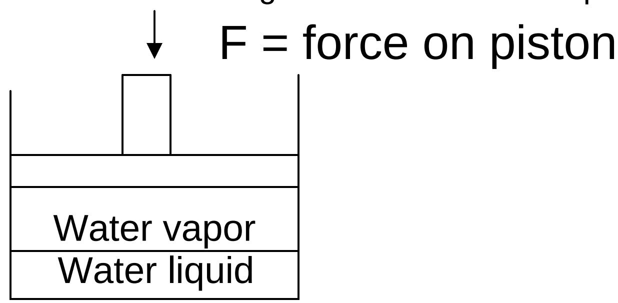
# WEEK 6

## Multiphase systems

# Multiphase systems

- P 237. Processes usually deal with material being transferred from one phase (gas, liquid, or solid) to another.
- 6.1a Phase diagrams



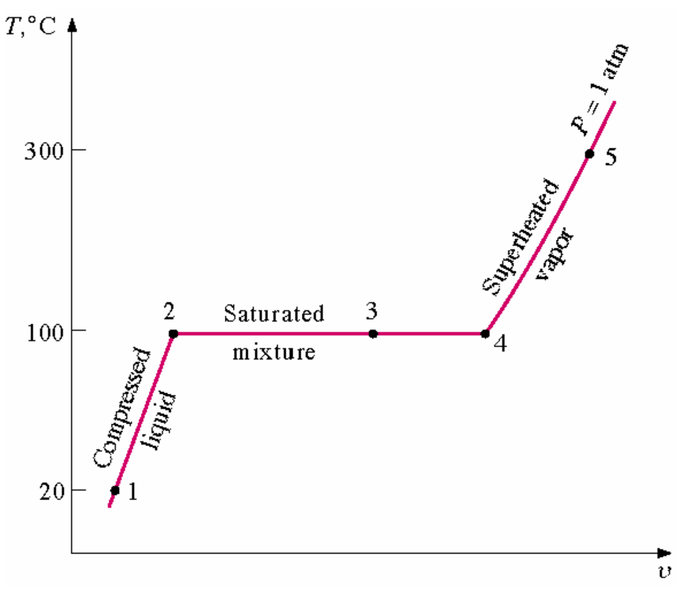

a) At time=0, system is at $20^{o}C$. Force is chosen so that P = 3 mm Hg
b) This is point A in Fig 6.1-1 on page 241. Everything evaporates. It's all vapor
c) Increase P to 760 mm Hg
d) Keep pressure at 760 mm Hg and increase T to $130^{o}C$
e) Consider the state of water throughout the process (A->B->C->D->E)

Note:

1) T and P on vapor-liquid equilibrium (points B and D); P= vapor pressure, T=boiling point temperature of water at P
2) The boiling point where P = 1 atm = normal boiling point of water
3) (T,P) on solid-liquid equilibrium curve: T is the melting point or freezing point at P
4) Solid-vapor equilibrium curve (T, P), P is the vapor pressure of solid at T; T is the sublimation point at P
5) (T, P) where solid, liquid, vapor phase coexist ---→ triple point of substance
6) Critical temperature and critical pressure: where vapor-liquid equilibrium stops. Above and to the right of the critical point, 2 separate phases never coexist

# Multiphase systems

- Compressed liquid: liquid is not about to vaporize: water at 20$^o$C and 1 atm.
- Saturated liquid: liquid is about to vaporize: water at 100$^o$C and 1 atm.
- Superheated vapor: vapor not about to condense: water vapor (steam) > 100$^o$C at 1 atm.
- Saturated vapor: vapor is about to condense: water at 100$^o$C and 1 atm.



# 6.1b Estimation of vapor pressure

- P243. Volatility: How easy the substance can go from liquid (or solid) state to a vapor phase
- Vapor pressure: measures volatility. High vapor pressure at given T -----→ High volatility
- Clapeyron equation:

  T : absolute temperature

$$\frac{dP^*}{dT} = \frac{\Delta\hat{H}_v}{T\left(\hat{V}_g - \hat{V}_L\right)}$$

$\hat{V}_g$ *and* $\hat{V}_L$ : Specific molar volume (volume/mole)

$\Delta\hat{H}_v$ : Latent heat of vaporization (energy required to vaporize one Mole of the liquid)

$\hat{V}_g >> \hat{V}_L$ : And assume ideal gas $\hat{V}_g = \frac{RT}{P^*}$

- We have the following equation: $$\frac{d\left(\ln P^*\right)}{d\left(1/T\right)} = \frac{-\Delta\hat{H}_v}{R}$$
- Methods can be use to determine heat of vaporization

# Estimation of vapor pressure

- If the heat of vaporization is known, Clausius-Clapeyron equation is used:

$$\ln P^* = \frac{-\Delta \hat{H}_v}{RT} + B$$ after integration of Clapeyron equation

- Example 6.1-1 page 244 in class
- We also use Antoine equation for vapor pressure and temperature relations (Page 640)

$$\log_{10}\left(P^*\right) = A - \frac{B}{T + C}$$

# 6.2 Gibbs Phase Rule

- Intensive variable: independent of size of the process
- Extensive variable: dependent of size
- The Gibbs phase rule deals with system at equilibrium
- DF = 2+c-$\Pi$ (no reaction)

DF: The number of intensive variables that must be specified for a system at equilibrium before the remaining intensive variables can be calculated

c: The number of components

$\Pi$: The number of phases at equilibrium

Intensive variables: T, P, concentration

Ex1: pure liquid water: DF = 2-1-1 = 2

Ex2: A mixture of liquid, solid, and vapor: DF = 2+1-3 = 0 (page 241)

# Fitting Polynomial and Correlation Equations to Vapor Pressure Data

- Often, it is necessary to fit a set of data to an equation (ex: y=a*x+b). Given (x,y) data, the goal is to find the coefficients a and b such that the line goes through the points.
- **Example in Matlab® and Excel ®**
  - Variance: $VarC_i = \dfrac{\left(P_i - 10^{A+\frac{B}{T}}\right)^2}{N-(n+1)}$ ← Ex: Clayperon Equation

n: degree of polynomial
N: number of data points

- Data correlation by a polynomial: $P_{calc} = a_0+a_1TK+a_2TK^2+a_3TK^3+a_4TK^4+a_5TK^5$
- Minimize a least-squares objective function:

$$\sum_{i=1}^{N}(P_{obs} - P_{calc})^2$$

- Confidence interval: uncertainty associated with a particular parameter
- Does the confidence interval include zero?
- Is the error randomly distributed with zero mean?

RMSD = Root mean square deviation

# Fitting Polynomial and Correlation Equations to Vapor Pressure Data

- Clapeyron Equation Data Correlation

$$\log(P) = A + \frac{B}{T}$$

  - Degree of freedom = #Component – 2 + #phase
  - Empirical equation relating temperature and vapor pressure
  - Confidence interval and variance are small
  - Difficult to compare variance of this model vs polynomial because different forms of the parameters were used

**Example in Matlab® and Excel ®**

# Fitting Polynomial and Correlation Equations to Vapor Pressure Data (Next)

- Riedel Equation Data Correlation

$$\log\left(P\right) = A + \frac{B}{T} + C\log\left(T\right) + DT^{\beta}$$

**Example in Matlab® and Excel ®**

HMK: **6.3, 6.22**