

MME 2009

Metallurgical

Thermodynamics

Sensible Heat and Enthalpy Calculations

Sensible Heat - The amount of heat that must be added when a substance undergoes a change in temperature from 298 K to an elevated temperature without a change in phase

$$\begin{aligned}\Delta H &= n \int_{298}^T C_P dT = \int_{298}^T a + bT + \frac{c}{T^2} \\ &= aT + \frac{b}{2}T^2 - \frac{c}{T} - \underbrace{a * 298 + \frac{b}{2}298^2 - \frac{c}{298}}_{\text{constant} = A}\end{aligned}$$

$$\Delta H = H_T - H_{298} = A + BT + CT^2 + \frac{D}{T} \quad \text{Enthalpy increment equation}$$

$$B = a, C = \frac{b}{2}, D = -c$$

Sensible heat at any temperature can be calculated by replacing that temperature in the enthalpy increment equation

Enthalpy increment equation can also be used to calculate enthalpy change between any two temperatures

$$\Delta H = H_{T_2} - H_{T_1} = (H_{T_2} - H_{298}) - (H_{T_1} - H_{298})$$

Enthalpy Increments with Phase Changes

Separate the enthalpy increments to steps when there is a phase change during heating of a substance, for example melting:

- 298 to T_m - Heat supplied increases the temperature of the solid phase

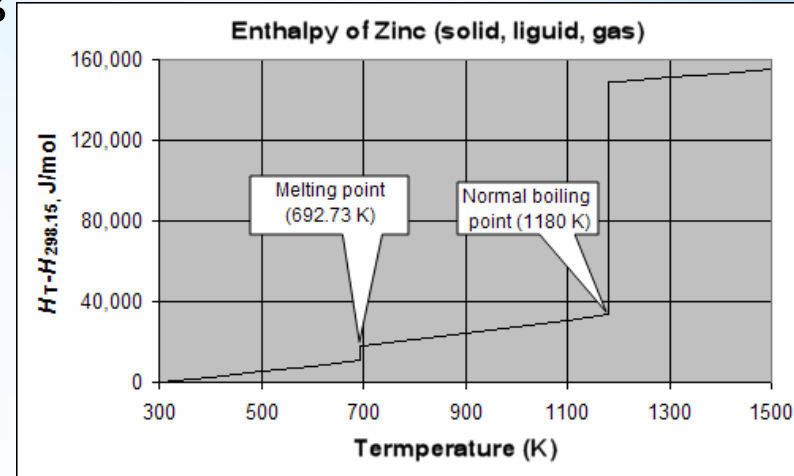
$$\Delta H = H_T - H_{298} = \int_{298}^T C_{P(s)} dT$$

- at T_m - Each mole of substance absorbs ΔH_m , latent heat of fusion or enthalpy of melting

$$\Delta H = n\Delta H_m$$

- T_m to T_v - Heat supplied increases the temperature of the liquid phase

$$\Delta H = H_T - H_{298} = \int_{298}^{T_m} C_{P(s)} dT + \Delta H_m + \int_{T_m}^T C_{P(l)} dT$$



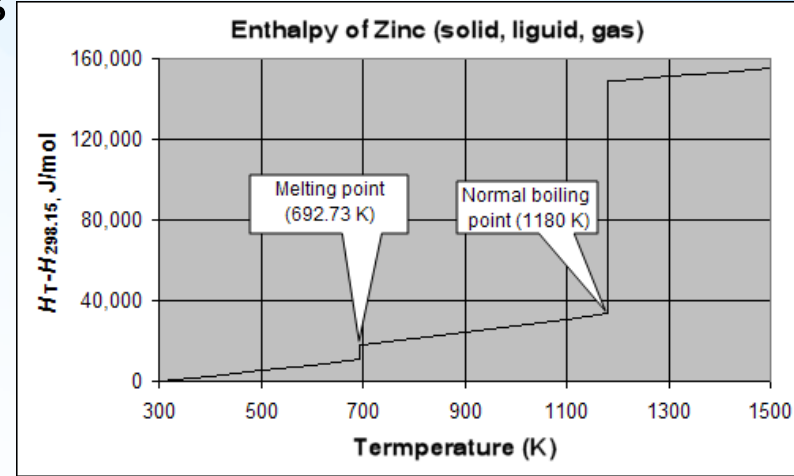
Enthalpy Increments with Phase Changes

Separate the enthalpy increments to steps when there is a phase change during heating of a substance, for example melting:

