Chemical Engineering Principles 2 (0905212)

Phase Change Operations

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Content

- ✓ Instruction
- ✓ Latent heat
- ✓ Estimation and Correlation of Latent Heats
- ✓ Energy Balances on Processes Involving Phase Changes
- ✓ Psychrometric Charts
- ✓ Adiabatic Cooling

Introduction

- Consider liquid water and water vapor, each at 100°C and 1 atm.

$$\hat{U}_{\text{vapor}} > \hat{U}_{\text{liquid}}$$

  - The molecules of a vapor, which can move around relatively freely, are much more energetic than the densely packed molecules of a liquid at the same *T and P.*
  - ✓ Liquid molecules are held in close proximity to each other by attractive forces between the molecules.
  - ✓ The energy required to overcome these forces when a liquid is vaporized is reflected in the higher internal energy of the vapor molecules.

		$\hat{V}(\text{m}^3/\text{kg})$		$\hat{U}(\text{kJ/kg})$		$\hat{H}(\text{kJ/kg})$		
T(°C)	P(bar)	Water	Steam	Water	Steam	Water	Evaporation	Steam
96	0.8767	0.001040	1.915	402.1	2501	402.2	2267	2669
98	0.9429	0.001042	1.789	410.6	2504	410.7	2262	2673
100	1.0131	0.001044	1.673	419.0	2507	419.1	2257	2676
102	1.0876	0.001045	1.566	427.1	2509	427.5	2251	2679

Latent Heat

For water at 100°C and 1 atm, $\hat{U}_\ell = 419$ kJ/kg and $\hat{U}_v = 2507$ kJ/kg.

$$\hat{U}_v - \hat{U}_\ell = 2008 \text{ kJ/kg}$$

- The specific enthalpy $(= \hat{U} + P\hat{V})$ $\hat{H}_\ell = 419.1$ kJ/kg and $\hat{H}_v = 2676$ kJ/kg.
- The difference $\Delta\hat{H} = \hat{H}_v - \hat{H}_\ell = 2257$ kJ/kg $= 40.6$ kJ/mol.

  Is the latent Heat of vaporization of water at 100°C and 1 atm (the specific enthalpy change for the transition of liquid water to steam at 100°C and 1 atm,)

- **Latent Heat of phase change:** is the specific enthalpy change associated with the transition of a substance from one phase to another at constant temperature and pressure.
- Phase changes such as melting and evaporation are usually accompanied by large changes in internal energy and enthalpy
- Heat transfer requirements in phase-change operations consequently tend to be substantial,

$$Q \approx \Delta U \text{ (closed constant-volume system)} \qquad \dot{Q} \approx \Delta\dot{H} \text{ (open system).}$$

Latent Heat

- Condensation is the reverse of vaporization and enthalpy is a state property,

The heat of condensation must be the negative of the heat of vaporization -40.6 kJ/mol

- Latent heats for the two most commonly encountered phase changes are:

1. ***Heat of fusion*** (or heat of melting). $\Delta\hat{H}_m(T, P)$ is the specific enthalpy difference between the solid and liquid forms of a species at T and P.[7]
2. ***Heat of vaporization.*** $\Delta\hat{H}_v(T, P)$ is the specific enthalpy difference between the liquid and vapor forms of a species at T and P.

- At a pressure of 1 atm, these quantities are referred to as standard heats of fusion and vaporization.
- The latent heat of a phase change may vary considerably with the temperature at which the change occurs but hardly varies at all with the pressure at the transition point.

Tabulated values of these two latent heats, such as those in Table B.1 and on pp. 2-151 through 2-160 of *Perry's Chemical Engineers' Handbook*,

Example

Heat of Vaporization

At what rate in kilowatts must heat be transferred to a liquid stream of methanol at its normal boiling point to generate 1500 g/min of saturated methanol vapor?

Example

- Propose a process path to calculate the heat required to vaporize isothermally a substance at 130°C, when the heat of vaporization is at 80°C is the only available data.

Example Cont.

Example ***Vaporization and Heating***

One hundred g-moles per hour of liquid *n*-hexane at 25°C and 7 bar is vaporized and heated to 300°C at constant pressure. Neglecting the effect of pressure on enthalpy, estimate the rate at which heat must be supplied.

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Example Cont.

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If a phase change takes place in a closed system, you must evaluate $\Delta\hat{U} = \Delta\hat{H} - \Delta(P\hat{V})$ for the phase change to substitute into the energy balance equation.

$$Q = \Delta U \quad \text{(closed system)}$$

- For phase changes such as fusion, which involve only liquids and solids, changes in $P\hat{V}$

$$\Delta\hat{U}_m \approx \Delta\hat{H}_m$$

For vaporization, $P\hat{V}$ for the vapor (which equals RT if ideal gas behavior may be assumed) is normally orders of magnitude greater than $P\hat{V}$ for the liquid, so that $\Delta(PV) \approx RT$, and

$$\Delta\hat{U}_v \approx \Delta\hat{H}_v - RT$$

Please bring a printed copy of the Psychrometric Charts in the next lectures

A simple formula for estimating a standard heat of vaporization ($\Delta\hat{H}_v$ at the normal boiling point) is **Trouton's rule**: (30% accuracy)

$$\Delta\hat{H}_v(\text{kJ/mol}) \begin{cases} \approx 0.088T_b(\text{K}) & \text{(nonpolar liquids)} \\ \approx 0.109T_b(\text{K}) & \text{(water, low molecular weight alcohols)} \end{cases}$$

where T_b is the normal boiling point of the liquid.

