

Physical Chemistry for Energy Engineering (15th: 2018/11/07)

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Seoul National University

*The class follows the text book: D.A. McQuarrie, J.D. Simon, "Physical Chemistry: A Molecular Approach", University Science Books (1997).

Course schedule (as of Nov. 5)

Deadline for appealing on exam-1 result: Nov. 12

Submission time of the homework-2: beginning of the class on Nov. 12.

	29-Oct	No lecture
	31-Oct	
14	5-Nov	2. Phase equilibrium-1
15	7-Nov	2. Phase equilibrium-2
16	12-Nov	3. Chemical equilibrium-1
17	14-Nov	Answers of homework-2
18	19-Nov	Exam-02 (2 hour)
19	21-Nov	3. Chemical equilibrium-2
20	26-Nov	3. Chemical equilibrium-3
21	28-Nov	3. Chemical equilibrium-4
22	3-Dec	3. Chemical kinetics-1
23	5-Dec	3. Chemical kinetics-2
24	10-Dec	3. Chemical kinetics-3
25	12-Dec	Answers of homework-3
26	17-Dec	Exam-03 (2 hour)

Modification in Homework-02

In HW02-07, the link to thermodynamic data is dead.

<http://courses.chem.indiana.edu/c360/documents/thermodynamicdata.pdf>

Instead, please use the file I uploaded on eTL.

In addition, you cannot find the standard entropy nor the standard Gibbs energy of formation. So, please [use 212 \[J/K/mol\] as the standard molar entropy of glucose.](#)

Molecular formula	Name	Crystal			
		$\Delta_f H^\circ$ kJ/mol	$\Delta_f G^\circ$ kJ/mol	S° J/mol K	C_p J/mol K
$C_6H_{12}O_6$	β -D-Fructose	-1265.6			
$C_6H_{12}O_6$	D-Galactose	-1286.3			
$C_6H_{12}O_6$	α -D-Glucose	-1273.3			
$C_6H_{12}O_6$	D-Mannose	-1263.0			
$C_6H_{12}O_6$	L-Sorbose	-1271.5			
$C_6H_{12}O_6$	Thiomannose				

Contents of today

<Last class>

2.3. Phase equilibrium-1: a typical case (1 component)

<Today's class>

2.3. Phase equilibrium-1: a typical case (1 component)

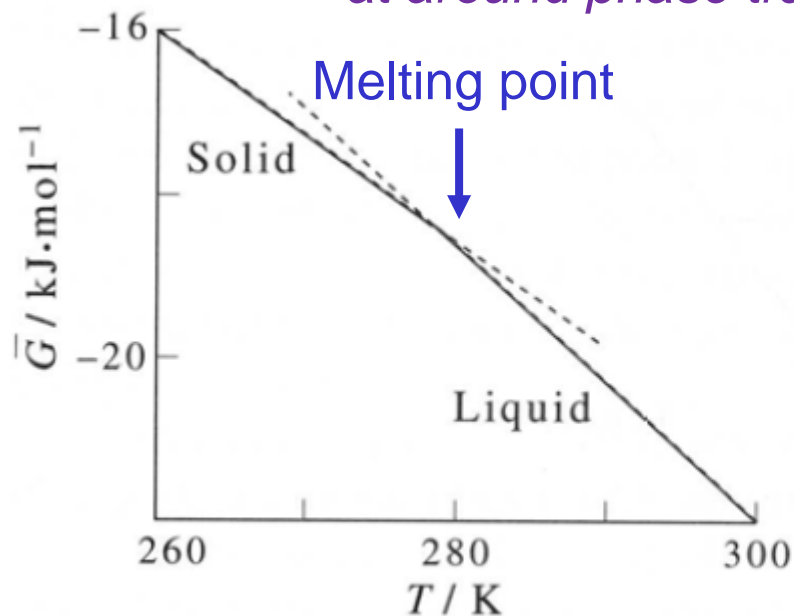
2.3.1. Chemical potential and phase rule

2.3.2. Freezing mechanism

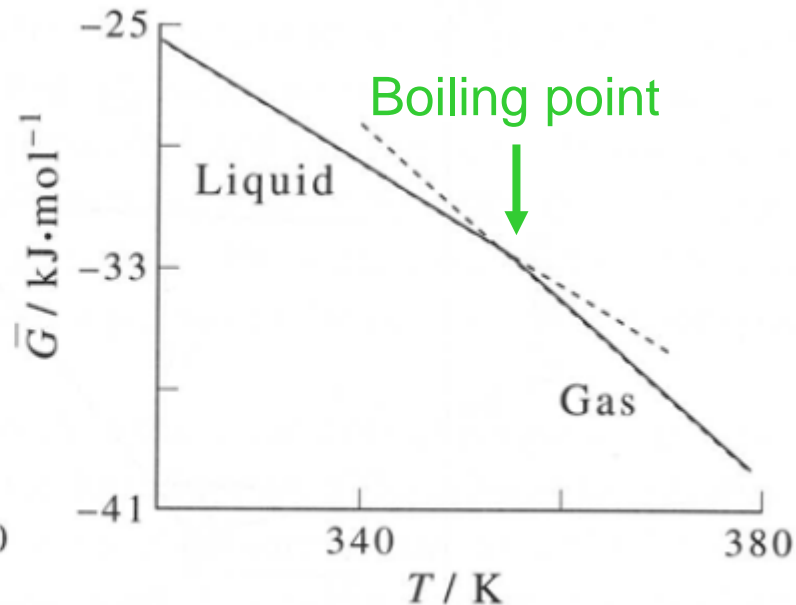
2.3. Phase equilibrium-1: a typical case (1 component)

- §23-2: The Gibbs energy of a substance has a close connection to its phase diagram -

Comparison of the molar Gibbs energies (\bar{G}) as a function of temperature at around phase transitions for benzen



(a)



(b)

- ✓ The molar Gibbs energy is a continuous function, but there is a discontinuity in its first derivative (by temperature) at phase transitions.
- ✓ The dotted line is theoretical: in experiment/reality, that state are unstable. The equilibrium phase the appear in experiment/reality has a phase of the lowest molar Gibbs energy.

