Lecture 23

Application of Thermodynamics in Phase Diagrams

The Clausius – Clapeyron Equation

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Today's Topics

- The Clapeyron equation
- Integration of the Clapeyron Equation
- The Clausius - Clapeyron Equation
- Applications of the Clausius - Clapeyron Equation

The Clapeyron Equation

- We have stated earlier that, for unary systems, the two phase equilibria curves in (P, T) space may each be described mathematically by the function **P = P (T).**
- **The Clapeyron equation** is a differential form of this equation.
- For any pair of coexisting phases in the unary system, integration of the Clapeyron equation yields a mathematical expression for the corresponding phase boundary on the phase diagram.

  Repeated application to all the pairs of phases that may exist in the system yields all possible two-phase domains. Intersections of the two-phase curves produce triple point where three phases coexist.
- Thus, **Clapeyron equation** is the only relation required for calculating a unary phase diagram.

Consider $\alpha \Leftrightarrow \beta$ Equilibrium

- Change in chemical potential of α phase when taken through any arbitrary change in its state

$$d\mu^{\alpha} = V^{\alpha}\, dP^{\alpha} - S^{\alpha}\, dT^{\alpha}$$

- Similarly, for any arbitrary change state of β phase, the change in chemical potential

$$d\mu^{\beta} = V^{\beta}\, dP^{\beta} - S^{\beta}\, dT^{\beta}$$

- For equilibrium, $\mathbf{d\mu^{\alpha} = d\mu^{\beta}}$, $\mathbf{dP^{\alpha} = dP^{\beta} = dP}$, and $\mathbf{dT^{\alpha} = dT^{\beta} = dT}$, so that

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

$$dP/dT = (S^{\beta} - S^{\alpha})/(V^{\beta} - V^{\alpha})$$

$$\mathbf{dP/dT = \Delta S/\Delta V}$$

$$dP/dT = \Delta S/\Delta V$$

- In experiments, change in S is not measure directly.

  Calorimetric measurements at constant pressure (i.e., Q_P) results values for heat of transformations (ΔH^F, ΔH^V, etc.).

  Since, for $\alpha \rightarrow \beta$ equilibrium, $\Delta G = 0 = \Delta H - T\Delta S$, we have $\mathbf{\Delta S = \Delta H/T}$.

- Thus, expression for Clapeyron equation becomes

$$\frac{dP}{dT} = \frac{\Delta H}{T\,\Delta V}$$

Check units:

LHS:

dP/dT = atm/deg

RHS:

ΔH = cal/mol, ΔV = cc/mol

$\Delta H/T\Delta V$ = cal/cc-deg

1 atm = 41.293 cal/cc

Applications of Clapeyron Equation

$$\frac{dP}{dT} = \frac{\Delta H}{T\,\Delta V}$$

1. **Predicting the effects of P on T_t (e.g., T_m, T_b)**

   describing the relationship between P and T at which α and β phases can exist in equilibrium

2. **Calculating precisely ΔH_t (e.g., ΔH^F, ΔH^G)**

   knowing the derivative (dP/dT), and ΔV of the transformation

3. **Obtaining an equation for a given equilibrium, P = P(T)**

   knowing any reference point to integrate dP/dT
   (e.g., normal melting point, normal boiling point)

Integration of Clapeyron Equation

$$\frac{dP}{dT} = \frac{\Delta H}{T\,\Delta V}$$

- Using appropriate reference points, the Clapeyron equation can be integrated for a two-phase equilibrium to yield the phase boundary P = P(T) for the equilibrium.

- While integrating, the dependency of ΔH and ΔV on P and T must, however, be considered first.

