

9/10/18 Review session CH 302 Grace JES A/21A

1. Key points in lectures (modules on canvas) (fast)
phase change and thermodynamics
heating curves
phase diagrams
Vapor pressure
 2. Example problems
(adapted from challenging ones in class and HWs)
 3. Review of Van't Hoff factor (solutions & colligative properties)
 4. Questions
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1.1 Phase change & thermodynamics (Definitions, signs)

Entropy S : about the number of potential microstates ↑ more chaotic
Gas > Liquid > solid

Enthalpy H : Energy Gas > Liquid > Solid

Gibbs free energy : $G = H - TS$

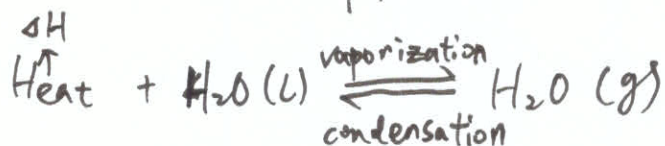
$$\Delta G = \Delta H - T\Delta S$$

$\Delta G \oplus$ non-spontaneous

$\Delta G \ominus$ spontaneous

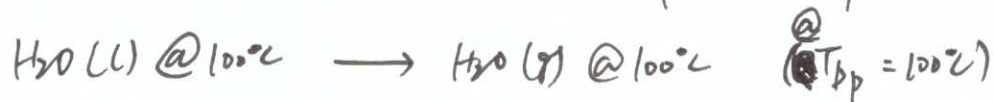
(matter wants the lowest possible free energy)

$\Delta G = 0$ physical equilibrium



$\text{l} \rightarrow \text{g}$ $\Delta H \oplus$: endothermic : add heat into the system

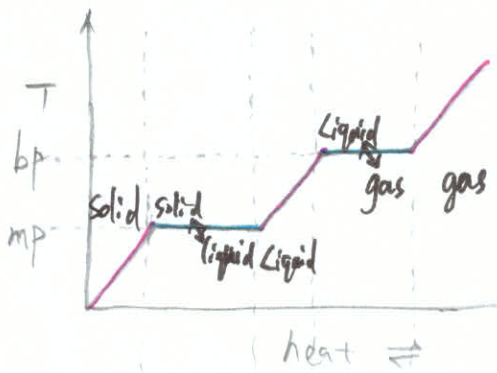
$\text{g} \rightarrow \text{l}$ $\Delta H \ominus$: exothermic : release heat from the system



$$\Delta H_{\text{vap}} = 40.7 \text{ kJ/mol}$$

$$\Delta H_{\text{vaporization}} = -\Delta H_{\text{condensation}}$$

1.2 Heating curve (calculate heat, temperature)



melting point (freezing & melting @ equil)

boiling point (boiling & condensation @ equil)

normal boiling point = T_{bp} @ $P = 1 \text{ atm}$

(Note: $P \downarrow, T_{bp} \downarrow$)

Phase change (constant T)

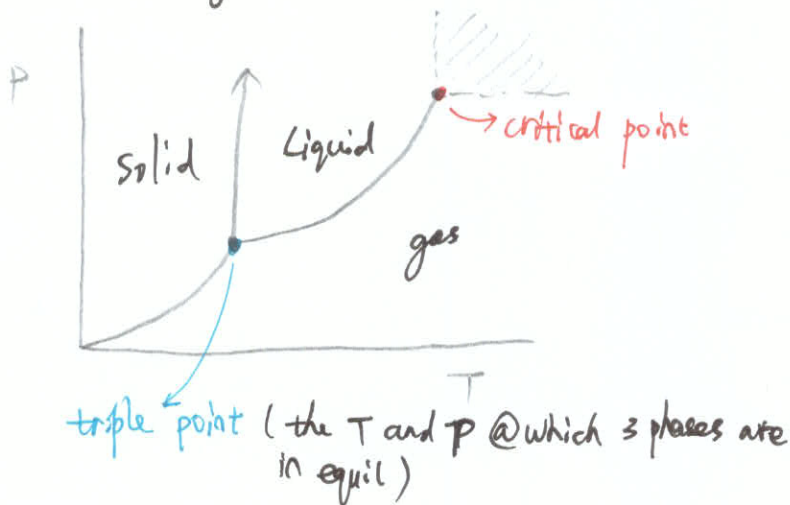
For phase change: $q = m \Delta H_{\text{fusion}}$

(take melting for example)

For heating/cooling a substance =

$$q = m C \Delta T$$

1.3 phase diagram (the points, the trends)

