

# 2015-2016 Spring Semester Material and Energy Balance Thermophysical & Related Properties of Materials

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23.02.2016

2<sup>nd</sup> Week

# Definitions

- The portion of the universe set aside for consideration is called a **system**. The remainder of the universe is called the **surroundings**.
- A **closed system** is enclosed by an impermeable boundary or wall that does not permit the transfer of matter but allows transfer of energy. The mass of a closed system remains constant.
- An **open system** is bounded by permeable walls that permit the transfer of both matter and energy across the walls.
- An **isolated system** is a system enclosed by impermeable walls that permit neither exchange of energy nor transfer of matter such walls are termed adiabatic walls.

# Definitions

- The system consists of a definite amount of matter, composed of one or more specific substances. Each substance may exist in various forms. We designate these forms of a substance as **phases**.
- A phase is a homogeneous, physically distinct, aggregate of matter which is mechanically separable from any other phases that may be present. A phase may exist in various **states**.
- We will designate the phases in a system using two special terms: **fluid** phases and **condensed** phases. The term fluid refers to the gas and liquid state. The term condensed refers to the liquid and solid state.
- There are two classes of state properties: **intensive** and **extensive**. An intensive property is independent of the mass, while an extensive property varies directly with mass. Temperature, pressure, and density are intensive properties, while mass and volume are extensive.

# Definitions

- A **homogeneous system** is one where the properties of the contents are the same throughout, with no apparent surfaces of discontinuity. A homogeneous system contains only one phase.
- A **heterogeneous system** contains two or more phases, which are separated from each other by phase boundaries. There may be large changes in properties across phase boundaries.
- In a heterogeneous system, each phase is an open system.



# The Gibbs Phase Rule

- Thermodynamic functions involving the free energy of phases were used by J. W. Gibbs to show that the number of phases that can be present at a particular temperature, pressure, and phase composition is limited.
- The state of a system is defined in terms of certain intensive (composition, temperature, pressure, and specific volume ), and extensive (mass, amount, volume) properties.

$$D = C - \phi + 2 \quad (\text{or } F = C - P + 2)$$

# The Gibbs Phase Rule

$$D = C - \phi + 2$$

D = # degrees of freedom

The number of intensive parameters that must be specified in order to completely determine the system, or the number of variables that can be changed independently and still maintain equilibrium