Chen's equation: (2% accuracy)

$$\Delta\hat{H}_v(\text{kJ/mol}) = \frac{T_b[0.0331(T_b/T_c) - 0.0327 + 0.0297 \log_{10} P_c]}{1.07 - (T_b/T_c)}$$

where T_b and T_c are the normal boiling point and critical temperature in kelvin and P_c is the critical pressure in atmospheres.

Estimation and Correlation of Latent Heats

A formula for approximating a standard heat of fusion is

$$\Delta\hat{H}_m(\text{kJ/mol}) \approx \begin{cases} 0.0092T_m(\text{K}) & \text{(metallic elements)} \\ 0.0025T_m(\text{K}) & \text{(inorganic compounds)} \\ 0.050T_m(\text{K}) & \text{(organic compounds)} \end{cases}$$

- Latent heats of vaporization may be estimated from vapor pressure data by using the Clausius-Clapeyron equation,

$$\ln p^* = -\frac{\Delta\hat{H}_v}{RT} + B$$

Provided that $\Delta\hat{H}_v$ is constant over the range of temperatures encompassed by the vapor pressure data, the latent heat of vaporization may be determined from a plot of $\ln p^*$ versus $1/T$.

$$\frac{d(\ln p^*)}{d(1/T)} = -\frac{\Delta\hat{H}_v}{R}$$

plotting $\ln p^*$ versus $1/T$, determining $[d(\ln p^*)/d(1/T)]$ at the temperature of interest as the slope of the tangent to the curve,

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Estimation and Correlation of Latent Heats

- A useful approximation for estimating the latent heat of vaporization at one temperature from a known value at any other temperature is **Watson's correlation**

$$\Delta\hat{H}_v(T_2) = \Delta\hat{H}_v(T_1)\left(\frac{T_c - T_2}{T_c - T_1}\right)^{0.38}$$

where T_c is the critical temperature of the substance.

Example *Estimation of a Heat of Vaporization*

The normal boiling point of methanol is 337.9 K, and the critical temperature of this substance is 513.2 K. Estimate the heat of vaporization of methanol at 200°C.

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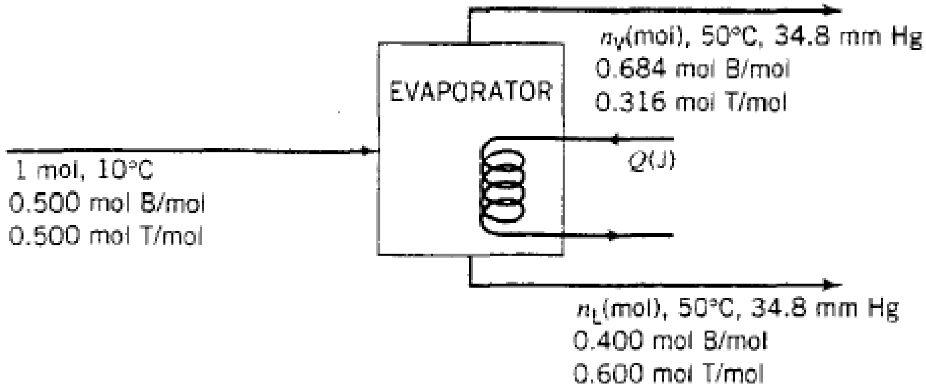
Energy Balances on Processes Involving Phase Changes

Example *Partial Vaporization of a Mixture*

An equimolar liquid mixture of benzene (B) and toluene (T) at 10°C is fed continuously to a vessel in which the mixture is heated to 50°C. The liquid product is 40.0 mole% B, and the vapor product is 68.4 mole% B. How much heat must be transferred to the mixture per g-mole of feed?



Example Cont.

Example Cont.

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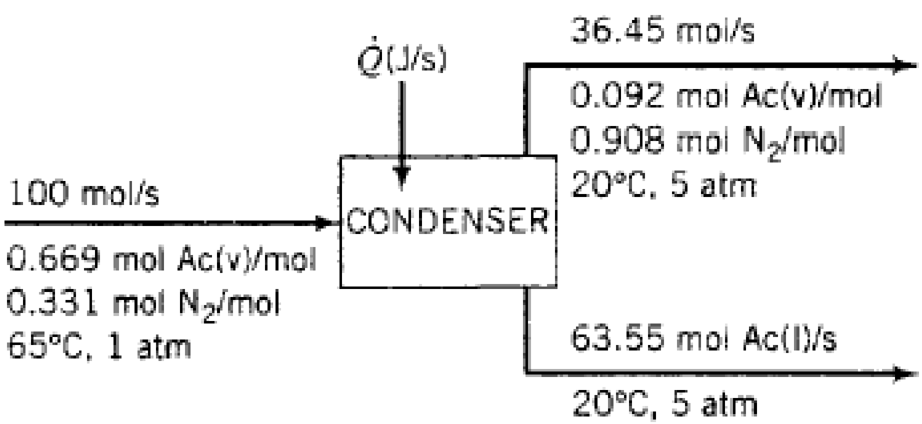
Example

Energy Balance on a Condenser

Acetone (denoted as Ac) is partially condensed out of a gas stream containing 66.9 mole% acetone vapor and the balance nitrogen. Process specifications and material balance calculations lead to the flowchart shown below. The process operates at steady state. Calculate the required cooling rate.