2.3. Phase equilibrium-1: a typical case (1 component)

- \$22-4: The enthalpy of an ideal gas is independent of pressure-

Maxwell relation for Gibbs energy (G)

Differential equation of Gibbs energy ($G = U - TS + PV$) is:

$$dG = dU - TdS - SdT + PdV + VdP$$

Considering a process along a reversible path, the first law is:

$$dU = \delta q_{rev} + \delta w_{rev} = TdS - PdV$$

Hence,

$$dG = -SdT + VdP$$

Here, we can compare it with the total derivative of $G = G(T, P)$

$$dG = \left(\frac{\partial G}{\partial T}\right)_P dT + \left(\frac{\partial G}{\partial P}\right)_T dP, \text{ then}$$

$$\left(\frac{\partial G}{\partial T}\right)_P = -S \text{ and } \left(\frac{\partial G}{\partial P}\right)_T = V$$

Since, the cross derivatives are equal as:

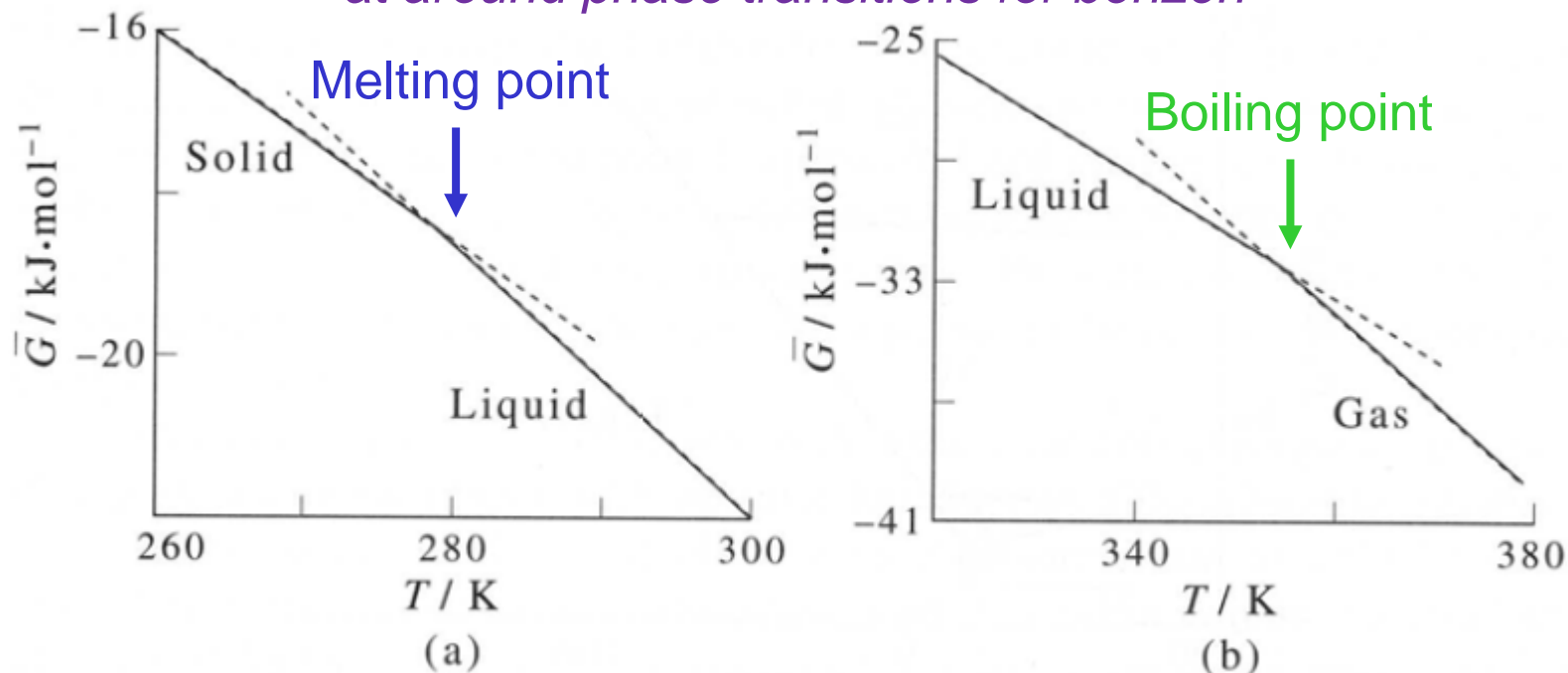
$$\left(\frac{\partial^2 G}{\partial T \partial P}\right) = \left(\frac{\partial^2 G}{\partial P \partial T}\right), \text{ then}$$
$$-\left(\frac{\partial S}{\partial P}\right)_T = \left(\frac{\partial V}{\partial T}\right)_P$$

This relation shows the enthalpy of an ideal gas is independent of pressure.