- at T_v - Each mole of liquid substance absorbs ΔH_v , latent heat of evaporation or enthalpy of evaporation

$$\Delta H = n\Delta H_v$$

- T_v to T - Heat supplied increases the temperature of the gas phase



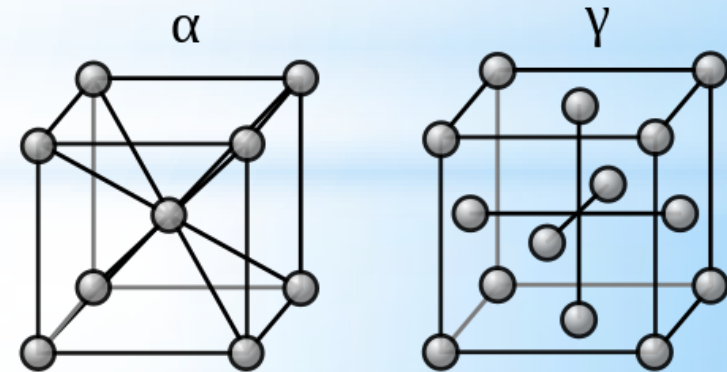
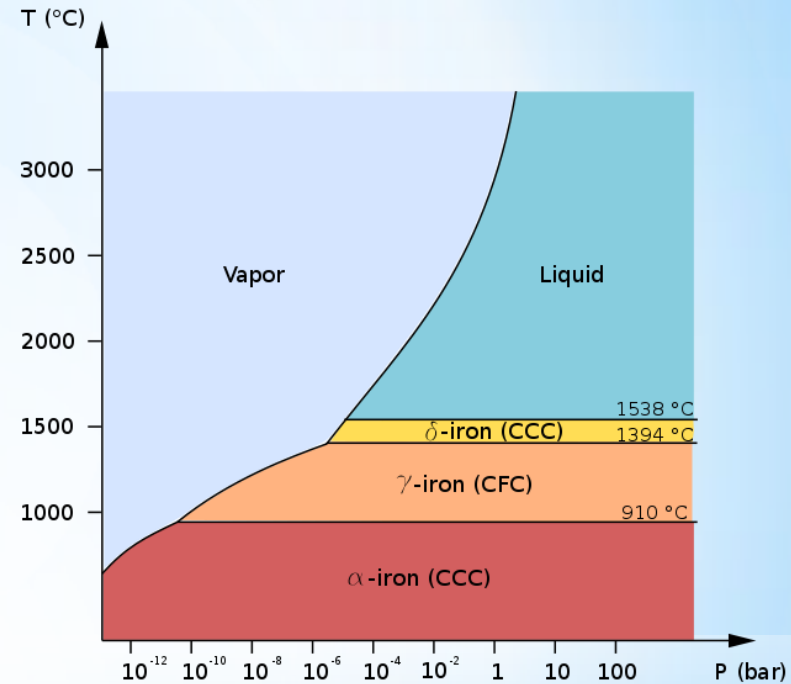
$$\Delta H = H_T - H_{298} = \int_{298}^{T_m} C_{P(s)} dT + \Delta H_m + \int_{T_m}^{T_v} C_{P(l)} dT + \Delta H_v + \int_{T_v}^T C_{P(g)} dT$$

Allotropic transformations are incorporated into enthalpy computations the same way as latent heats of melting and evaporation

Allotropes are different structural modifications of an element. The atoms of the element are bonded together in a different form

Allotropy refers only to different forms of an element within the same phase

For example there are three allotropic forms of solid iron at atmospheric pressure: alpha iron (α) ferrite, gamma iron (γ) austenite, and delta iron