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Example Cont.

1. *Perform required material balance calculations.* None are required

2. *Write and simplify the energy balance.*

$$\dot{Q} - \dot{W}_s = \Delta\dot{H} + \Delta\dot{E}_k + \Delta\dot{E}_p.$$

$$\dot{W}_s = 0.$$

There are no moving parts in the system

- No significant vertical distance separates the inlet and outlet ports $\Delta\dot{E}_p \approx 0.$
- Phase changes and nonnegligible temperature changes occur $\Delta\dot{E}_k \approx 0$ (relative to $\Delta\dot{H}$).

$$\dot{Q} = \Delta\dot{H} = \sum_{out} \dot{n}_i\hat{H}_i - \sum_{in} \dot{n}_i\hat{H}_i$$

3. *Choose reference states for acetone and nitrogen.*

Example Cont.

Table B.8lists specific enthalpies of nitrogen relative to N_2(g, 25°C, 1 atm)

4. *Construct an inlet–outlet enthalpy table.*

References: Ac(l, 20°C, 5 atm), N_2(g, 25°C, 1 atm)

Substance	$\dot{n}_{in}$ (mol/s)	$\hat{H}_{in}$ (kJ/mol)	$\dot{n}_{out}$ (mol/s)	$\hat{H}_{out}$ (kJ/mol)
Ac(v)	66.9	$\hat{H}_1$	3.35	$\hat{H}_3$
Ac(l)	—	—	63.55	0
N_2	33.1	$\hat{H}_2$	33.1	$\hat{H}_4$

5. *Calculate all unknown specific enthalpies.*

$$\text{Ac(l, 20°C, 5 atm)} \xrightarrow{\Delta\hat{H}_{1a}} \text{Ac(l, 20°C, 1 atm)} \xrightarrow{\Delta\hat{H}_{1b}} \text{Ac(l, 56°C, 1 atm)}$$

$$\xrightarrow{\Delta\hat{H}_{1c}} \text{Ac(v, 56°C, 1 atm)} \xrightarrow{\Delta\hat{H}_{1d}} \text{Ac(v, 65°C, 1 atm)}$$

Example Cont.

$$\hat{H}_1 = \Delta\hat{H}_{path} = \Delta\hat{H}_{1a} + \Delta\hat{H}_{1b} + \Delta\hat{H}_{1c} + \Delta\hat{H}_{1d}$$

6. *Calculate $\Delta\dot{H}$.*

$$\Delta\dot{H} = \sum_{out} \dot{n}_i\hat{H}_i - \sum_{in} \dot{n}_i\hat{H}_i$$

7. *Calculate nonzero work, kinetic energy, and potential energy terms.* $\dot{W}_s = 0$.

$\Delta\dot{E}_p \approx 0$. $\Delta\dot{E}_k \approx 0$ (relative to $\Delta\dot{H}$).

8. *Solve the energy balance for $\dot{Q}$.* $\dot{Q} = \Delta\dot{H}$

Example Cont.

Psychrometric Charts

- **Psychrometric chart (or humidity chart)** is a chart on which several properties of a gas-vapor mixtures are cross-plotted, providing a concise compilation of a large quantity of physical property data.
- **Psychrometric chart** of the air-water system at 1 atm-is used extensively in the analysis of humidification, drying, and air-conditioning processes.
- Humid air contains one phase and two components $F = 2 + 2 - 1 = 3$

Properties of humid air at 1 atm that appear on the psychrometric chart

1. ***Dry-bulb temperature,*** T-the abscissa of the chart.
   - ***This is the air temperature as measured*** by a thermometer, thermocouple, or other conventional temperature-measuring instrument.
2. ***Absolute humidity,*** (h_a [kg $H_2O(v)$/kg DA]) called **moisture content (**the ordinate of the chart).

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Psychrometric Charts

- For an the absolute humidity 0.0150 kg H_2O/kg DA
  - For every kilogram of dry air there is 0.015 kg of water vapor, for a total of 1.015 kg.
  - The mass fraction of water is

$$(0.0150 \text{ kg } H_2O)/(1.015 \text{ kg humid air}) = 0.0148 \text{ kg } H_2O/\text{kg}$$

3. ***Relative humidity***, $h_r = [100 \times p_{H_2O}/p^*_{H_2O}(T)]$.

