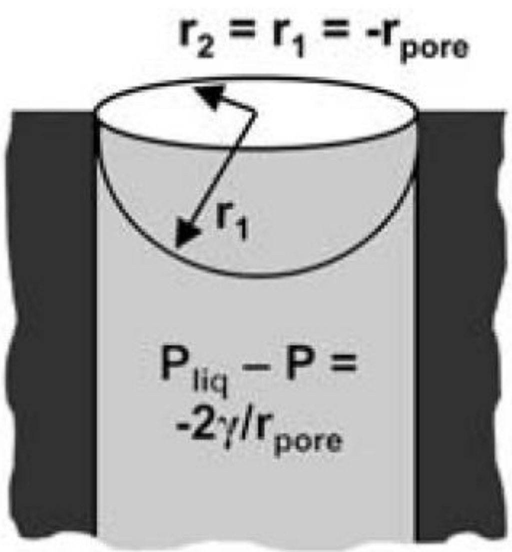
Pressure in Bubbles and Pores

$$\ln \frac{p_{sat}}{p_{sat}^{\infty}} = \frac{V_{liq}\gamma}{RT} \cdot \frac{2}{r_{droplet}} \quad \text{and} \quad \ln \frac{p_{sat}}{p_{sat}^{\infty}} = -\frac{V_{liq}\gamma}{RT} \cdot \frac{2}{r_{bubble}}$$



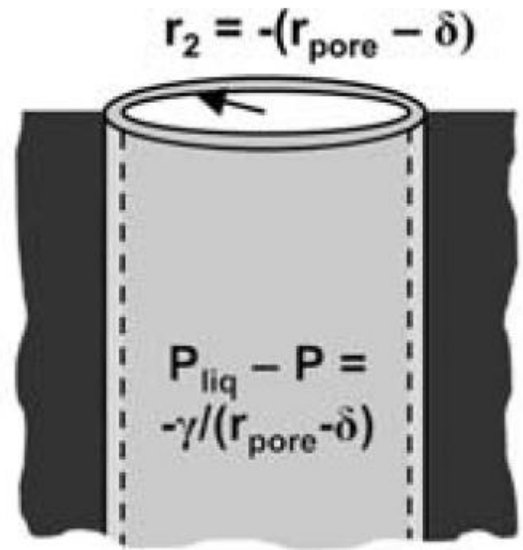
Higher pressure in droplets, lower in bubbles

Pressure in Bubbles and Pores



$$p_{sat} = p_{sat}^{\infty} \exp\left(-\frac{V_{liq}}{RT} \frac{2\gamma}{r_{pore}} \right)$$

