1. *Understand* ***chemical potential*** *and the* ***thermodynamic conditions for equilibrium****, from which are derived all the important relations that you need. Be prepared to derive any of them starting from the first and second law of thermodynamics.*

- *The Clapeyron eq. for any two phases*
- *The Phase Rule* $F = C - P + 2$ (for T and p)
- $\mu_{A,\text{ liquid}} - \mu^*_{A,\text{ liquid}} = RT \ln x_A$
- *boiling point elevation (in terms of mole fraction or activity or molality)*
- *freezing point depression (")*
- *osmotic pressure (")*
- *definitions of activity*

Be prepared to apply the thermodynamic conditions for equilibrium to a new practical problem or application.

2. *Understand quantitatively p vs. x and T vs. x phase diagrams for two component systems involving gas, liquid, and solid, miscible and otherwise. Be prepared to describe completely (how many phases, composition of each phase, how much of each phase, how many degrees of freedom) any state point, and any p-changing or T-changing process in a phase diagram. Understand the relation between experimental cooling curves and the phase diagram.*

Summary of activities, solvent, solute

Definition	Rational	Practical
applied to→	solvent	solute
basis	x_A	x_B
basis	*Raoult*	*Henry*
definition of activity $\boldsymbol{a}$	$\boldsymbol{a}_A \equiv f_A/f^*_A$ $[\boldsymbol{a}_A = p_A/p^*_A]$	$\boldsymbol{a}_B \equiv p_B/K_H$
definition of activity coeff γ	$\gamma_A \equiv \boldsymbol{a}_A/x_A$	$\gamma_B \equiv \boldsymbol{a}_B/x_B$
limiting behavior $\gamma \to 1$	as $x_A \to 1$ $\gamma_A \to 1$ $\boldsymbol{a}_A \to x_A$	as $x_B \to 0$ $\gamma_B \to 1$ $\boldsymbol{a}_B \to x_B$
ideal solution $\gamma=1$	$\boldsymbol{a}_{A,ideal} = x_A$	$\boldsymbol{a}_{B,\ ideal} = x_B$
$\boldsymbol{a}=1$, $\mu_T = \mu^{\ominus}_T$ for standard state at 1 bar	pure liquid *A* $\mu_A{}^{\ominus}{}_T = \mu_A{}^*{}_T$	fictitious solution having $p_B = K_H$

Summary of activities, solute:

Definition	Practical, m_B	Practical
applied to→	solute	solute
basis	m_B	x_B
basis	Henry	Henry
definition of activity $\boldsymbol{a}$	$\boldsymbol{a}_B \equiv p_B/K'_H$ $p_B = K'_H\, m_B$ $\boldsymbol{a}_B \equiv \gamma_B(m_B/1)$	$\boldsymbol{a}_B \equiv p_B/K_H$
definition of activity coeff γ	$\gamma_B \equiv \boldsymbol{a}_B/m_B$	$\gamma_B \equiv \boldsymbol{a}_B/x_B$
limiting behavior $\gamma \to 1$	as $x_B \to 0$ $\gamma_B \to 1$ $\boldsymbol{a}_B \to m_B$	as $x_B \to 0$ $\gamma_B \to 1$ $\boldsymbol{a}_B \to x_B$
ideal solution $\gamma=1$	$\boldsymbol{a}_{B,\ ideal} = m_B$	$\boldsymbol{a}_{B,\ ideal} = x_B$
$\boldsymbol{a}=1$ for standard state $\mu^{\ominus}_T$ at 1 bar	fictitious Henry's law solution of unit molality	fictitious solution having $p_B = K_H$

Summary of activities:

Definition	Rational	Practical
applied to	solvent	solute
basis	x_A	x_B
definition of activity a	$a_A \equiv f_A/f^*_A$ $[a_A = p_A/p^*_A]$	$a_B \equiv p_B/K_H$
definition of activity coeff γ	$\gamma_A \equiv a_A/x_A$	$\gamma_B \equiv a_B/x_B$
limiting behavior	as $x_A \to 1$ $\gamma_A \to 1$ $a_A \to x_A$	as $x_B \to 0$ $\gamma_B \to 1$ $a_B \to x_B$
how to measure a	$\ln a_A = -\Delta_{fus}H/R \cdot \{(1/T_f)-(1/T_f^*)\}$ $\ln a_A = -\Delta_{vap}H/R \cdot \{-(1/T_b)+(1/T_b^*)\}$ $\ln a_A = -V_m\pi/RT$ $a_A = p_A/p^*_A$	$a_B = \Delta_{fus}H/R \cdot \{(1/T_f)-(1/T_f^*)\}$ $a_B = \Delta_{vap}H/R \cdot \{-(1/T_b)+(1/T_b^*)\}$ $a_B = V_m\pi/RT$ $a_B \equiv p_B/K_H$

Summary of activities $\mu_T = \mu^\ominus_T + RT\ln a$

Definition		
applied to→	gas mixture	pure gas
standard state at 1 bar $\mu^\ominus_T$	fictitious pure gas at 1 bar behaving ideally	fictitious gas at 1 bar behaving ideally
definition of activity, a (or f fugacity for gases)	$a_A \equiv f_A$	$RT\ln a = \int V dp$ $a = f$ $\ln(f/p) \equiv \int_0^p [Z-1]dp/p$
definition of activity coeff γ	$\gamma_A \equiv f_A/p_A$	$\gamma \equiv f/p$
limiting behavior $\gamma \to 1$	as $p \to 0$ $\gamma_A \to 1$ $f_A \to x_A p$	as $p \to 0$ $\gamma \to 1$ $f \to p$
ideal gas $\gamma = 1$	$f_{A,ideal} = p_A = x_A p$	$f_{ideal} = p$

AVOID	Instead, **DO THIS**
`d`T` = 0 since adiabatic`	adiabatic means q**=0**, and T **has to change** [except if ideal gas and W=0].
$\Delta\boldsymbol{U}=\Delta\boldsymbol{H}=0$ *since isothermal*	**only** happens for **ideal gas** under p,V changes
$\Delta\boldsymbol{U} = q$	$\int d\boldsymbol{U} = \int C_V dT + \int(\partial\boldsymbol{U}/\partial V)_T dV$ leads to $\Delta\boldsymbol{U}_V = \int C_V dT = q_{\boldsymbol{V}}$
$\Delta\boldsymbol{H} = q$	$\int d\boldsymbol{H} = \int C_p dT + \int(\partial\boldsymbol{H}/\partial p)_T dp$ leads to $\Delta\boldsymbol{H}_p = \int C_p dT = q_{\boldsymbol{p}}$
$\Delta\boldsymbol{S}_T = q/T$	$\int d\boldsymbol{S} = \int dq_{\boldsymbol{REV}}/\mathrm{T}$ leads to $\Delta\boldsymbol{S}_T = q_{\boldsymbol{REV}}/T$
$\Delta\boldsymbol{A}_T = W$	$\int d\boldsymbol{A} = \int -p dV - \int \boldsymbol{S} dT$ leads to $\Delta\boldsymbol{A}_T = W_{\boldsymbol{REV}}$