Curves on the psychrometric chart correspond to specified values of h_r (100%, 90%, 80%, etc.). The curve that forms the left boundary of the chart is the **100% relative humidity curve**, also known as the **saturation curve.**

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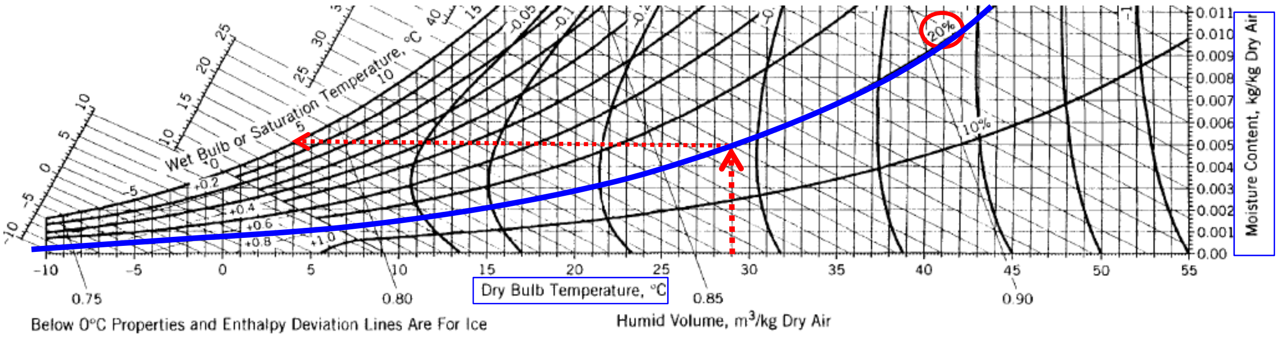
Psychrometric Charts

4. Dew point, T_{dp}

The temperature at which humid air becomes saturated if it is cooled at constant pressure.

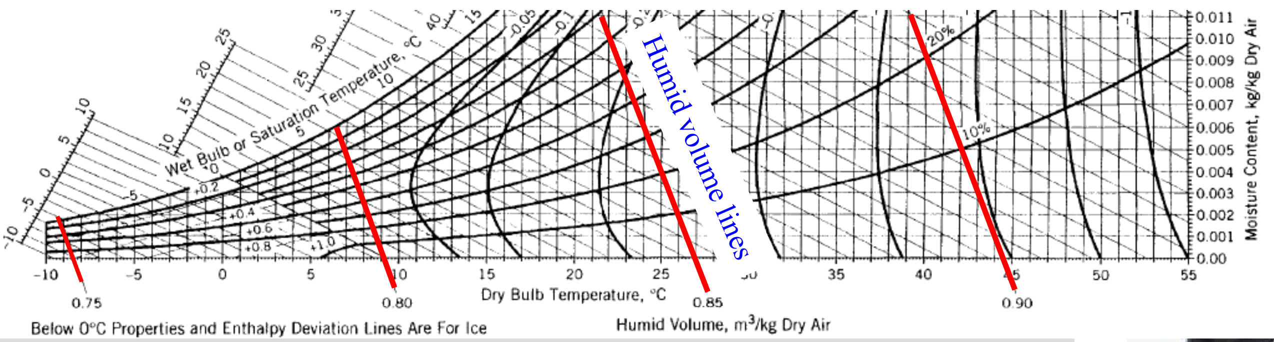
- Example: For air at 29°C and 20% relative humidity. Cooling this air at constant pressure (1 atm) corresponds to moving horizontally (at constant absolute humidity) to the saturation curve. T_{dp} is the temperature at the intersection, or 4°C.