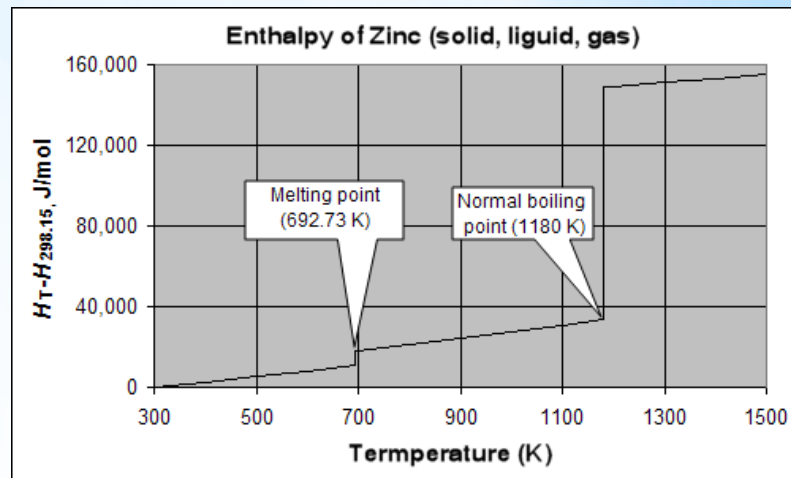


$$\Delta H = H_{1500} - H_{298} = \int_{298}^{1183} C_{P(s(\alpha\text{-iron}))} dT + \Delta H_A + \int_{1183}^{1500} C_{P(s(\gamma\text{-iron}))} dT$$

Enthalpy increment equations incorporate phase transformations

Example - Calculate the heat required to heat 500 gram of zinc from room temperature to 1500 K

a) Using heat capacities



$$C_p(s) = 22.4 + 0.01005 \cdot T \text{ J/mol K}$$

$$C_p(l) = 31.4 \text{ J/mol K}$$

$$C_p(g) = 20.76 \text{ J/mol K}$$

$$\Delta H_m = 7388 \text{ J/mol at } 693 \text{ K}$$

$$\Delta H_v = 115366 \text{ J/mol at } 1180 \text{ K}$$

$$(H_T - H_{298})_{Zn(g)} = 124376 + 20.76 \cdot T \text{ J/mol}$$

b) Using enthalpy increment equations

Phase transformations result in the coexistence of two phases

Gibbs' phase rule requires that a two phase system consisting of a single species is univariant and its state is determined by specification of one intensive property: T

$$\frac{dP^{sat}}{dT} = \frac{\Delta H^{\alpha\beta}}{T\Delta V^{\alpha\beta}}$$

$$\Delta H^{\alpha\beta} = T\Delta V^{\alpha\beta} \frac{dP^{sat}}{dT}$$

Clapeyron equation helps calculate the latent heats of transformation $\Delta H^{\alpha\beta}$

When Clapeyron equation is applied to the vaporization of a pure liquid, $\frac{dP^{sat}}{dT}$ is the slope of the vapor pressure-temperature curve at a temperature T, $\Delta V^{\alpha\beta}$ is the difference between molar volumes of saturated vapor and saturated liquid and $\Delta H^{\alpha\beta}$ is the latent heat of vaporization

Latent heats may be measured calorimetrically and experimental values at selected temperature are available for many substances

Estimation of the latent heats, especially latent heats of vaporization is possible by approximate methods:

$$\frac{\Delta H_n}{RT_n} \approx 10$$

Trouton's rule gives rough estimates of latent heats of vaporization for pure liquids at their normal boiling points

$$\frac{\Delta H_n}{RT_n} = \frac{1.092(\ln P_c - 1.013)}{0.930 - T_{rn}}$$

Riedel's equation is an accurate approximation of latent heat of vaporization where P_c is the critical pressure, T_{rn} is the reduced temperature or T_n/T_c

For example, applied to water it gives:

$$\frac{\Delta H_n}{RT_n} = \frac{1.092(\ln 220.55 - 1.013)}{0.930 - 0.577} = 13.56$$

$$\Delta H_n = (13.56)(8.314)(373.15) = 42.065 \text{ J/m} \quad 3.4\% \text{ higher than real}$$

Estimates of the latent heat of vaporization of a pure liquid at any temperature from the known value at a single temperature is derived from Riedel's equation by Watson:

$$\frac{\Delta H_2}{\Delta H_1} = \left(\frac{1 - T_{r2}}{1 - T_{r1}} \right)^{0.38}$$