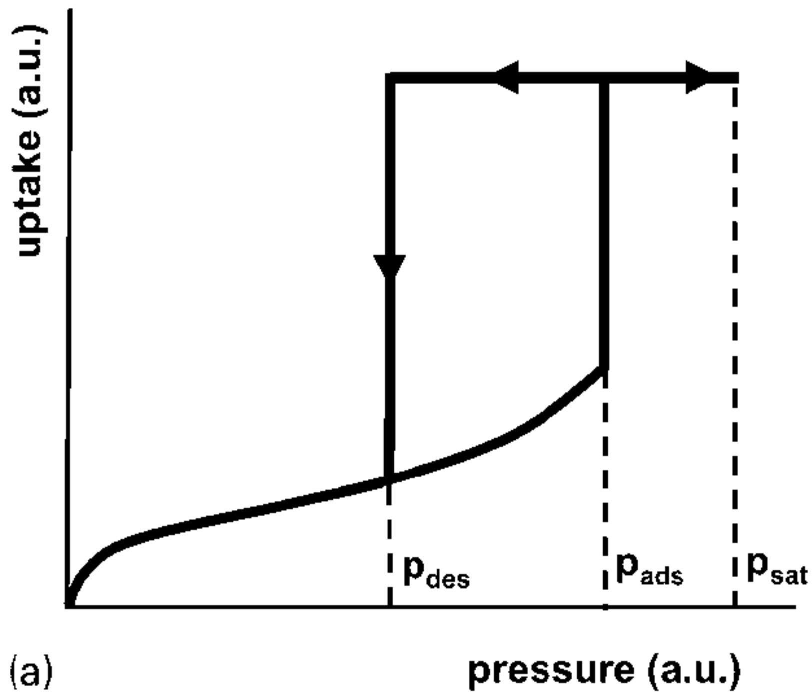
Pressure to empty pore

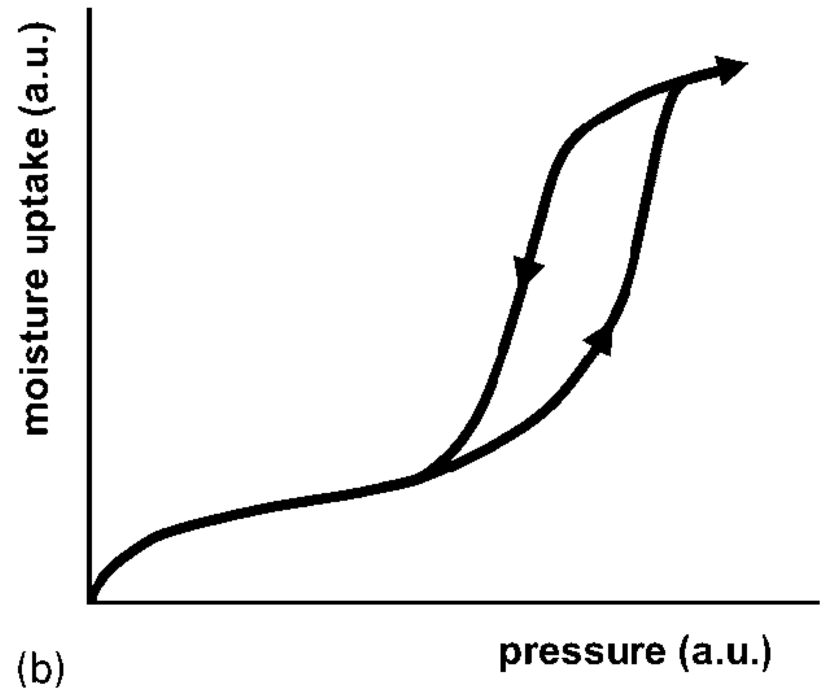


$$p_{sat} = p_{sat}^{\infty} \exp\left(-\frac{V_{liq}}{RT} \frac{\gamma}{r_{pore} - \delta} \right)$$