Psychrometric Charts

5. Humid volume, $\hat{V}_H$ (m^3/kg DA).

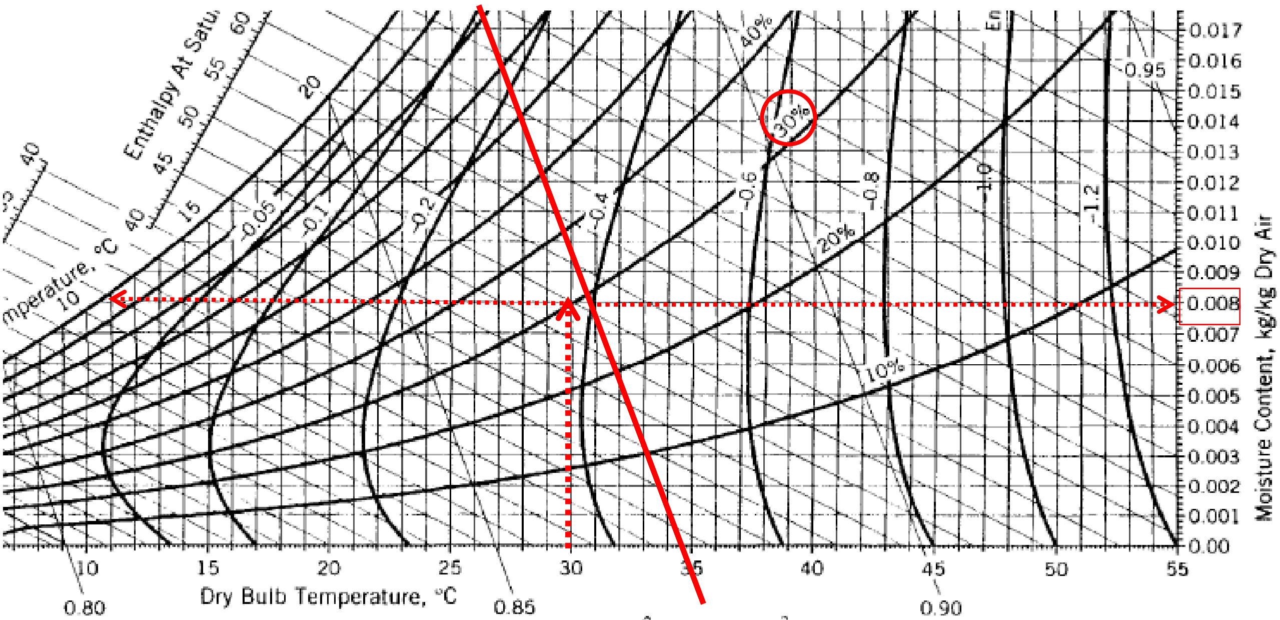
- The volume occupied by 1 kg of dry air plus the water vapor that accompanies it.
- Lines of constant humid volume on the psychrometric chart are steep and have negative slopes.
- Humid volume lines are shown corresponding to 0.75, 0.80, 0.85, and 0.90 m^3/kg dry air.
- Can be used to determine the volume of a given mass of wet air.



Psychrometric Charts

What is the volume occupied by 150 kg of humid air at $T = 30^{\circ}C$ and $h_r = 30\%$

$h_a = 0.0080 \text{ kg } H_2O(v)/\text{kg DA}$ $\hat{V}_H \approx 0.87 \text{ m}^3/\text{kg DA}$



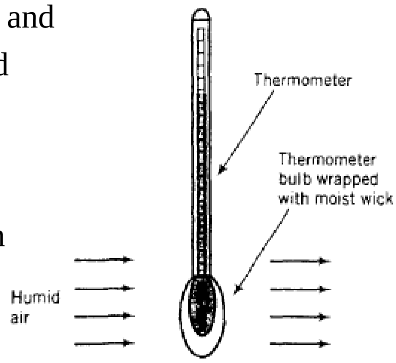
$\hat{V}_H \approx 0.87 \text{ m}^3/\text{kg DA}$

Psychrometric Charts

$$V = \frac{150 \text{ kg humid air}}{} \left| \frac{1.00 \text{ kg DA}}{1.008 \text{ kg humid air}} \right| \frac{0.87 \text{ m}^3}{\text{kg DA}} = 129 \text{ m}^3$$

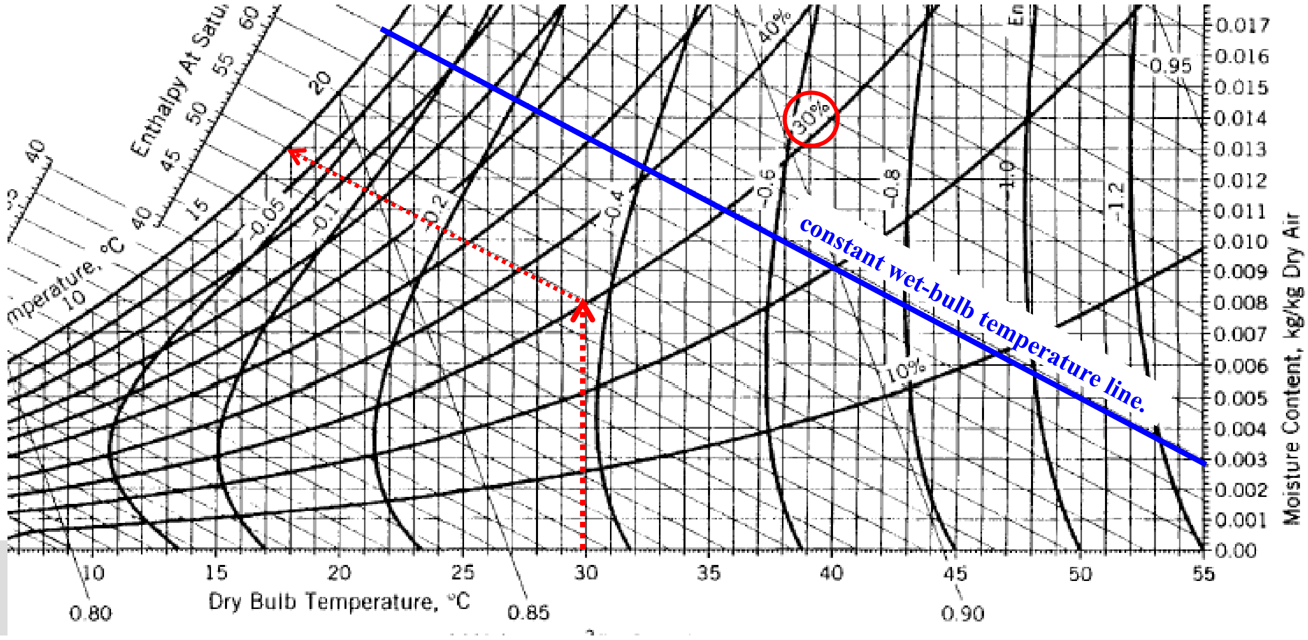
6. Wet-bulb temperature, T_{wb}.