- To obtain $\Delta H = \Delta H\,(P, T)$ for $\alpha \leftrightarrows \beta$ equilibrium:

$$d\,(\Delta H) = dH^{\beta} - dH^{\alpha}$$

- Now, for the function $H = H\,(P, T)$:

$$dH = C_P dT + V(1 - T\alpha)\,dP$$

- For all practical purposes, dependency of H on P can be ignored. Thus, $\mathbf{dH_P = C_P dT}$, and

$$d\,(\Delta H) \cong \Delta C_p\,dT \qquad (7.21)$$

where $\Delta C_P = C_P^{\beta} - C_P^{\alpha} = \Delta a + \Delta bT + \Delta cT^{-2}$

- Eq (7.21) is often known as the **Kirchhoff's equation.**

- To obtain $\Delta V = \Delta V\ (P, T)$ for $\alpha \leftrightarrows \beta$ equilibrium:

$$d\,(\Delta V) = dV^{\beta} - dV^{\alpha}$$

- **If β is an ideal gas phase** and α is either a solid or liquid phase, then $V^{\beta} >> V^{\alpha}$, and

$$\Delta V = V^G - V^{\alpha} \cong V^G = RT/P \quad \text{(for ideal gas)}$$

At STP, molar volume of:
Gas = 22400 cc
Solid/Liquid ≈ 10 cc

- **If both β and α phases are condensed phases** (solid or liquid),

For an approximate calculation (where P < a few tens of atm), ΔV can be treated as constant.

For a precise calculation, dependency of V on P and T must be considered according to the familiar formula

$$V = V\,(P,T): \qquad dV = V\alpha\, dT - V\beta\, dP$$

The Clausius - Clapeyron Equation

- Consider the equilibrium between the condensed phase and its vapour phase, i.e., ($\alpha \Leftrightarrow G$) equilibrium

- If $C_P^G = C_P^{\alpha}$, then ΔH is independent of T. Then

$$dP / dT = \Delta H / T\Delta V$$

$$dP / dT \cong \Delta H^G / TV^G = P\Delta H^G / RT^2$$

$$dP / P = (\Delta H^G / RT^2)\, dT$$

$$d \ln P = \frac{\Delta H^G}{T^2}\, dT \qquad (7.25)$$

- Eq. (7.25) is known as the **Calusius - Clapeyron equation**.
This is an approximate equation, derived by assuming that
  1. **ΔH^G is constant**
  2. **$V^G >> V^{\alpha}$ so that $\Delta V \cong V^G$.**
  3. **Vapour phase behaves ideally.**

Integration of Clausius - Clapeyron Equation

$$d \ln P = (\Delta H^G / RT^2)\, dT$$

- Integrating between the limits (P_1, T_1) and (P_2, T_2):

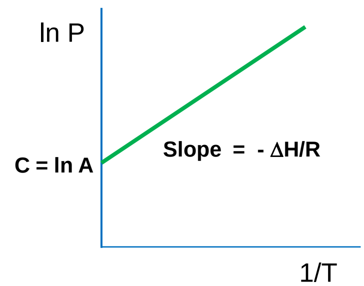
$$\ln \left(\frac{P_2}{P_1} \right) = - \left(\frac{\Delta H^G}{RT} \right) \ln \left(\frac{1}{T_2} - \frac{1}{T_1} \right)$$

- Integrating indefinitely:

$$\ln P = -(\Delta H^G / RT) + C$$

$$\mathbf{P = A \exp(-\Delta H^G / RT)}$$

where $A = \ln C$



The Condensed Phase Equilibria

- The Clausius – Clapeyron equation is applied only when there is a gas phase involved in the equilibra.

  Example: **S** ⇔ **G** equilirbium, **L** ⇔ **G** equilirbium, etc.

- For all other equilibria involving condensed phases only (**e.g.,** $\alpha \Leftrightarrow \beta$ equilirbium, **S** ⇔ **L** equilirbium, etc), the Clausius-Clapeyron equation cannot be applied.

- In such cases, the original Clapeyron equation should be used.

$$\frac{dP}{dT} = \frac{\Delta S}{\Delta V}$$

- **For a precise calculation**, T and P dependency of S and V must be considered while integrating the Clapeyron equation.