$\phi$  = # of phases

phases are mechanically separable constituents

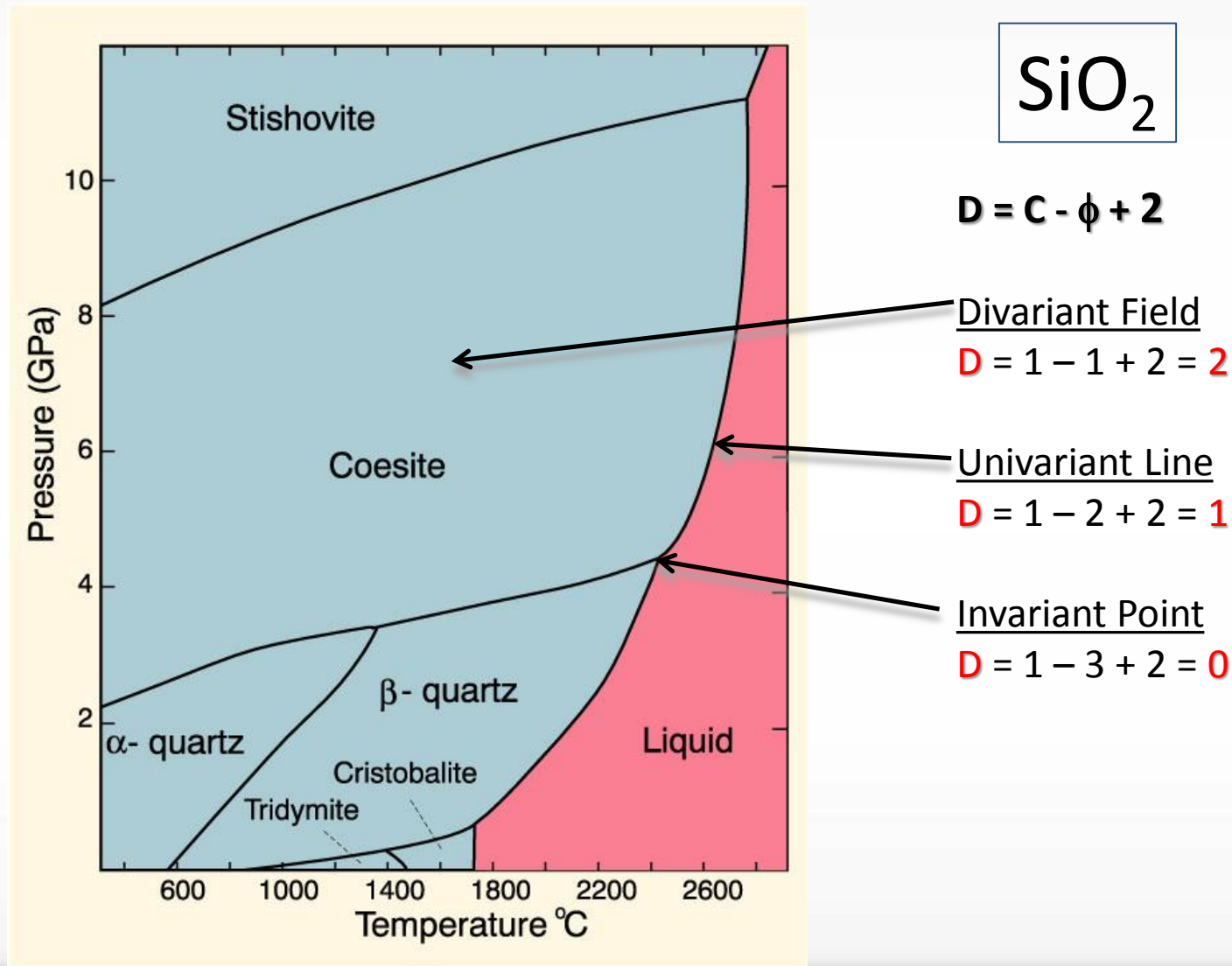
C = minimum # of components (chemical constituents that must be specified in order to define all phases)