2.3. Phase equilibrium-1: a typical case (1 component)

- §23-2: The Gibbs energy of a substance has a close connection to its phase diagram -

Comparison of the molar Gibbs energies (\bar{G}) as a function of temperature at around phase transitions for benzen



- ✓ The left figure is $\bar{G} - P$ graph around solid-liquid phase transition (melting, fusion)
 - $(\partial\bar{G}/\partial T)_P = -\bar{S}$, which corresponds to the slope in figures.
 - As liquid is more disordered than solid, $\bar{S}^l > \bar{S}^s$.
 - Thus, as $\bar{G} = \bar{H} - T\bar{S}$, $\bar{G}^l < \bar{G}^s$ must be achieved at high temperatures.
- ✓ The same thing is realized in liquid-gas phase transition (boiling), as given in the right figure.

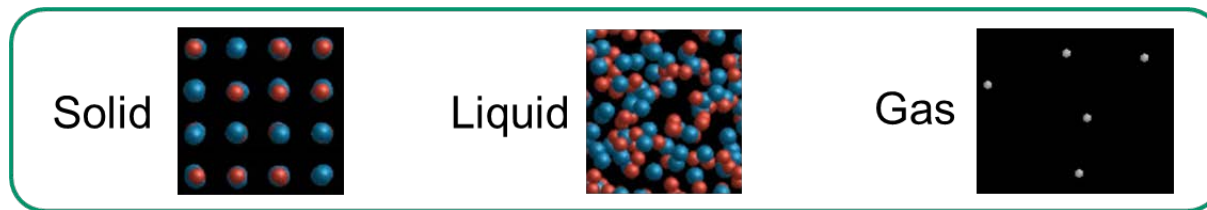
2.3. Phase equilibrium-1: a typical case (1 component)

- \$23-2: The Gibbs energy of a substance has a close connection to its phase diagram -

- ✓ As we have learned, the (molar) Gibbs energy indicates which state (phase) appears at equilibrium under constant-T constant-P condition.
 - ✓ Be careful that **a smaller Gibbs energy means more stable**.
- ✓ As $G = H - TS$ ($\bar{G} = \bar{H} - T\bar{S}$), the enthalpy term (H) plays a dominant role at low temperatures, while the entropy term ($-TS$) at high temperatures.
- ✓ In comparison of gas/liquid/solid phases, as we have learned:

$$\bar{S}^g \gg \bar{S}^l > \bar{S}^s (\geq 0) \quad (\text{due to disorder})$$

$$\Delta_f H^g > \Delta_f H^l > \Delta_f H^s \quad (\text{due to bonding nature})$$

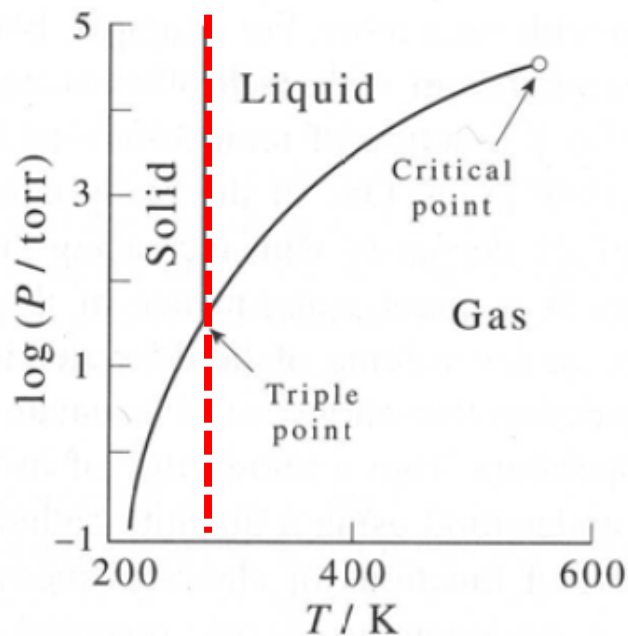


- ✓ Hence, comparing the Gibbs energies, we can say the following points in general:
 - At low temperatures, a solid phase is **always** favored due to its low enthalpy. So, every substance becomes solid at sufficiently low temperatures.
 - At high temperatures, a gaseous phase is **always** favored due to its high entropy. So, every substance becomes gas at sufficiently high temperatures.
 - At intermediate temperatures, a liquid phase is **often (not always)** favored as a balance between enthalpy and entropy.

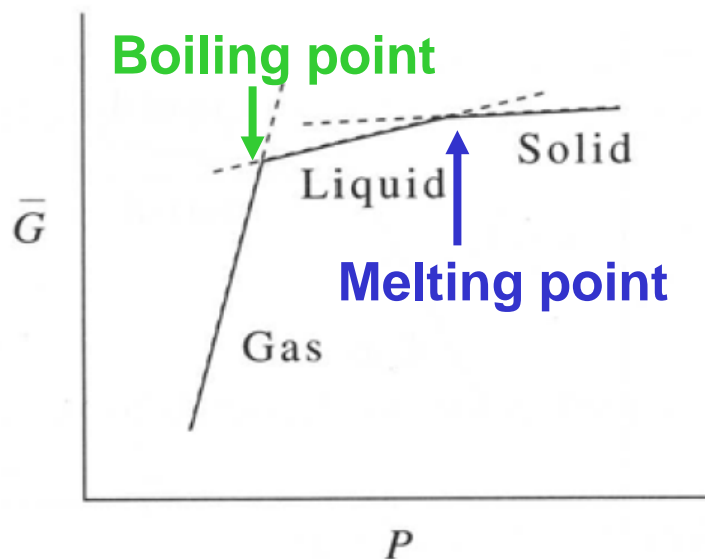
2.3. Phase equilibrium-1: a typical case (1 component)