AVOID	Instead, **DO THIS**
$\Delta \boldsymbol{S}_{T,p} = \Delta \boldsymbol{H}_{trans}/T_{trans}$	At constant T and p, $q_p = \Delta \boldsymbol{H}$ but $q_p = q_{REV}$ ***only when*** the 2 phases are at equilibrium at this (T,p)
$\Delta \boldsymbol{S}_T = -R\ln p_2/p_1$	$\mathrm{d}\boldsymbol{S} = (\partial \boldsymbol{S}/\partial T)_p \mathrm{d}T + (\partial \boldsymbol{S}/\partial p)_T \mathrm{d}p$ $\Delta \boldsymbol{S}_T = \int (\partial \boldsymbol{S}/\partial p)_T \mathrm{d}p$ $(\partial \boldsymbol{S}/\partial p)_T = -(\partial V/\partial T)_p$ $= -R/p$ **only for** an ideal gas
$\Delta \boldsymbol{G}_T = RT\ln p_2/p_1$	$\mathrm{d}\boldsymbol{G} = V\mathrm{d}p - \boldsymbol{S}\mathrm{d}T$ $\Delta \boldsymbol{G}_T = \int V\mathrm{d}p$ $V = RT/p$ **only for** an ideal gas
$p_C = x_C p_C^*$ or $p_C = x_C K_{H,C}$	$\lim_{x_C \to 0} p_C = x_C K_{H,C}$ $p_C = a_C p_C^*$ (rational) or $p_C = a_C K_{H,C}$ (practical) where $\gamma_C = a_C/x_C$

- When integrating:

(a) Must integrate **both** sides of an equation in order for the equality to hold.
(b) Must integrate using **the same state point** for the lower limit on **both** sides of the equation. Likewise must integrate using the same state point for the upper limit on **both** sides of the equation.

- **If no phase or chemical changes**, can use $\Delta \boldsymbol{H} = \int(\partial \boldsymbol{H}/\partial T)_p \, dT + \int(\partial \boldsymbol{H}/\partial p)_T dp$

$\Delta \boldsymbol{U} = \int(\partial \boldsymbol{U}/\partial T)_V \, dT + \int(\partial \boldsymbol{U}/\partial V)_T dV$
$\Delta \boldsymbol{S} = \int(\partial \boldsymbol{S}/\partial T)_p \, dT + \int(\partial \boldsymbol{S}/\partial p)_T dp$
$\Delta \boldsymbol{S} = \int(\partial \boldsymbol{S}/\partial T)_V \, dT + \int(\partial \boldsymbol{S}/\partial V)_T dV$
$\Delta \boldsymbol{G} = \int(\partial \boldsymbol{G}/\partial T)_p \, dT + \int(\partial \boldsymbol{G}/\partial p)_T dp$
where $(\partial \boldsymbol{G}/\partial T)_p = -\boldsymbol{S}$ and $(\partial \boldsymbol{G}/\partial p)_T = V$
otherwise there is a $\Delta_{vap}\boldsymbol{U}$, $\Delta_{vap}\boldsymbol{H}$, $\Delta_{vap}\boldsymbol{S}$, $\Delta_{vap}\boldsymbol{H}$, $\Delta_{vap}\boldsymbol{G}$ for a phase change itself and there is a $\Delta_{rxn}\boldsymbol{U}$, $\Delta_{rxn}\boldsymbol{H}$, $\Delta_{rxn}\boldsymbol{S}$, $\Delta_{rxn}\boldsymbol{H}$, $\Delta_{rxn}\boldsymbol{G}$ for a chemical change.

- **Only when** the phase change occurs reversibly (that is the two phases are at equilibrium with each other during the phase change) we can use
$\Delta_{vap}\boldsymbol{S} = \Delta_{vap}\boldsymbol{H}/T_b$ and $\Delta_{vap}\boldsymbol{G} = 0$.
At any other (T,p) conditions, can not use these. It is always possible to find $\Delta\boldsymbol{U}$, $\Delta\boldsymbol{H}$, $\Delta\boldsymbol{S}$, $\Delta\boldsymbol{H}$, $\Delta\boldsymbol{G}$ for a (for example irreversible) process by using an algebraic sum of alternate (for example, reversible) paths from initial to final states.

- A tie line provides, at each of its ends, a description (what phases and what compositions in each phase) of the nature of the phases at equilibrium.

- A pure substance does not have variable composition! A phase that has variable x_A can not be a pure substance!