2 = Two intensive parameters

Usually = temperature and pressure

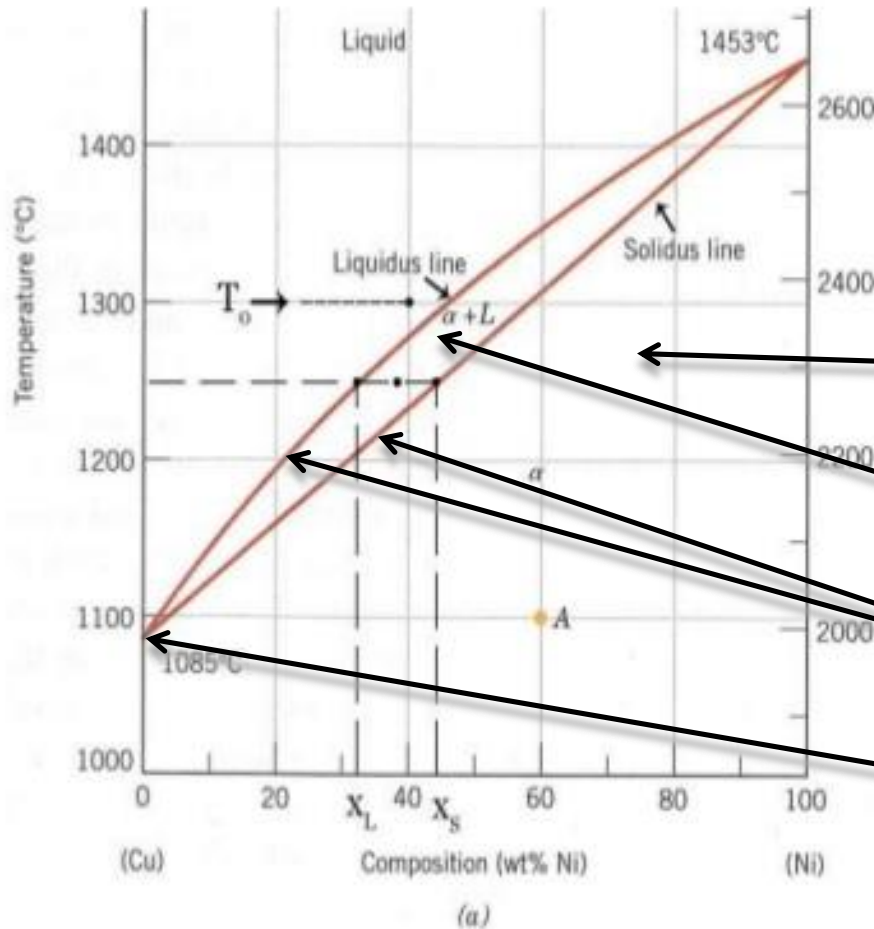
**ONLY APPLIES TO SYSTEMS IN CHEMICAL EQUILIBRIUM!!**

# Phase Rule in a One-Component System



# Phase Rule in a Two-Component System

System: Cu-Ni Binary  
 Phases: Liquid and  $\alpha$   
 Components: (Cu) and (Ni)



$$D = C - \phi + 1$$

(only 1 variable since P is constant)