- §23-2: The Gibbs energy of a substance has a close connection to its phase diagram -

The phase diagram of benzene



The molar Gibbs energies (\bar{G}) as a function of pressure at around the triple point for benzene

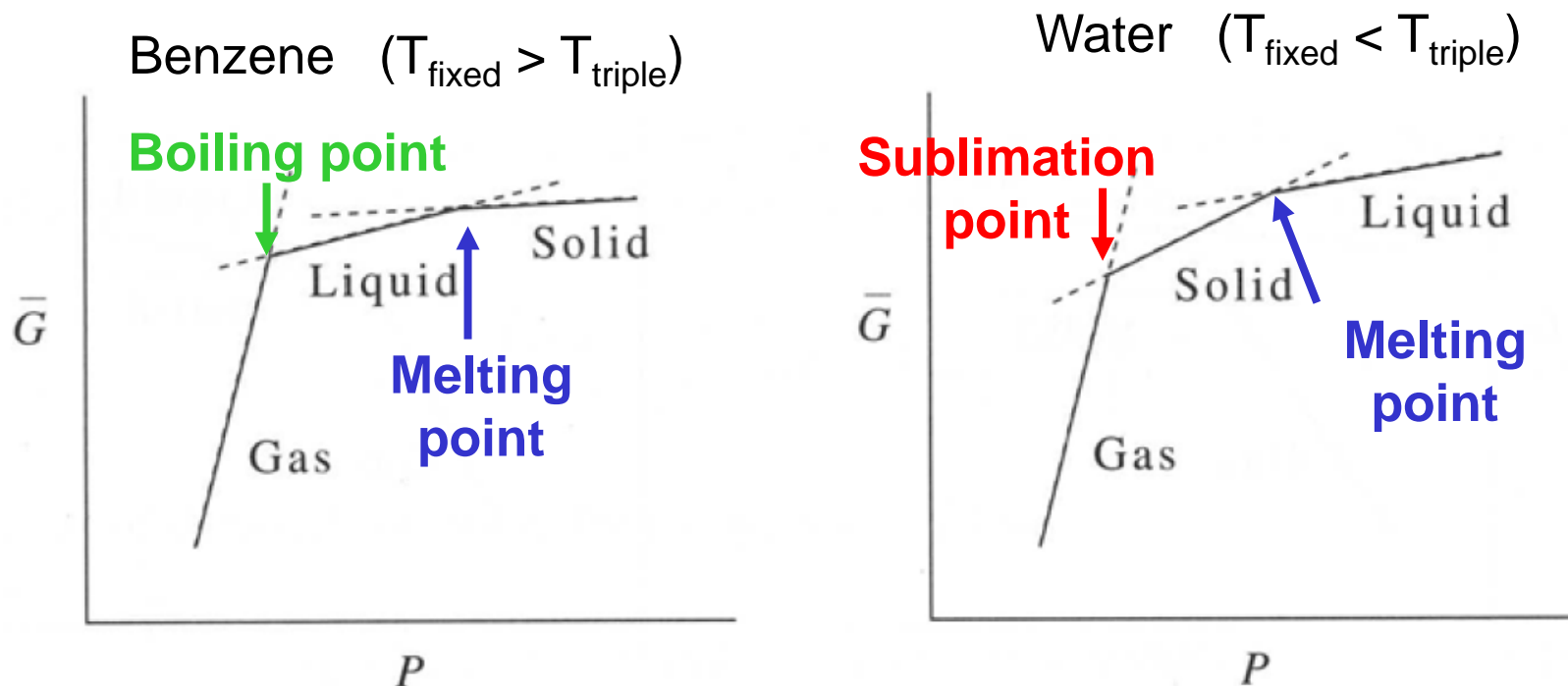


- ✓ Because the solid-liquid coexistence curve has a positive slope for most substances including benzene, to observe both gas-liquid and liquid-solid intersects in $\bar{G} - P$ graph, the temperature should be fixed at one slightly higher than the triple point temperature.
 - Otherwise, only a gas-solid intersect appears (no stable liquid phase)
- ✓ For water, where the slope of solid-liquid coexistence curve is negative, we can see solid-liquid intersect at a high pressure.

2.3. Phase equilibrium-1: a typical case (1 component)

- \$23-2: The Gibbs energy of a substance has a close connection to its phase diagram -

The molar Gibbs energy (\bar{G}) as a function of pressure at around the triple point