Example - Estimate the latent heat of vaporization for water at 300 C, given that its latent heat of vaporization at 100 C is 2257 J/g

$$T_{r1} = \frac{T_1}{T_c} = \frac{373.15}{647.1} = 0.577$$

$$T_{r2} = \frac{T_1}{T_c} = \frac{573.15}{647.1} = 0.886$$

$$\frac{\Delta H_2}{\Delta H_1} = (2257) \left(\frac{1-0.886}{1-0.577} \right)^{0.38} = (2257)(0.270)^{0.38} = 1371 \text{ J/g}$$

The value given in steam tables is 1406 J/g

One can determine the amount of heated material through division of the amount of heat given by the heat required per mole

Example - What is the amount of ice cube at 0.0°C added to 500 mL of tea at 20.0°C to make ice tea if the temperature of the tea when the ice cube has just melted is 11.0°C ?

Take the density of water (and ice tea) constant = 1.00 g/mL over the range 0°C - 20°C

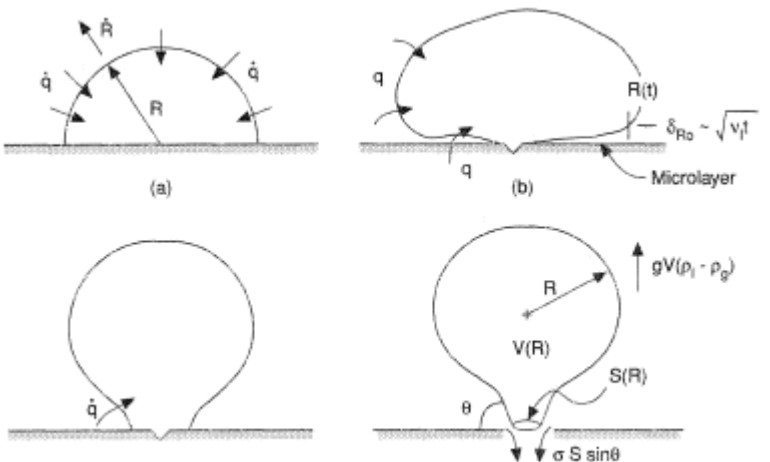
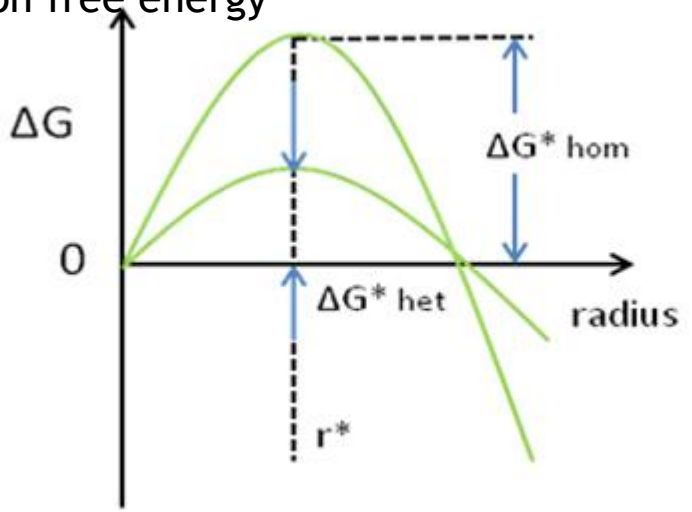
$$C_p(\text{l}) = 75.312\text{ J}/(\text{mol}\cdot\text{K})$$

$$C_p(\text{s}) = 37.116\text{ J}/(\text{mol}\cdot\text{K}),$$

$$\Delta H_m = 6.01\text{ kJ/mol}.$$

Superheating or boiling delay is the phenomenon by which a liquid is heated to a temperature higher than its boiling point
 Superheating is achieved by heating a homogeneous substance in a clean container, free of nucleation sites