- It is the temperature the air flowing measured
  - When a porous material like cloth or cotton is soaked in water and wrapped around the bulb of a thermometer to form a *wick,* and
  - The thermometer is placed in a stream of flowing air.
  - Evaporation of water from the wick into the flowing air is accompanied by a transfer of heat from the bulb, which in turn causes a drop in the bulb temperature and hence in the thermometer reading.
  - Provided that the wick remains moist, the bulb temperature falls to a certain value and remains there.
  - The wet-bulb temperature of humid air depends on both the dry-bulb temperature and the moisture content of the air.



Psychrometric Charts

- If the air is saturated (100% relative humidity), no water evaporates from the wick, and the wet-bulb and dry-bulb temperatures are the same.
- The lower the humidity, the greater the difference between the two temperatures
- For humid air at $T = 30^{\circ}\mathrm{C}$ and $h_r = 30\%$, the wet bulb temperature is 18°C



Psychrometric Charts

➢ This means that if you wrap a wet wick around a thermometer bulb and blow air with $T = 30^{\circ}\mathrm{C}$ and $h_r = 30\%$ past the bulb, the thermometer reading will drop and eventually stabilize at 18°C

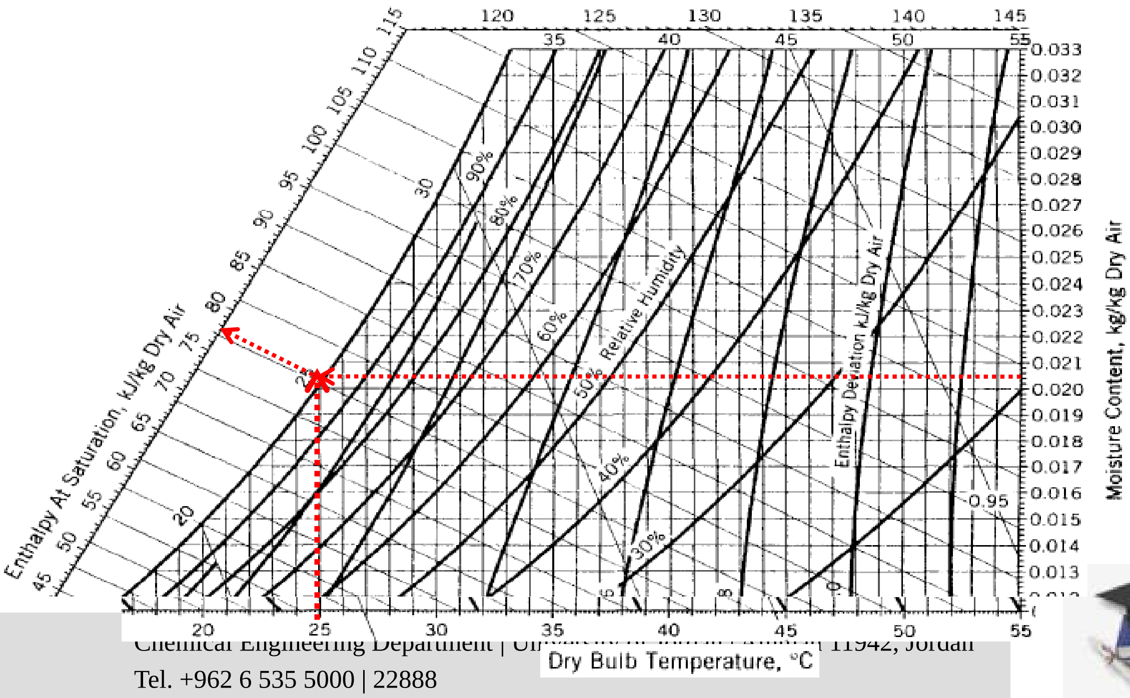
7. Specific enthalpy of saturated air

- The diagonal scale above the saturation curve on the psychrometric chart shows the enthalpy of a unit mass (1 kg or 1 Ibm) of dry air plus the water vapor it contains **at saturation.**
- The reference states are liquid water at 1 atm and 0°C (32°F) and dry air at 1 atm and 0°C.
- To determine the enthalpy from the chart, follow the constant wet-bulb temperature line from the saturation curve at the desired temperature to the enthalpy scale.

Psychrometric Charts

saturated air at 25°C and 1 atm—which has an absolute humidity $h_a = 0.0202$ kg H_2O/kg DA

➡ specific enthalpy of 76.5 kJ/kg DA.