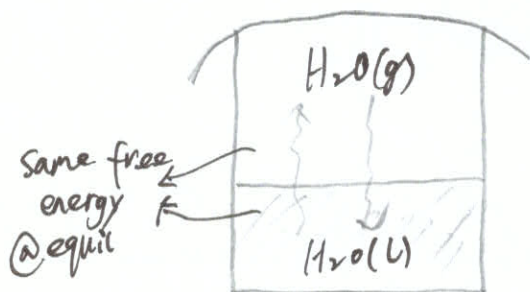


Points: Triple point, Critical point

trends: ZMFs \sim bp

$\downarrow \quad \downarrow$

1.4 Vapor pressure (calculate VP, calculate $\Delta H, \Delta S \dots$)



sealed

@ equilibrium $\Delta G = 0$

rate of evaporation = rate of condensation

$P_{\text{H}_2\text{O}}$ = constant and dependent on T

For equil @ specific T : $\Delta G = \Delta H - T \Delta S = 0$

For change @ variant T s: clausius-clapeyron equation

(If the pressure of the headspace is lower than the vapor pressure, the liquid will keep on vaporizing, until the pressure of the head space = vapor pressure)

2. Example problems

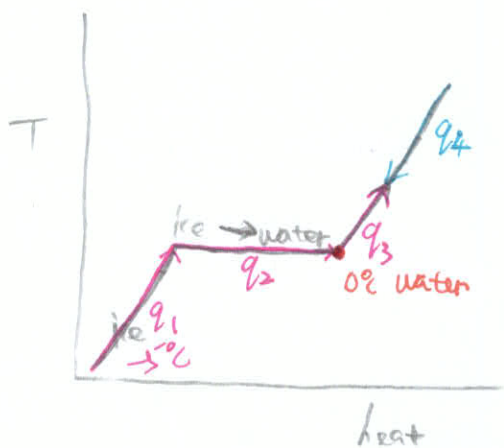
2.1 ice water problem

If 100g ice @ -5°C is dropped into 1000g warm water @ 20°C , after stirring for a while, ~~the~~ the system has reached its final temperature. What will be the final temperature?

$$C_{\text{ice}} = 2.09 \text{ J/g}\cdot^{\circ}\text{C} \quad C_{\text{water}} = 4.184 \text{ J/g}\cdot^{\circ}\text{C}$$

$$\Delta H_{\text{fusion}} = 6.01 \text{ kJ/mol}$$

Heating problem, find the subprocesses on heating curve



$$q_1 + q_2 + q_3 + q_4 = 0$$

Ice:
 q_1 : heat ice @ -5°C to 0°C
 q_2 : melt ice @ 0°C to water @ 0°C
 q_3 : resulting H_2O heats to T_f

Warm water

q_4 : warm water cools from 20°C to T_f

Method 1: Pick 0°C water as an intermediate point

The ice

2 steps: heat ice @ -5°C to 0°C (q_1)
 melt ice @ 0°C to water @ 0°C (q_2)

$$\begin{aligned} \text{heating } q_1 &= m_{\text{ice}} C_{\text{ice}} \Delta T \\ &= 100 \text{ g} \times 2.09 \text{ J/g}\cdot^{\circ}\text{C} \times (0^{\circ}\text{C} - (-5^{\circ}\text{C})) \\ &= 1045 \text{ J} \end{aligned}$$

$$\begin{aligned} \text{phase change } q_2 &= m_{\text{ice}} \Delta H_{\text{fusion}} \\ &= \frac{100 \text{ g}}{18 \text{ g/mol}} \times 6.01 \times 10^3 \text{ J/mol} \\ &= \del{33388.9} \text{ J} \end{aligned}$$

Warm water

1 step: drop from 20°C to 0°C (q)

$$\begin{aligned} \text{cooling } q &= m_{\text{H}_2\text{O}} C_{\text{water}} \Delta T \\ &= 1000 \text{ g} \times 4.184 \text{ J/g}\cdot^{\circ}\text{C} \times (20^{\circ}\text{C} - 0^{\circ}\text{C}) \\ &= 83680 \text{ J} \end{aligned}$$

Compare = Will the heat released from warm H₂O (20°C → 0°C) be enough to ~~turn~~ all the ice @ -5°C to resulting water @ 0°C?

$$q_1 + q_2 < q \Rightarrow \text{Yes.}$$

$$\text{And } q - (q_1 + q_2) = 49246.1 \text{ J (leftover heat)}$$

Now we have 100g water @ 0°C (from ice), 1000g water @ 0°C (from warm water), and 49246.1 J (leftover heat)