Nucleation free energy



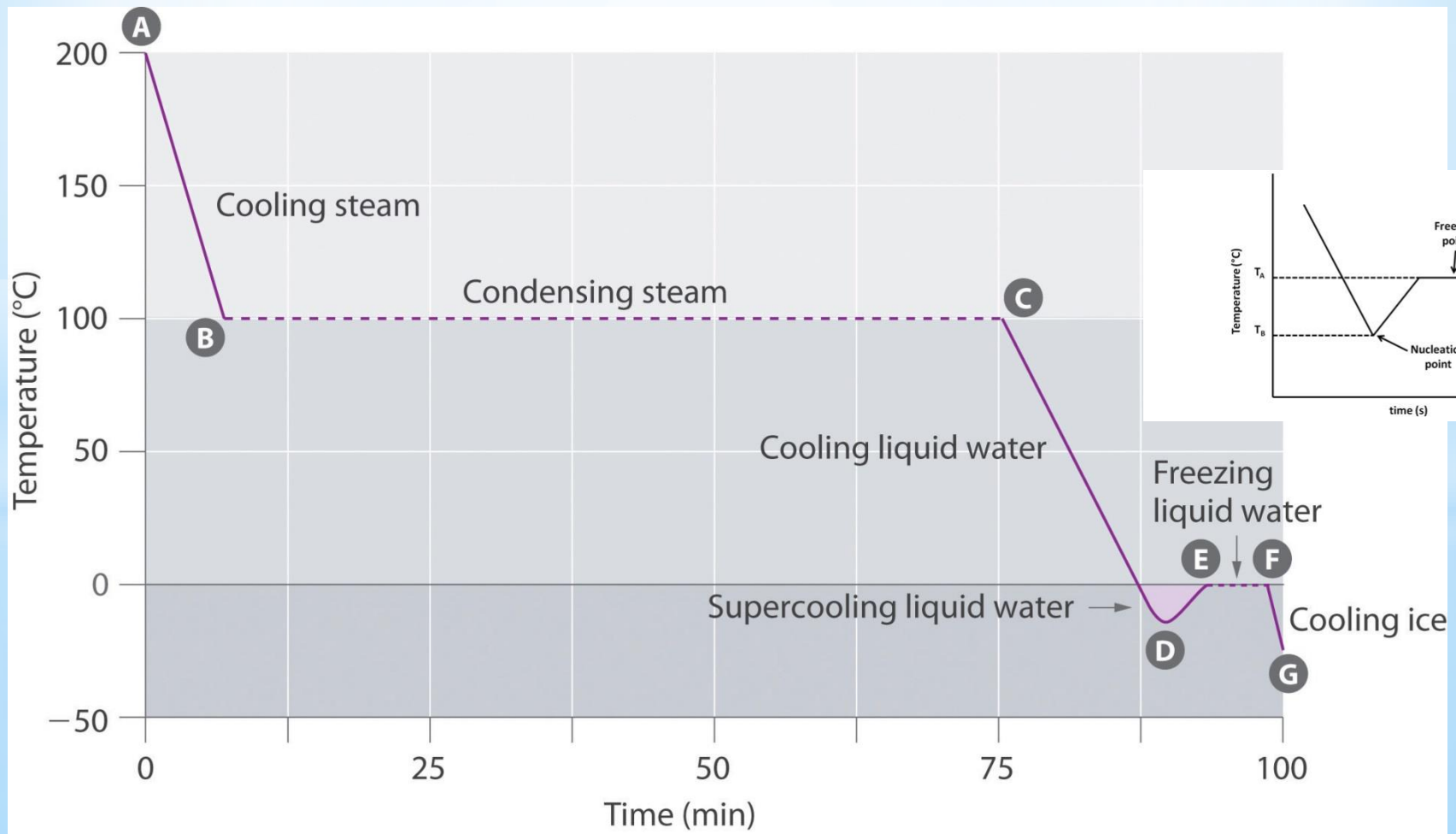
Heterogeneous nucleation around a surface pit



Supercooling or freezing delay is the phenomenon by which a liquid is cooled below its freezing point

A liquid below its freezing point will crystallize in the presence of a seed crystal around which a crystal structure can form creating a solid

Liquid phase can be maintained while cooling to the temperature at which crystal homogeneous nucleation occurs