- **An approximate calculation** of the phase boundaries between two condensed phases can be made by ignoring T and P dependency of H and V.

- In such cases, considering ΔS and ΔV as constant, integration of the Clapeyron equation becomes straightforward:

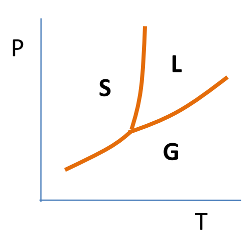
$$P_2 - P_1 = \frac{\Delta S}{\Delta V} (T_2 - T_1)$$

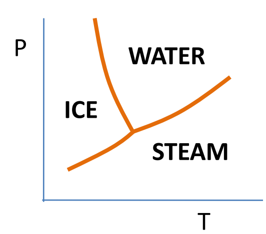
$$P_2 - P_1 = \frac{\Delta H}{\Delta V} \left(\frac{T_2 - T_1}{T_1} \right)$$

ΔH = latent heat of fusion, etc.

- The gradient of P = P (T) line (i.e. $\Delta S/\Delta V$) for **S** ⇔ **L** equilibrium for most substances is positive, which means that ΔV for the transformation is positive (since ΔS is always positive), i.e., the volume expands.

  The only exception is water, for which the slope is negative, since ice contracts when it becomes water.





Trouton's rule

The entropy of vapourisation of most elements is constant.

$$\Delta S^G = \frac{\Delta H^G}{T_b} \cong 21 \ \ \text{cal/deg-mol}$$

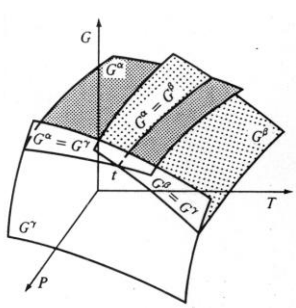
Richards' rule

The entropy of fusion of most elements is constant.

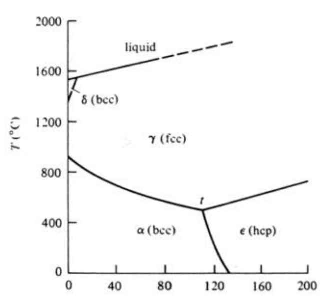
$$\Delta S^F = \frac{\Delta H^F}{T_F} \cong 9 \ \ \text{J/mol-K}$$

The Triple Point

- At the triple point, **S** $\Leftrightarrow$ **L**, **L** $\Leftrightarrow$ **G**, and **S** $\Leftrightarrow$ **G** equilibrium lines meet.



At the triple point, $G^\alpha = G^\beta = G^\gamma$



P – T diagram for pure iron

- For most elements and compounds, the triple point pressure is well below the atmospheric pressure.

  The only exception is CO_2, for which P_{tp} = 0.006 atm.

- The triple point of **S**, **L** and **G** phases can be determined if any two of the three equilibrium **(S ⇔ L, L ⇔ G, S ⇔ G)** lines are known.

- Using the equations for **L ⇔ G** and **S ⇔ G** equilibrium lines, the triple point temperature and pressure is calculated as follows:

$$P^G = A^G \exp\left(-\Delta H^G / RT\right)$$

$$P^S = A^S \exp\left(-\Delta H^S / RT\right)$$

- At the triple point **(P_{tp}, T_{tp})**, these two lines intersect. Thus

$$P_{tp} = A^G \exp\left(-\Delta H^G / RT_{tp}\right) = A^S \exp\left(-\Delta H^S / RT_{tp}\right)$$

$$\mathbf{T_{tp} = \frac{\Delta H^S - \Delta H^G}{R \ln (A^S/A^G)}} \quad ; \quad \mathbf{P_{tp} = A^S \exp\left(\frac{\Delta H^G}{\Delta H^G - \Delta H^S}\right)}$$

Next Class

Lecture 24

Application of Thermodynamics in Phase Diagrams

The Free Energy – Composition Diagrams