Pressure to Fill pore

Drying Porous Solids

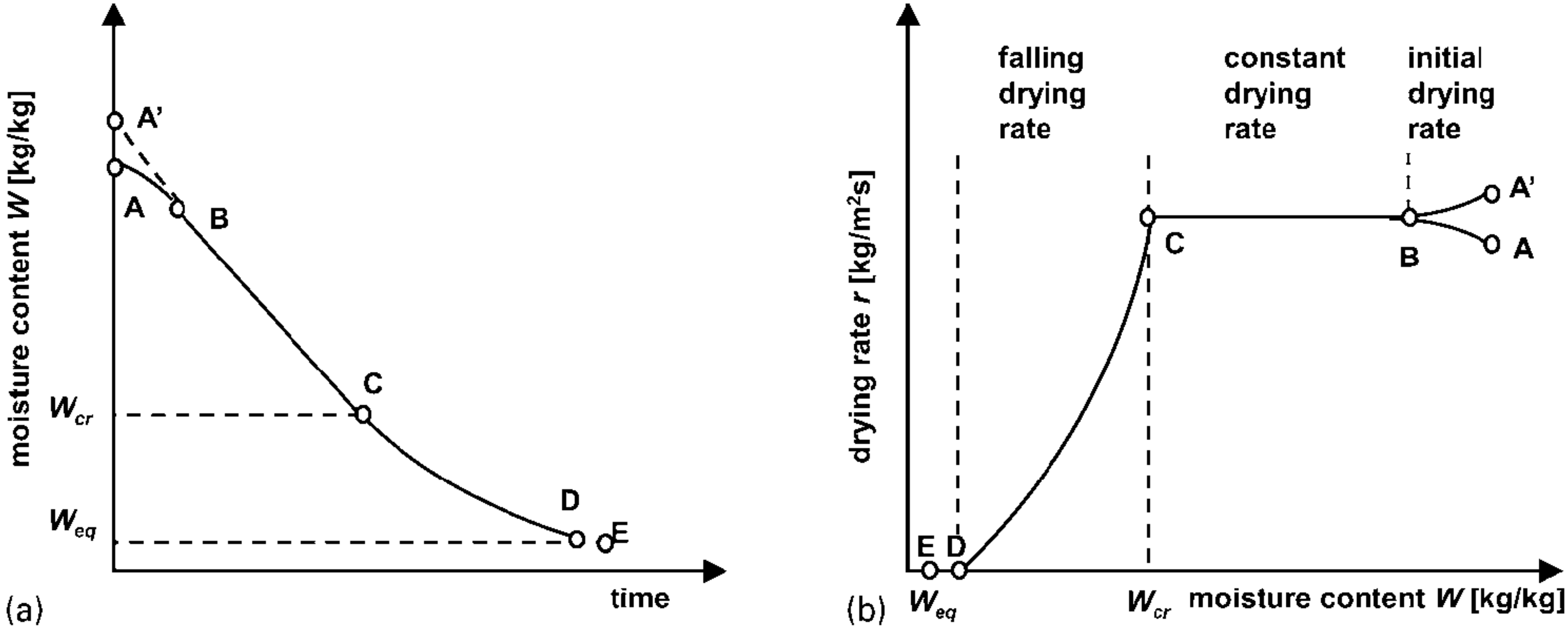




Ideal Cyllinder Pores **Irregular Pores**

Adsorption/ desorption hysteresis

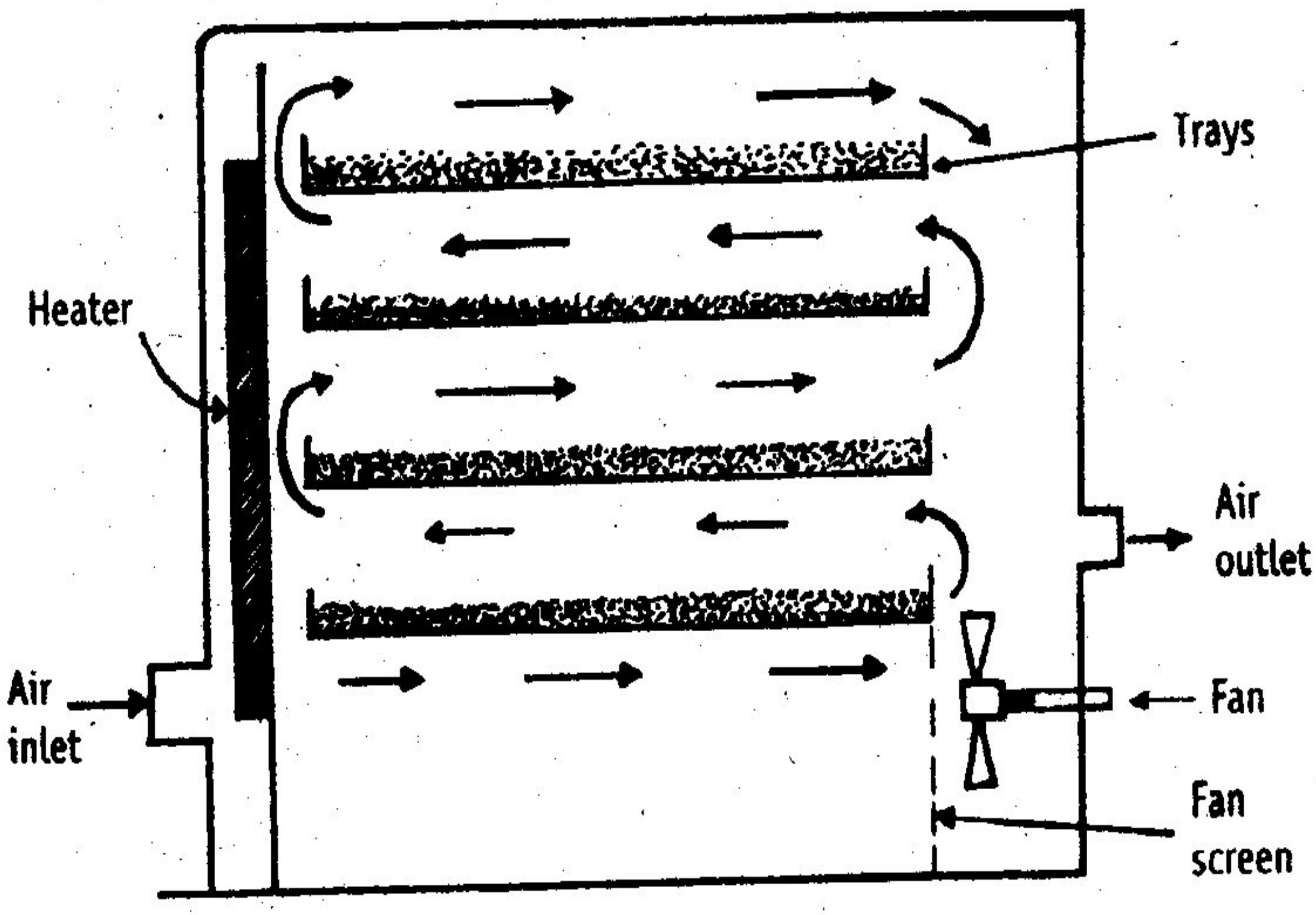