Psychrometric Charts

➢ The enthalpy is the sum of the enthalpy changes for 1.00 kg dry air and 0.0202 kg water going from their reference conditions to 25°C.

$$1.00 \text{ kg DA}(0^\circ\text{C}) \rightarrow 1 \text{ kg DA}(25^\circ\text{C})$$

$$\Delta H_{\text{air}} = (1.00 \text{ kg DA})\left(\frac{1 \text{ kmol}}{29.0 \text{ kg}}\right)\left[\int_0^{25} C_{p,\text{air}}(T)\,dT\right]\left(\frac{\text{kJ}}{\text{kmol}}\right) = 25.1 \text{ kJ}$$

$$0.0202 \text{ kg } H_2O(\text{l}, 0^\circ\text{C}) \rightarrow 0.0202 \text{ kg } H_2O(\text{v}, 25^\circ\text{C})$$

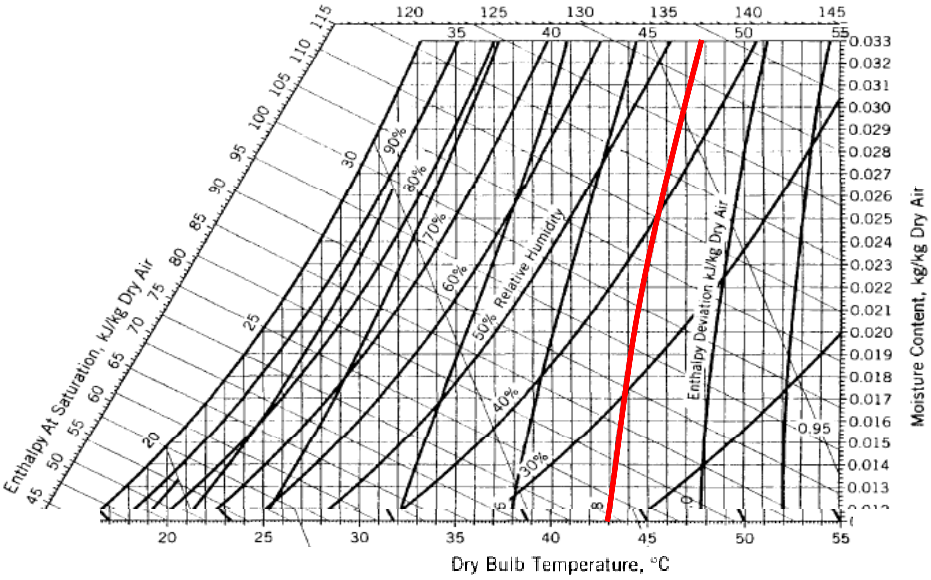
$$\Delta H_{\text{water}} = (0.0202 \text{ kg})[\hat{H}_{H_2O(\text{v},25^\circ\text{C})} - \hat{H}_{H_2O(\text{l},0^\circ\text{C})}]\left(\frac{\text{kJ}}{\text{kg}}\right) = 51.4 \text{ kJ}$$

$$\hat{H} = \frac{(\Delta H_{\text{air}} + \Delta H_{\text{water}})(\text{kJ})}{1.00 \text{ kg DA}} = \frac{(25.1 + 51.4) \text{ kJ}}{1.00 \text{ kg DA}} = 76.5 \text{ kJ/kg DA}$$

Psychrometric Charts

8. Enthalpy deviation

➢ The enthalpy of humid air that is **not saturated** (The units of these numbers are kJ/kg DA)