Heat the remaining water by leftover heat

$$\Delta T = \frac{49246.1 \text{ J}}{4.184 \text{ J/g}\cdot\text{C} \cdot (100 \text{ g} + 1000 \text{ g})} = 10.7 \text{ }^\circ\text{C}$$

$$q = cm\Delta T$$
$$\Delta T = \frac{q}{cm}$$

$$\Delta T = T_f - 0^\circ\text{C} = 10.7^\circ\text{C}$$

$$T_f = 10.7^\circ\text{C}$$

Method 2:

the ice

3 steps: q_1 heat ice @ -5°C to 0°C

q_2 melt ice @ 0°C to water @ 0°C

q_3 heat resulting water @ 0°C to T_f

$$q_1 = m_{\text{ice}} C_{\text{ice}} \Delta T = 1045 \text{ J}$$

$$q_2 = m_{\text{ice}} \Delta H_{\text{fusion}} = 33388.9 \text{ J}$$

$$q_3 = m_{\text{resulting water}} C_{\text{water}} \Delta T$$

$$= m_{\text{resulting water}} C_{\text{water}} (T_f - 0^\circ\text{C})$$

$$= 100 \text{ g} \times 4.184 \text{ J/g}\cdot\text{C} \times (T_f - 0^\circ\text{C})$$

warm water

1 step: q_4 drop from 20°C to T_f

$$q_4 = M_{\text{warm water}} C_{\text{water}} \Delta T$$

$$= M_{\text{warm water}} C_{\text{water}} (T_f - 20^\circ\text{C})$$

$$= 1000 \text{ g} \times 4.184 \text{ J/g}\cdot\text{C} \times (T_f - 20^\circ\text{C})$$

No heat exchange with the environment

$$q_1 + q_2 + q_3 + q_4 = 0$$

absorbing

$$1045\text{J} + 33388.9\text{J} + 100\text{g} \times 4.184\text{J/g}\cdot^\circ\text{C} \times (T_f - 0^\circ\text{C}) + 100\text{g} \times 4.184\text{J/g}\cdot^\circ\text{C} \times (T_f - 20^\circ\text{C}) = 0$$

Solve for T_f

$$T_f = 10.7^\circ\text{C}$$

2.2 What is the vapor pressure of CH_3OH (methanol) @ its normal boiling point?
A. 2 atm B. 1 atm C. Not enough info D. 22.4 atm

Standard $P = 1\text{atm}$

The boiling point is the temperature @ which the vapor pressure equals the total pressure

2.3 What is the change in entropy (ΔS) for the vaporization of methanol ($\Delta H_{\text{vap}} = 35.2\text{ kJ/mol}$) at its normal boiling point (64.7°C)?

$$\Delta G = \Delta H - T\Delta S = 0$$

$$\Delta S = \frac{\Delta H}{T}$$

$$= \frac{35.2\text{ kJ/mol}}{(64.7 + 273.15)\text{ K}}$$

$$= 0.104\text{ kJ}\cdot\text{mol}^{-1}\cdot\text{K}^{-1}$$

@ boiling point

T

evaporation & condensation @ equilibrium

Free energy of methanol vapor is the same as that of the methanol liquid

Review of the Van't Hoff factor

Def: ratio between the actual concentration of particles when the substance is dissolved, and the concentration of the substance as calculated from its molecular mass.

Non-electrolyte in H₂O Van't Hoff factor $i=1$

(molecular species do not dissociate in solution)

Examples		i	Identify anions
	NaCl	$i=2$	
	CaCl ₂	$i=3$	NO ₃ ⁻
$\frac{3}{1} \rightarrow 3$ $\frac{1+2}{1} \rightarrow 3$	<u>K₂SO₄</u>	$i=3$	Cl ⁻
$\frac{2+1}{1} \rightarrow 3$	Mg ₃ (PO ₄) ₂	$i=5$	SO ₄ ²⁻
			PO ₄ ³⁻
			OH ⁻

What is the total moles of ions in $\frac{1.5}{\sqrt{}} \text{ L}$ of $\frac{2 \text{ M}}{\text{concentration}}$ NaCl aqueous solution?

$$M = \text{mol/L}$$



$$\text{Total moles of ions (Na}^+, \text{Cl}^-) = C \times V \times i$$

$$= 2 \frac{\text{mol}}{\text{L}} \times 1.5 \text{ L} \times 2$$

$$= 6 \text{ moles}$$