Drying Solids



Drying Curve **Drying Rate**

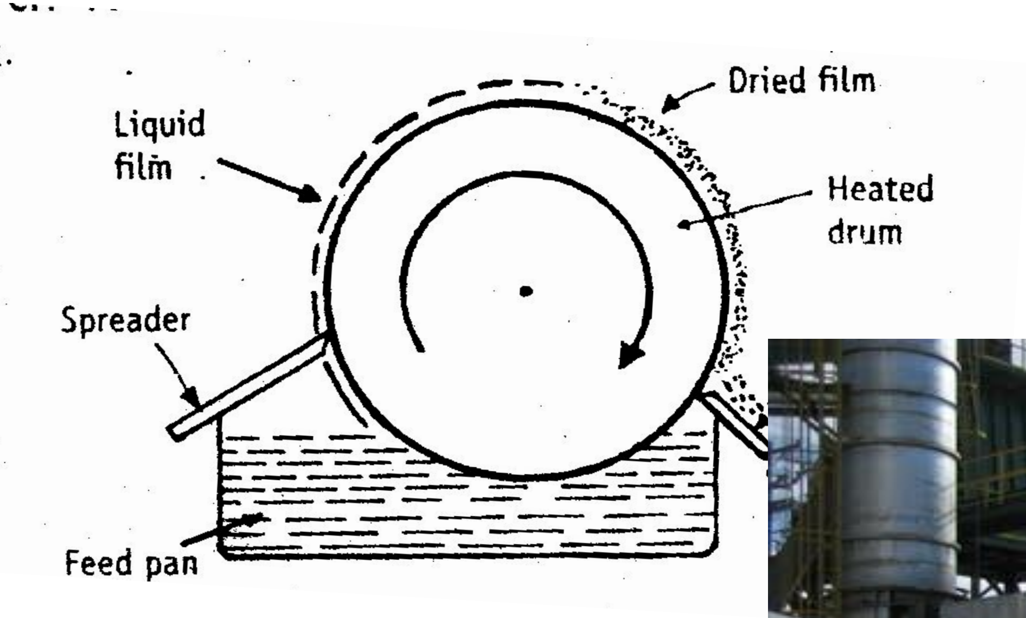
At Critical moisture, surface is dry, water is deeper,
Comes to the surface by diffusion or capillary flow