Divariant Field

$$D = 2 - 1 + 1 = 2$$

Univariant Field

$$D = 2 - 2 + 1 = 1$$

Univariant Lines

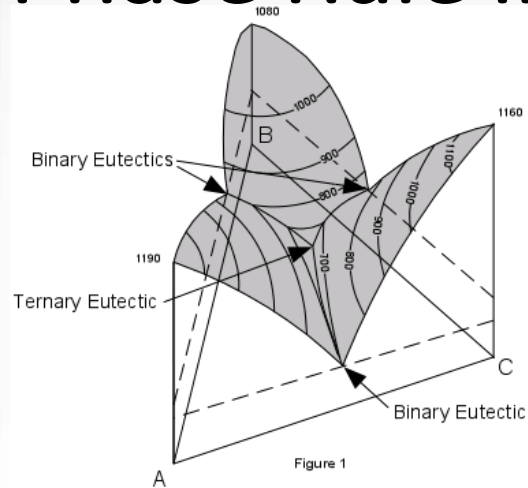
$$D = 2 - 2 + 1 = 1$$

Invariant Point

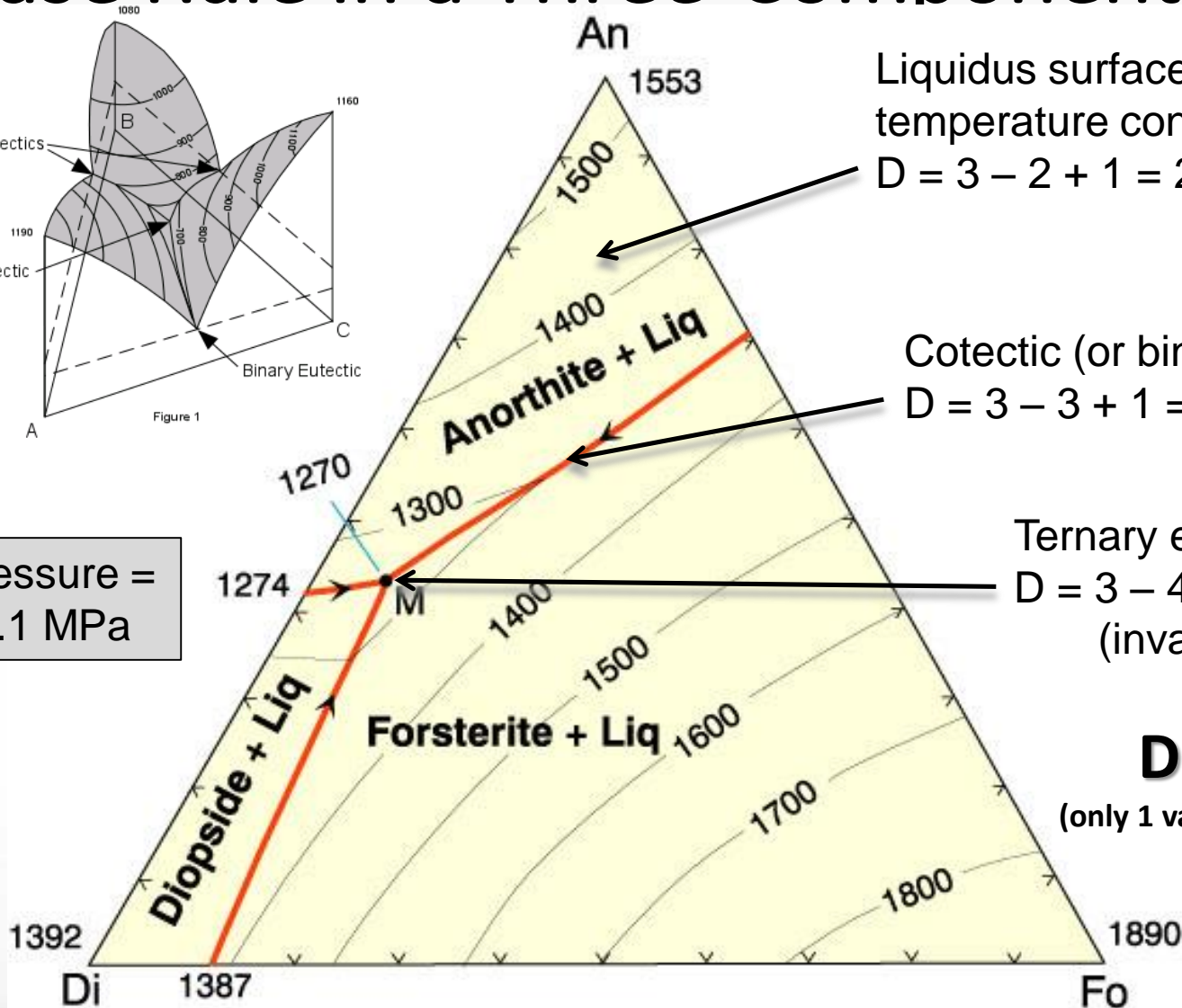
$$D = 1 - 2 + 1 = 0$$



# Phase Rule in a Three-Component System



Pressure =  
0.1 MPa



Liquidus surface showing  
temperature contours

$D = 3 - 2 + 1 = 2$  (divariant field)

Cotectic (or binary eutectic)

$D = 3 - 3 + 1 = 1$  (univariant line)

Ternary eutectic

$D = 3 - 4 + 1 = 0$   
(invariant point)

$$D = C - \phi + 1$$

(only 1 variable since P is constant)

# The Ideal Gas Law

- An ideal gas is a theoretical substance in which the particles are assumed to be totally free of mutual interaction. Most gases involved in materials production and processing are at sufficiently high temperature and/or at sufficiently low pressure such that deviations from the ideal gas law are small.
- Ideal gases obey the ideal gas law represented as:

$$P V = n R T$$

Where  $P$ ,  $V$  and  $T$  are the pressure, volume and absolute temperature of the gas. The number of moles of gas is  $n$ , and  $R$  is the ideal gas constant.

## Values of the Universal Gas Constant R

Values of R	Units		Values of R	Units
8.314472	$\text{J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$		83.14472	$\text{L}\cdot\text{mbar}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$
0.082057	$\text{L}\cdot\text{atm}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$		$8.314472 \times 10^{-5}$	$\text{m}^3\cdot\text{bar}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$
$8.205745 \times 10^{-5}$	$\text{m}^3\cdot\text{atm}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$		10.73159	$\text{ft}^3\cdot\text{psi}\cdot^{\circ}\text{R}^{-1}\cdot\text{lb}\cdot\text{mol}^{-1}$
8.314472	$\text{L}\cdot\text{kPa}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$		0.73024	$\text{ft}^3\cdot\text{atm}\cdot^{\circ}\text{R}^{-1}\cdot\text{lb}\cdot\text{mol}^{-1}$
8.314472	$\text{m}^3\cdot\text{Pa}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$		1.98588	$\text{Btu}\cdot^{\circ}\text{R}^{-1}\cdot\text{lb}\cdot\text{mol}^{-1}$
82.05745	$\text{cm}^3\cdot\text{atm}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$		62.36367	$\text{L}\cdot\text{torr}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$