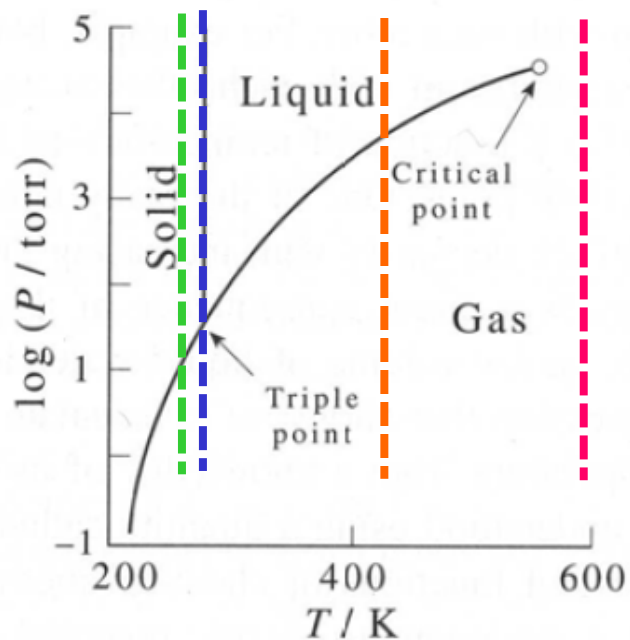
✓ In $G - P$ graph:

- $(\partial \bar{G} / \partial P)_T = \bar{V} > 0$. Thus the slope in this graph must be positive.
- In most substances including benzene, $\bar{V}^g \gg \bar{V}^l > \bar{V}^s$. Hence the slopes are given as in the left figure.
- In some substances like water, however, $\bar{V}^g \gg \bar{V}^s > \bar{V}^l$. Thus, the slopes are given as in the right figure.

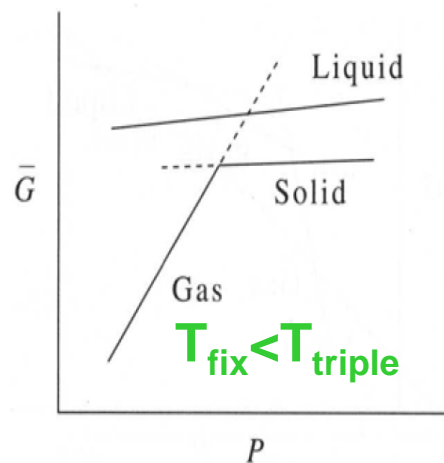
2.3. Phase equilibrium-1: a typical case (1 component)

- §23-2: The Gibbs energy of a substance has a close connection to its phase diagram -

The phase diagram of benzene



The molar Gibbs energies (\bar{G}) as a function of pressure with different T_{fixed}



$$T_{\text{fix}} = T_{\text{triple}}$$

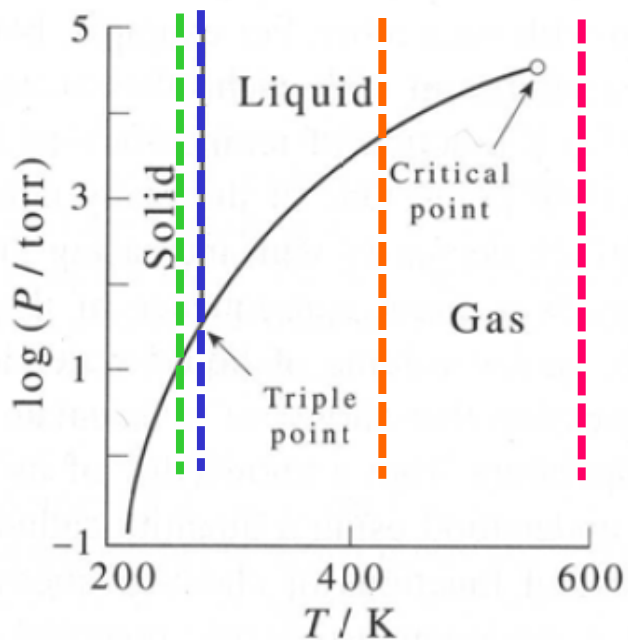
$$T_{\text{fix}} \gg T_{\text{triple}}$$

$$T_{\text{fix}} > T_{\text{critical}}$$

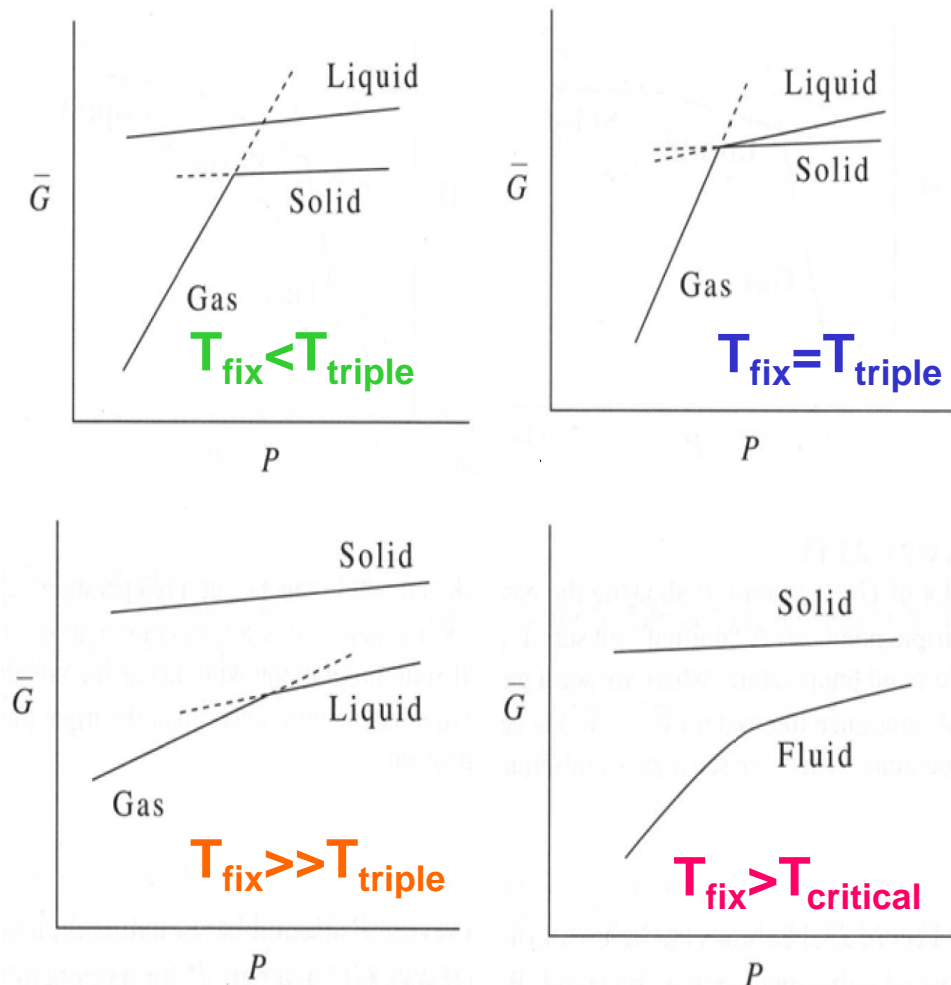
2.3. Phase equilibrium-1: a typical case (1 component)