Drying Solids – Drying Equipment



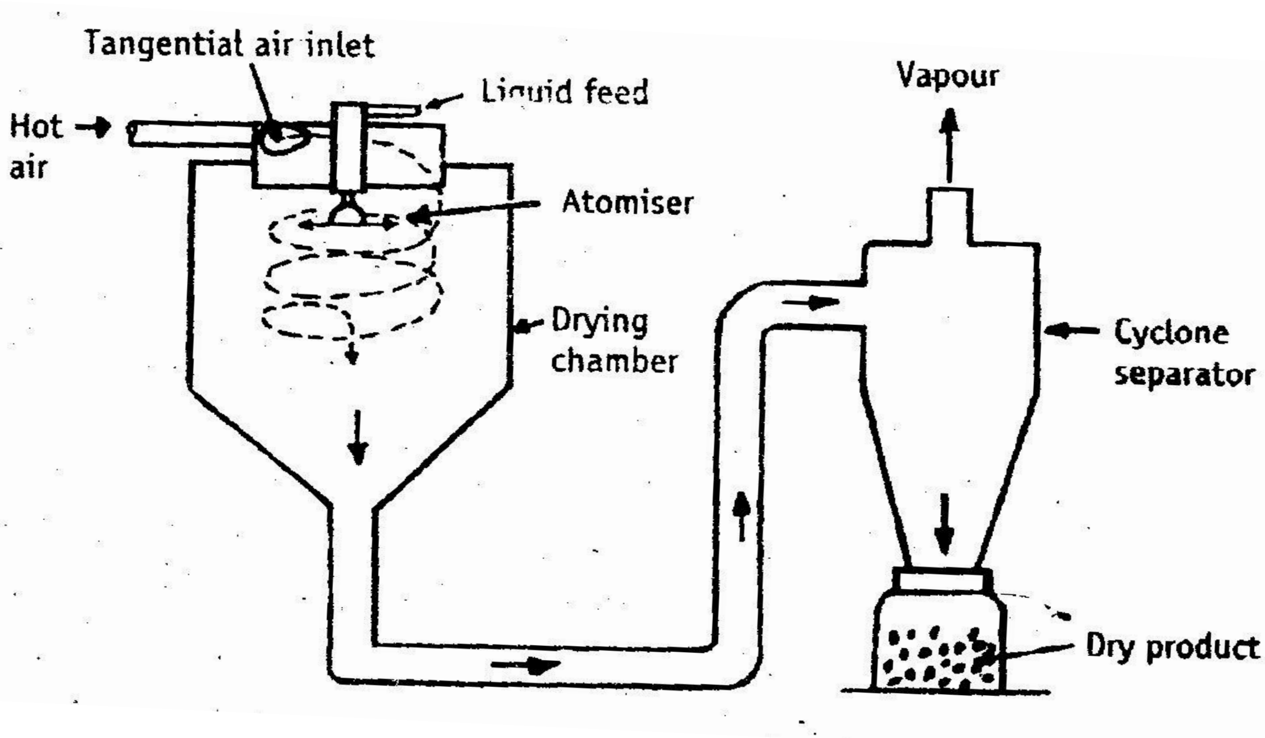
Tray Dryer – Gentle handling – but not very fast