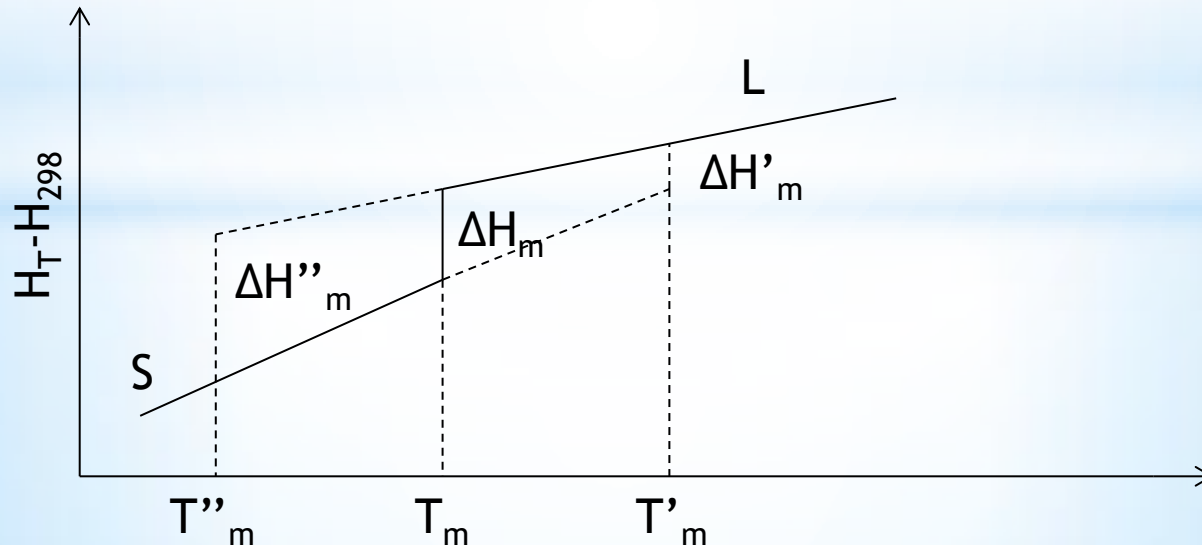


Enthalpy change for transformations of superheated and supercooled matter

A solid at a higher temperature T'_m than its melting point is a superheated solid. Enthalpy change for the transformation of superheated solid to liquid phase is $\Delta H'_m$

A liquid at a lower temperature T''_m than its freezing point is a supercooled liquid. Enthalpy change for the transformation of supercooled liquid to solid phase is $\Delta H''_m$

T_m is reversible melting point



Enthalpy change for transformations of superheated and supercooled matter

Enthalpy change through ABC and ADC paths are equal since enthalpy is a state function

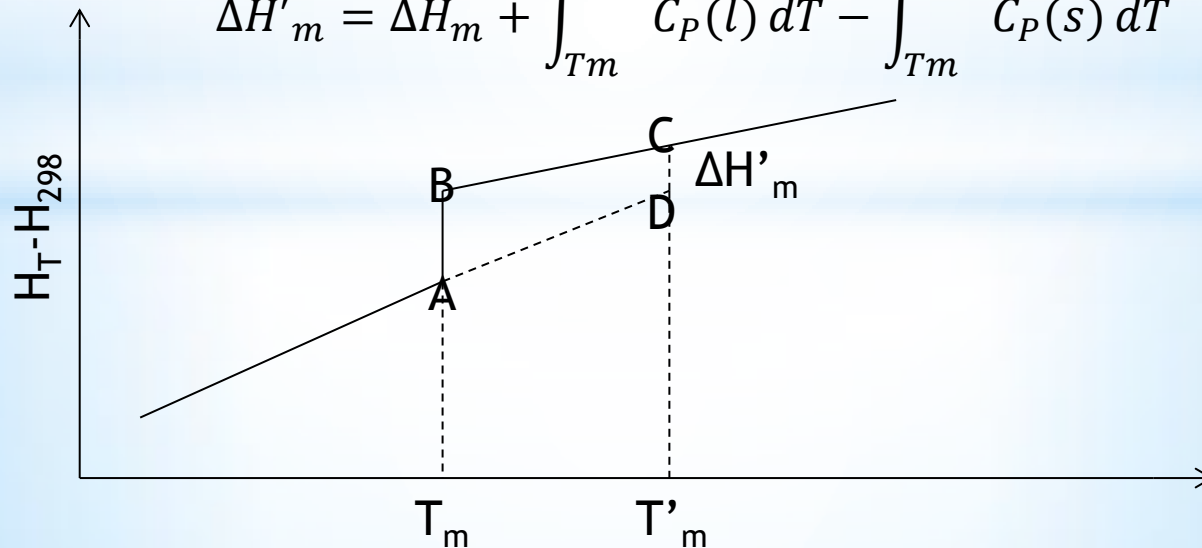
$\Delta H'_m$ can be calculated using the known enthalpy change values along these paths