- §23-2: The Gibbs energy of a substance has a close connection to its phase diagram -

The phase diagram of benzene



The molar Gibbs energies (\bar{G}) as a function of pressure with different T_{fixed}



2.3. Phase equilibrium-1: a typical case (1 component)

- §23-3: The chemical potentials of a pure substance in two phases in equilibrium are equal -

We consider a system consisting of two phases of a pure substance (1-component) in equilibrium each other. (liquid and gas, for example here)

The Gibbs energy of this system is given by

$$G = G^l + G^g$$

where G^l and G^g are the Gibbs energies of the liquid and the gas phase.

Now, suppose dn mole are transferred from the liquid to the solid phase, where T and P are kept constant. The infinitesimal change in Gibbs energy for this process is:

$$dG = \left(\frac{\partial G^g}{\partial n^g} \right)_{P,T} dn^g + \left(\frac{\partial G^l}{\partial n^l} \right)_{P,T} dn^l$$

As $dn^l = -dn^g$, then

$$dG = \left[\left(\frac{\partial G^g}{\partial n^g} \right)_{P,T} - \left(\frac{\partial G^l}{\partial n^l} \right)_{P,T} \right] dn^g$$

Here, we define *chemical potentials*, $\mu^g = \left(\frac{\partial G^g}{\partial n^g} \right)_{P,T}$ and $\mu^l = \left(\frac{\partial G^l}{\partial n^l} \right)_{P,T}$, then

$$dG = [\mu^g - \mu^l] dn^g \quad (\text{constant T and P})$$

2.3. Phase equilibrium-1: a typical case (1 component)

- §23-3: The chemical potentials of a pure substance in two phases in equilibrium are equal -

We consider a system consisting of two phases of a pure substance (1-component) in equilibrium each other. (liquid and gas, for example here)

$$dG = [\mu^g - \mu^l]dn^g \quad (\text{constant } T \text{ and } P)$$

where *chemical potentials* are $\mu^g = \left(\frac{\partial G^g}{\partial n^g}\right)_{P,T}$ and $\mu^l = \left(\frac{\partial G^l}{\partial n^l}\right)_{P,T}$.

- ✓ If the two phases are in equilibrium with each other, then $dG = 0$.
- ✓ And because we suppose some amount of the liquid phase is transferred to the gas phase (dn^g) here, to make $dG = 0$ in this condition, $\mu^g = \mu^l$ is needed.
 - If $\mu^g < \mu^l$, $[\mu^g - \mu^l] < 0$. Thus, the process of $dn^g > 0$ (transfer from the liquid phase to the gas phase) spontaneously takes place as $dG < 0$ is achieved by the transfer.
 - Likewise, if $\mu^g > \mu^l$, $dn^g < 0$.
 - Hence, in general, the mass transfer occurs from the phase with higher chemical potential to the phase with lower chemical potential.

2.3. Phase equilibrium-1: a typical case (1 component)

- §23-3: The chemical potentials of a pure substance in two phases in equilibrium are equal -

- ✓ The chemical potential is defined as:

$$\mu = \left(\frac{\partial G}{\partial n} \right)_{P,T}$$

- ✓ Because G is proportional to the size/amount of a system $G \propto n$, namely an extensive thermodynamic function, we can express it as:

$$G(n, T, P) = n\mu(T, P)$$

Apparently, $\mu(T, P)$ corresponds to molar Gibbs energy as

$$\mu(T, P) = G(n, T, P)/n = \bar{G}(T, P)$$

- ✓ Indeed, this equation is consistent with the definition of chemical potential:

$$\mu = \left(\frac{\partial G}{\partial n} \right)_{P,T} = \left(\frac{\partial [n\mu(T, P)]}{\partial n} \right)_{P,T} = \mu(T, P)$$

which means $\mu(T, P)$, the chemical potential, is the same quantity as the molar Gibbs energy and it is an intensive quantity.