# The Ideal Gas Law

- At any given temperature and pressure, the volume per mole of any ideal gas is the same.

$$\frac{V}{n} = \frac{RT}{P}$$

- For material balances involving gases, it is convenient to convert the listed volumes to a certain temperature and pressure: the standard temperature and pressure, abbreviated STP.
- Most gas volumes have been reported at 273.15 K (0°C) and 101.325 kPa (1 atm) pressure considered as STP.

$$1 \text{ mol gas} = 22.4 \times 10^{-3} \text{ m}^3$$



## EXAMPLE Removal of Air by a Vacuum Pump

- A vacuum furnace has a radius of 1.00 m and a height of 2.00 m. The air initially inside is at a temperature of 302 K and a pressure of 760.0 mm Hg, and must be pumped out until the internal pressure is 1.00 mm Hg. Calculate the mass of air that will be removed by the pump.

$$P V = n R T$$

$$V = \pi(1)^2(2) = 6.28 \text{ m}^3$$

we need a value of R in units of  $\text{m}^3$  and mm Hg

$$R = 0.06236 \text{ m}^3 \cdot \text{mm Hg}/(\text{mol} \cdot \text{K}).$$

$$760 \text{ mmHg}(6.28 \text{ m}^3) = n[0.06236 \text{ m}^3 \cdot \text{mmHg}/(\text{mol} \cdot \text{K})](302 \text{ K})$$

$$n = 253.4 \text{ mol}$$

# EXAMPLE Removal of Air by a Vacuum Pump

$$P V = n R T$$

$$n = 253.4 \text{ mol @ } 760 \text{ mm Hg}$$

After vacuum 1 mm Hg

$$1 \text{ mmHg}(6.28 \text{ m}^3) = n[0.06236 \text{ m}^3 \cdot \text{mmHg}/(\text{mol} \cdot \text{K})](302 \text{ K})$$

$$n = 0.33 \text{ mol @ } 1 \text{ mm Hg}$$

$$253.4 - 0.33 = 253.07 \text{ mol dry air pumped}$$

$$(253.07 \text{ mol})(28.84 \text{ g/mol})(1/1000 \text{ g/kg}) = 7.29 \text{ kg}$$

# Properties of Solutions

- Very often, the first metallic phase produced in the extractive flowsheet is a liquid solution, containing one or more impurities that must subsequently be removed. Other solution phases are slags (mixtures of molten oxides), mattes (mixtures of molten sulfides), and molten salts. The final product of a materials production process is often a solid solution, such as an iron-carbon alloy.
- Only two types of solution behavior will be discussed: an *ideal* and a *regular* solution.

# Ideal Solutions — Raoult's Law

- We describe ideal behavior in terms of the partial pressure of the pure component and its partial pressure in the dissolved-state. For a two component system A and B, where  $p^\circ$  is the vapor pressure of the pure component:

$$p_A = p_A^\circ(x_A)$$

- where  $x_A$  refers to the mole fraction of component A in the condensed-phase solution.
- Unfortunately, Raoult's law has very limited applicability in describing the behavior of most solutions encountered in material processing. We are forced to use Raoult's law when we have no other information about a system.



# Non-Ideal Solutions — Activity Coefficients

- solution phases encountered in materials processing are seldom ideal, and some are very far from ideal. One way to describe the behavior of a solute is to define how far it deviates from ideality. A parameter that describes such deviation is called the activity coefficient and has the symbol  $\gamma$ .
- Raoult's law is altered to include an activity coefficient to define the "extent of non-ideality". In terms of constituent A:

$$a_A = \text{activity of A} = (\gamma_A)(x_A) = p_A/p_A^\circ$$

If Raoult's law is valid,  $\gamma = 1$ .