$$\Delta H_{ABC} = \Delta H_{ADC}$$

$$\Delta H_{AB} + \Delta H_{BC} = \Delta H_m + \int_{T_m}^{T'_m} C_P(l) dT$$

$$\Delta H_{AD} + \Delta H_{DC} = \int_{T_m}^{T'_m} C_P(s) dT + \Delta H'_m$$

$$\Delta H'_m = \Delta H_m + \int_{T_m}^{T'_m} C_P(l) dT - \int_{T_m}^{T'_m} C_P(s) dT$$



$$\Delta H'_m = \Delta H_m + \int_{T_m}^{T'_m} C_P(l) - C_P(s) dT$$

$$\Delta H'_v = \Delta H_v + \int_{T_v}^{T'_v} C_P(g) - C_P(l) dT$$

$$\Delta H_{\text{solidification}} = - \Delta H_m$$

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

Example - Derive an equation for the enthalpy of melting for lead as a function of temperature

$$C_p(s) = 24.36 + 0.00796 * T \text{ J/mol K}$$

$$C_p(l) = 28.46 \text{ J/mol K}$$

$$T_m = 600\text{K}$$

$$\Delta H_m = 5128 \text{ J/mole}$$

$$\Delta H'_m = \Delta H_m + \int_{T_m}^{T'_m} C_P(l) - C_P(s) dT$$

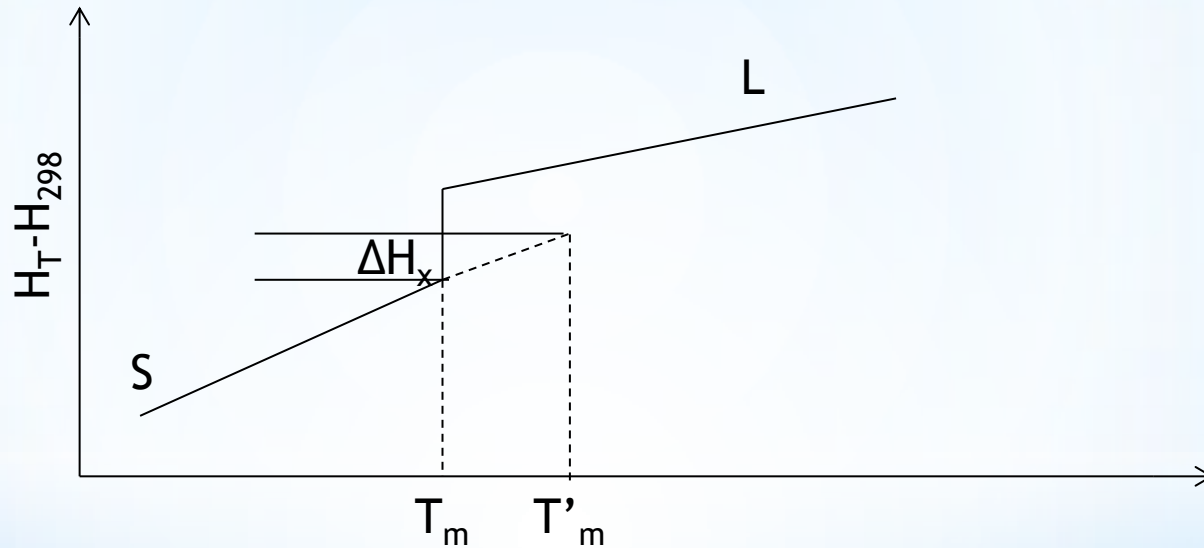
Enthalpy of melting at any temperature T is $\Delta H_m(T) = \Delta H'_m$