(Appendix) more about chemical potential

- ✓ The following definition is for single component at const.-T const.-P condition:

$$\mu(T, P) = \left(\frac{\partial G}{\partial n} \right)_{T, P} = \bar{G}(T, P)$$

- ✓ If the condition becomes const.-T const.-V:

$$\mu(T, V) = \left(\frac{\partial A}{\partial n} \right)_{T, V} = \bar{A}(T, V)$$

- ✓ If the condition becomes const.-U and const.-V:

$$\mu(U, V) = -T \left(\frac{\partial S}{\partial n} \right)_{U, V} = -T \bar{S}(U, V)$$

- ✓ For multiple components and const.-T const.-P condition,

$$\mu_i(T, P, \mathbf{n}) = \left(\frac{\partial G}{\partial n_i} \right)_{T, P, n_{j \neq i}}$$

$$G(T, P, \mathbf{n}) = \sum_i n_i \mu_i(T, P, \mathbf{n})$$

2.3. Phase equilibrium-1: a typical case (1 component)

- §23-3: The chemical potentials of a pure substance in two phases in equilibrium are equal -

We consider two phases (α and β) are in equilibrium each other.

As they are in equilibrium,

$$\mu^\alpha(T, P) = \mu^\beta(T, P)$$

Now take the differentials of both sides

$$d\mu^\alpha(T, P) = d\mu^\beta(T, P)$$

$$\left(\frac{\partial\mu^\alpha}{\partial P}\right)_T dP + \left(\frac{\partial\mu^\alpha}{\partial T}\right)_P dT = \left(\frac{\partial\mu^\beta}{\partial P}\right)_T dP + \left(\frac{\partial\mu^\beta}{\partial T}\right)_P dT$$

Since μ is simply the molar Gibbs energy for a single substance, utilizing $\left(\frac{\partial G}{\partial P}\right)_T =$

V and $\left(\frac{\partial G}{\partial T}\right)_P = -S$ (*these were previously derived along Maxwell relations)

$$\left(\frac{\partial\mu}{\partial P}\right)_T = \left(\frac{\partial\bar{G}}{\partial P}\right)_T = \bar{V} \quad \text{and} \quad \left(\frac{\partial\mu}{\partial T}\right)_P = \left(\frac{\partial\bar{G}}{\partial T}\right)_P = -\bar{S}$$

where \bar{V} and \bar{S} are the molar volume and the molar entropy. Then,

$$\bar{V}^\alpha dP - \bar{S}^\alpha dT = \bar{V}^\beta dP - \bar{S}^\beta dT$$

$$\frac{dP}{dT} = \frac{\bar{S}^\beta - \bar{S}^\alpha}{\bar{V}^\beta - \bar{V}^\alpha}$$

2.3. Phase equilibrium-1: a typical case (1 component)

- §23-3: The chemical potentials of a pure substance in two phases in equilibrium are equal -

We consider two phases (α and β) are in equilibrium each other.

$$\bar{V}^{\alpha} dP - \bar{S}^{\alpha} dT = \bar{V}^{\beta} dP - \bar{S}^{\beta} dT, \quad \frac{dP}{dT} = \frac{\bar{S}^{\beta} - \bar{S}^{\alpha}}{\bar{V}^{\beta} - \bar{V}^{\alpha}}$$

We apply this equation to a phase transition (e.g. melting),

$$\frac{dP_{trs}}{dT_{trs}} = \frac{\bar{S}^{\beta} - \bar{S}^{\alpha}}{\bar{V}^{\beta} - \bar{V}^{\alpha}} = \frac{\Delta_{trs}\bar{S}}{\Delta_{trs}\bar{V}}$$

As the phase transition occurs at a certain (fixed) temperature and pressure, we have the following relation (please check the material on #13)

$$\Delta_{trs}\bar{S} = \frac{\Delta_{trs}\bar{H}}{T_{trs}}$$

Then, using this relation, we achieve

$$\frac{dP_{trs}}{dT_{trs}} = \frac{\bar{S}^{\beta} - \bar{S}^{\alpha}}{\bar{V}^{\beta} - \bar{V}^{\alpha}} = \frac{\Delta_{trs}\bar{S}}{\Delta_{trs}\bar{V}} = \frac{\Delta_{trs}\bar{H}/T_{trs}}{\Delta_{trs}\bar{V}} = \frac{\Delta_{trs}\bar{H}}{T_{trs}\Delta_{trs}\bar{V}}$$

The equation $\frac{dP_{trs}}{dT_{trs}} = \frac{\Delta_{trs}\bar{H}}{T_{trs}\Delta_{trs}\bar{V}}$ is called the *Clapeyron equation*, which relates “the slope of the two-phase boundary line in a phase diagram with the values of $\Delta_{trs}\bar{H}$ and $\Delta_{trs}\bar{V}$ for a transition between these two phases”.

2.3.1. Chemical potential and phase rule

- \$23-3: The chemical potentials of a pure substance in two phases in equilibrium are equal -