# Non-Ideal Solutions — Activity Coefficients

- Where it is not,  $\gamma$  is some function of composition and temperature.
- The activity coefficient may be greater than one, in which case the solution component is said to deviate positively from Raoult's law. A negative deviation occurs when  $\gamma$  is less than one.
- In cases where the deviation from ideality is fairly symmetrical across the range of composition, a one-parameter equation has been found to be useful — the regular solution approximation.

$$R T \ln(\gamma_A) = \alpha(x_B)^2$$

- where  $\alpha$  is a constant, independent of temperature and composition, with the same value for both constituents of a binary solution

# Non-Ideal Solutions — Activity Coefficients

- We see that as  $x_A \rightarrow 1$ ,  $\gamma_A \rightarrow 1$  (Raoult's law)
- The solvent constituent becomes more ideal as its composition increases.
- as  $x_A \rightarrow 0$ , the activity coefficient of the dilute solute ( $\gamma_A$ ) approaches a limiting value, designated  $\gamma_A^\circ$ .
- The use of a fixed activity coefficient for a very dilute solute is designated as the Henry's law approximation, and  $\gamma_A^\circ$  is called the Henry's law activity coefficient.
- Quite often, the Henry's law coefficient is satisfactory for dilute solutions up to a mole fraction of solute of 0.02.

## Example - Evaporation from Liquid Cd - Mg Alloys

- Mixtures of Cd and Mg are heated to 700 °C to form a liquid solution. A 10.00 kg melt contained initially  $w_{\text{Cd}} = 40.0 \%$ . The melt lost 2.5 g by evaporation.
- Calculate the composition of the vapor.
- Data. Cd - Mg liquid alloys obey the regular solution approximation, with  $\alpha = -4100$ .
- The vapor pressure equations for liquid Cd and Mg are:

$$\log(p^\circ_{\text{Cd}}) = -5250/T + 5.05 \qquad \log(p^\circ_{\text{Mg}}) = -6900/T + 5.10$$

$$MW_{\text{Cd}} = 112.4 \text{ g} \quad MW_{\text{Mg}} = 24.305 \text{ g} \quad R = 1.987 \text{ cal/g-mol K}$$

$$R T \ln(\gamma_A) = \alpha(x_B)^2 \qquad (\gamma_A)(x_A) = p_A/p^\circ_A$$



## Example - Evaporation from Liquid Cd - Mg Alloys

$$n_{\text{Cd}}=4000/112.4 = 35.58 \quad n_{\text{Mg}}=6000/24.305=246.86$$

$$x_{\text{Cd}}=35.58/(35.58+246.86)=0.126 \quad x_{\text{Mg}}=1-0.126=0.874$$

$$1.987(973)(\ln \gamma_{\text{Cd}}) = -4100(0.874)^2 \rightarrow \gamma_{\text{Cd}} = 0.198$$

$$1.987(973)(\ln \gamma_{\text{Mg}}) = -4100(0.126)^2 \rightarrow \gamma_{\text{Mg}} = 0.967$$

$$\log(p^{\circ}_{\text{Cd}}) = -5250/T + 5.05 \rightarrow p^{\circ}_{\text{Cd}} = 0.451 \text{ @973K}$$

$$\log(p^{\circ}_{\text{Mg}}) = -6900/T + 5.10 \rightarrow p^{\circ}_{\text{Mg}} = 0.0102 \text{ @973K}$$

$$p_{\text{Cd}} = 0.451(0.198)(0.126) = 0.0113 \text{ atm}$$

$$p_{\text{Mg}} = 0.0102(0.967)(0.874) = 0.00862 \text{ atm}$$

$$x_{\text{Cd}}=0.0113/(0.0113+0.00862)=0.567 \quad x_{\text{Mg}}=0.433$$

$$w_{\text{Cd}}=85.8\%$$

$$w_{\text{Mg}}=14.2\%$$

# Next Week

- **Statistical Concepts Applied to Measurement and Sampling**
- **HSC Chemistry ©Outetec programme**
- **Completion of team and group assignments**