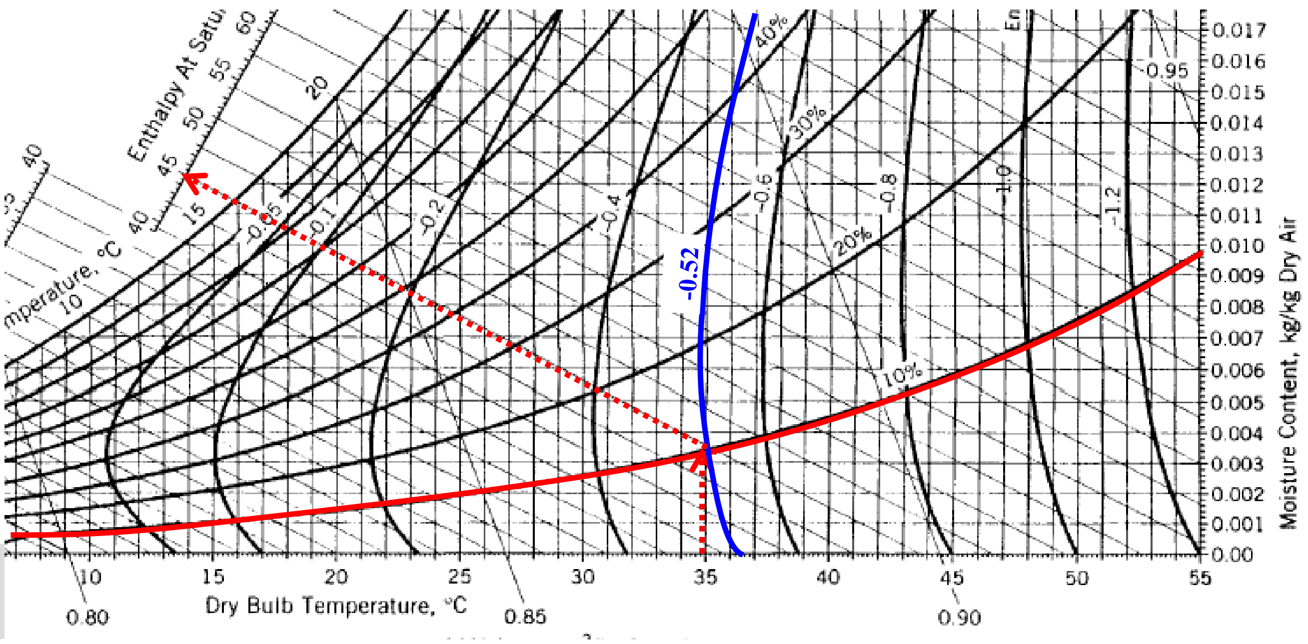


Psychrometric Charts

For air at 35°C and 10% relative humidity ➡ the enthalpy deviation of about −0.52 kJ/kg DA.

The specific enthalpy of saturated air at the same wet-bulb temperature is 45.0 kJ/kg DA.

The specific enthalpy of the humid air is (45.0 − 0.52) kJ/kg DA = 44.5 kJ/kg DA.



Example

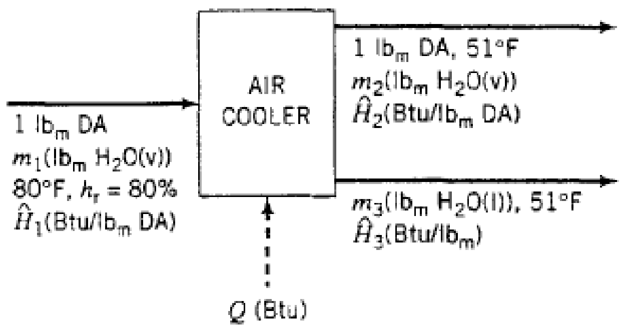
The Psychrometric Chart

Use the psychrometric chart to estimate (1) the absolute humidity, wet-bulb temperature, humid volume, dew point, and specific enthalpy of humid air at 41°C and 10% relative humidity, and (2) the amount of water in 150 m^3 of air at these conditions.

Example Cont.

Example ***Material and Energy Balances on an Air Conditioner***

Air at 80°F and 80% relative humidity is cooled to 51°F at a constant pressure of 1 atm. Use the psychrometric chart to calculate the fraction of the water that condenses and the rate at which heat must be removed to deliver 1000 ft^3/min of humid air at the final condition.



Example Cont.

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Adiabatic Cooling

- In adiabatic cooling,
  - A warm gas is brought into contact with a cold liquid, causing the gas to cool and some of the liquid to evaporate.
  - Heat is transferred from the gas to the liquid but no heat is transferred between the gas-liquid system and its surroundings (hence "adiabatic“ cooling).
- Some common processes of this type
  - ✓ Spray cooling, spray humidification.
  - ✓ Spray dehumidification
  - ✓ Drying
  - ✓ Spray drying

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Adiabatic Cooling

- Air undergoing adiabatic cooling through contact with liquid water moves along a constant wet-bulb temperacure line on the psychrometric chart from its initial condition to the 100% relative humidity curve.
- Further cooling of the air below its saturation temperature leads to condensation and hence dehumidification.
- Heating or cooling humid air at temperatures above the dew point corresponds to horizontal movement on the psychrometric chart
- If superheated humid air is cooled at 1 atm, the system follows a horizontal path to the left on the chart until the saturation curve (dew point) is reached; thereafter, the gas phase follows the saturation curve

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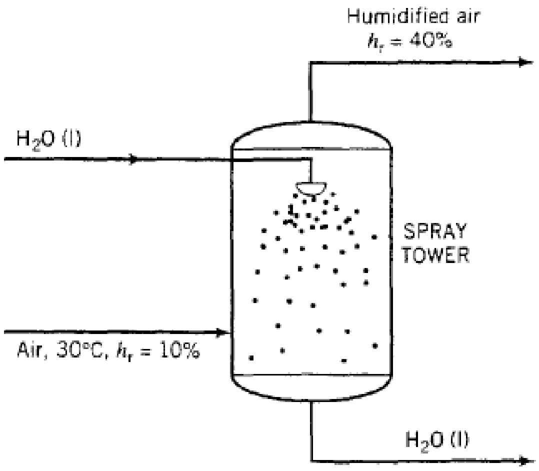
Example

Adiabatic Humidification

A stream of air at 30°C and 10% relative humidity is humidified in an adiabatic spray tower operating at $P \approx 1$ atm. The emerging air is to have a relative humidity of 40%.

1. Determine the absolute humidity and the adiabatic saturation temperature of the entering air.
2. Use the psychrometric chart to calculate
   (i) The rate at which water must be added to humidify 1000 kg/h of the entering air, and
   (ii) The temperature of the exiting air.



Example Cont.

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