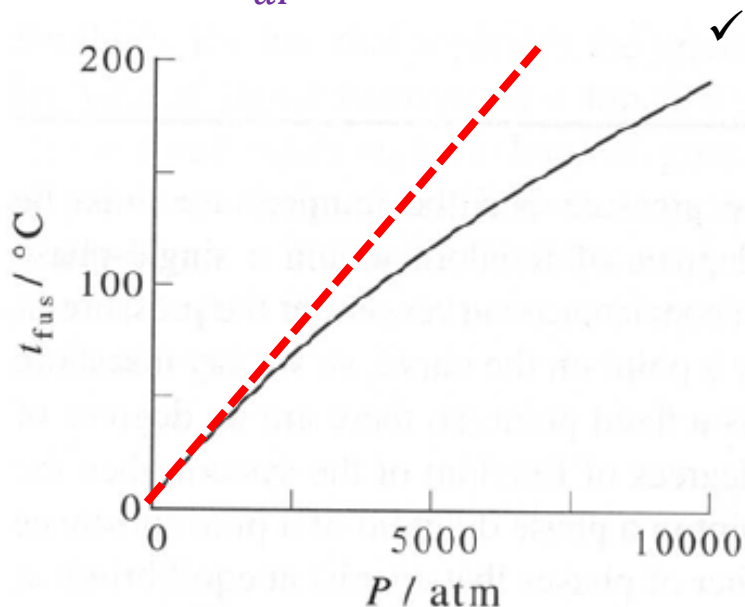
Exampe-1) Solid-liquid coexistence curve at around 1 atm for Benzene

- ✓ $\Delta_{fus}\bar{H} = 9.95 \text{ kJ mol}^{-1}$ and $\Delta_{fus}\bar{V} = 10.3 \text{ cm}^3 \text{ mol}^{-1}$ at the normal melting point (278.7 K).
- ✓ Thus, dP/dT at the normal melting point of benzene is:

$$\frac{dP}{dT} = \frac{\Delta_{trs}\bar{H}}{T\Delta_{trs}\bar{V}} = \frac{9.95 \text{ kJ mol}^{-1}}{(278.7 \text{ K})(10.3 \text{ cm}^3 \text{ mol}^{-1})} = 34.2 \text{ atm K}^{-1}$$

Here, by taking the reciprocal of this result:

$$\frac{dT}{dP} = 0.0292 \text{ K atm}^{-1}$$



- ✓ Using the above result ($0.0292 \text{ K atm}^{-1}$) and assuming $\Delta_{fus}\bar{H}$ and $\Delta_{fus}\bar{V}$ are independent of pressure, we predict the melting point as:

- 308 K at 1000 atm (experimental value is 306 K)
- 570 K at 10000 atm (exp. value $\sim 460 \text{ K}$)

*as clearly seen in the left figure, $\Delta_{fus}\bar{H}$ and $\Delta_{fus}\bar{V}$ are not independent of pressure at high-pressure region

*D.A. McQuarrie, J.D. Simon, "Physical Chemistry: A Molecular Approach", University Science Books (1997).

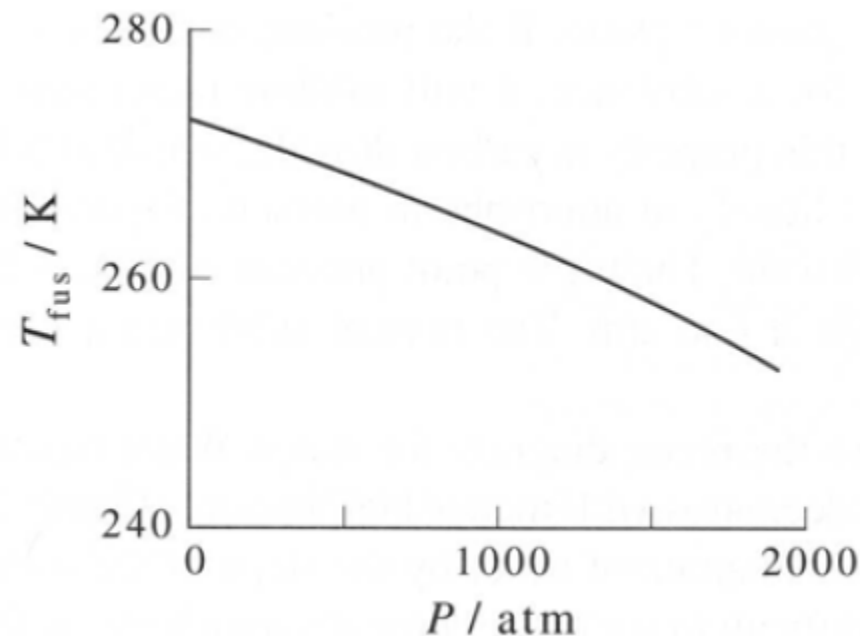
2.3.1. Chemical potential and phase rule

- \$23-3: The chemical potentials of a pure substance in two phases in equilibrium are equal -

Exampe-2) Solid-liquid coexistence curve at around 1 atm for water

- ✓ $\Delta_{fus}\bar{H} = 6.01 \text{ kJ mol}^{-1}$ and $\Delta_{fus}\bar{V} = -1.63 \text{ cm}^3 \text{ mol}^{-1}$ at the normal melting point (273.15 K).
- ✓ Thus, dP/dT at the normal melting point of water is:

$$\frac{dT}{dP} = \frac{T\Delta_{trs}\bar{V}}{\Delta_{trs}\bar{H}} = \frac{(273.15 \text{ K})(-1.63 \text{ cm}^3 \text{ mol}^{-1})}{6.01 \text{ kJ mol}^{-1}} = -0.00751 \text{ K atm}^{-1}$$



- ✓ As already mentioned, the melting point of ice decreases with increasing pressure. Hence, the solid-liquid coexistence curve in P-T phase diagram has a negative slope.
- ✓ This clearly comes from the fact that $\Delta_{fus}\bar{V} < 0$ (the molar volume is larger in solid than that in liquid at around melting point, 1atm)

*D.A. McQuarrie, J.D. Simon, "Physical Chemistry: A Molecular Approach", University Science Books (1997).