Drying Solids – Drying Equipment



Drum Dryer – Continuous, faster

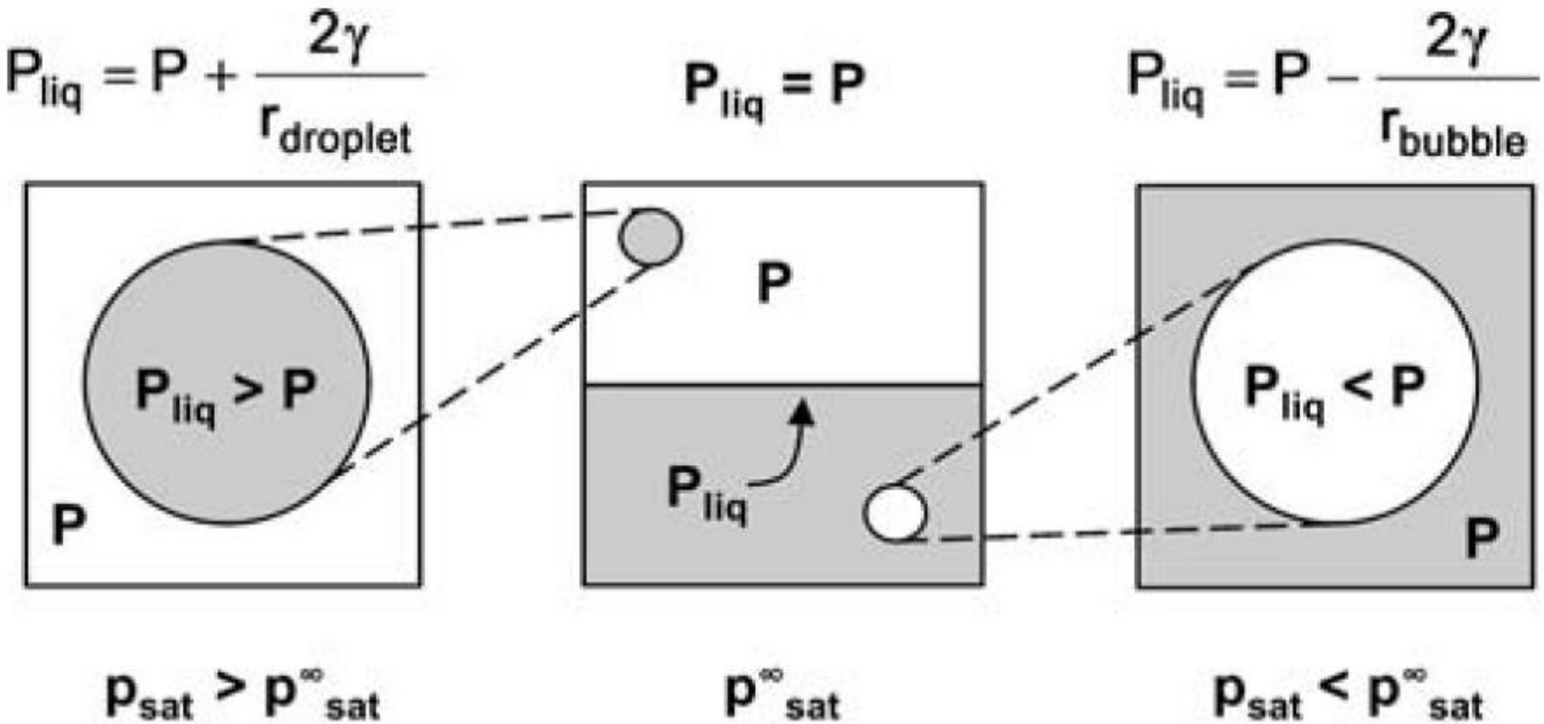
Drying Solids – Drying Equipment



Spray Dryer – Bulky and expensive but
Very fast – large surface area and capillary speedup

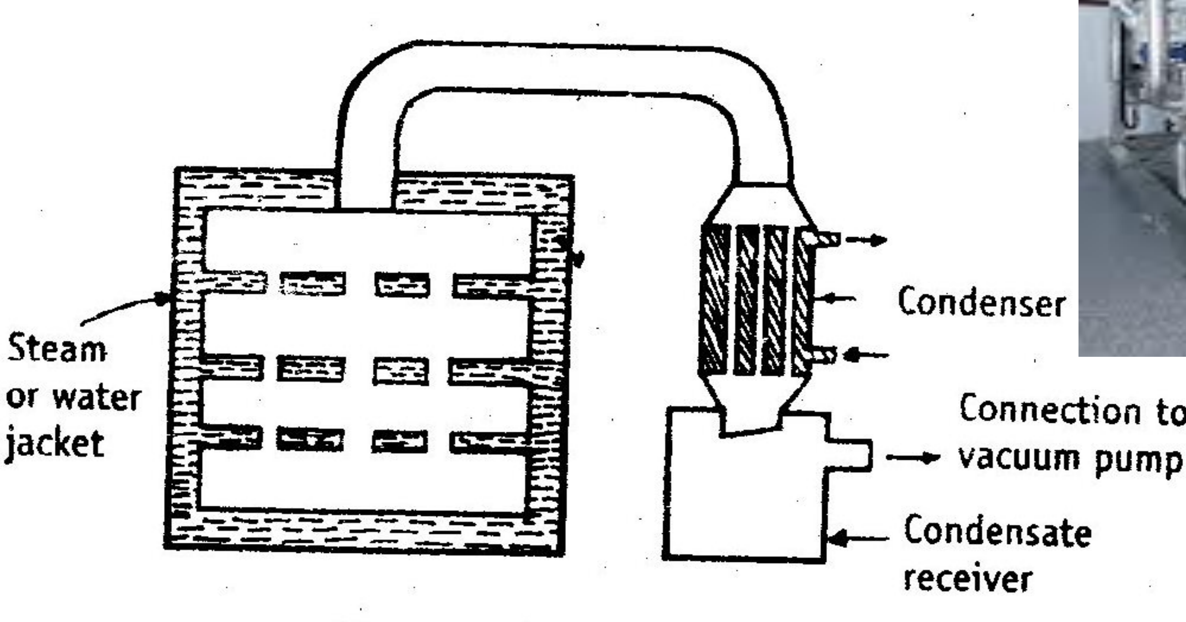
Pressure in Bubbles and Pores

$$\ln \frac{p_{sat}}{p_{sat}^{\infty}} = \frac{V_{liq}\gamma}{R\,T} \cdot \frac{2}{r_{droplet}} \quad \text{and} \quad \ln \frac{p_{sat}}{p_{sat}^{\infty}} = -\frac{V_{liq}\gamma}{R\,T} \cdot \frac{2}{r_{bubble}}$$



Higher pressure in droplets, lower in bubbles

Drying Solids – Drying Equipment



Vacuum Dryer – Slow and expensive but can dry temperature sensitive compounds