Hence

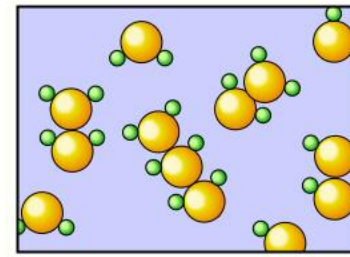
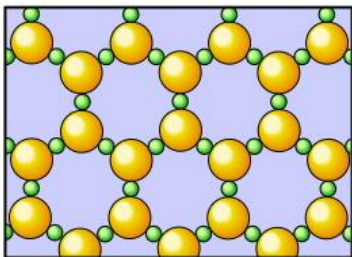
$$\Delta H_m(T) = 5128 + \int_{600}^T (28.46 - 24.36 - 0.00796 * T) dT$$

$$\Delta H_m(T) = 4101 + 4.1 * T - 0.00398 * T^2 \text{ J/mole}$$

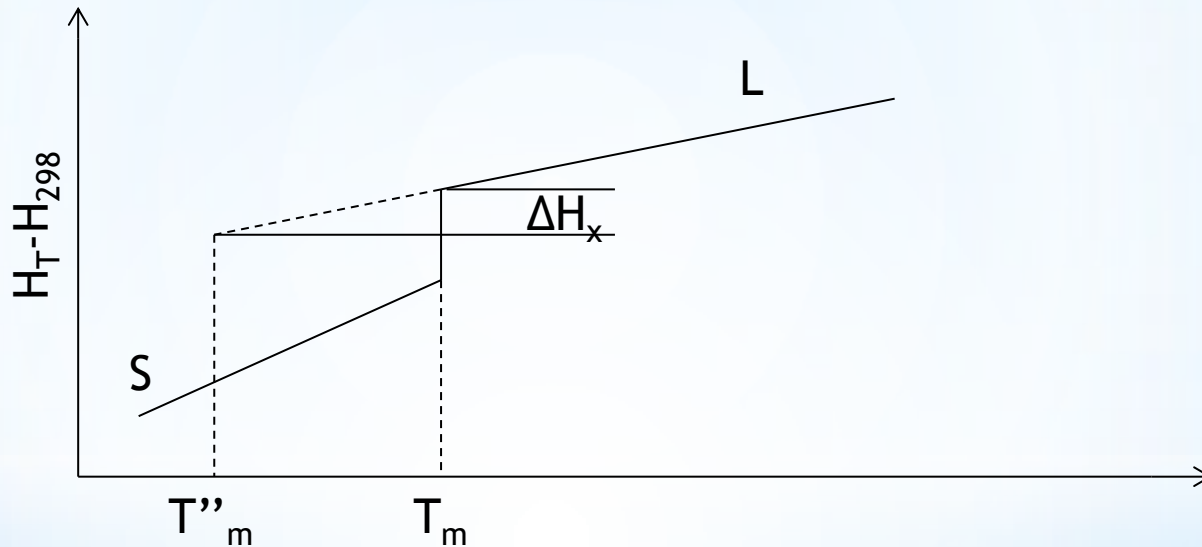
When a superheated material is kept in an adiabatic enclosure, fraction of the liquid may be determined from the ratio of extra heat supplied ΔH_x to enthalpy of melting



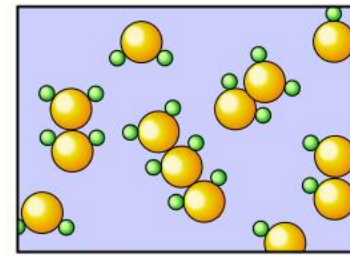
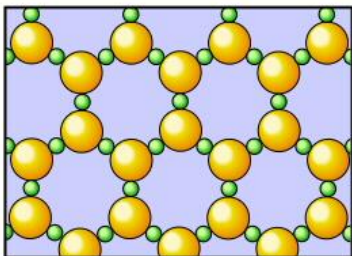
$$X_l = \frac{\Delta H_x}{\Delta H_m}$$



When a supercooled material is kept in an adiabatic enclosure, fraction of the solid may be determined from the ratio of extra heat ΔH_x taken from the liquid below its melting point to the enthalpy of melting



$$X_s = \frac{\Delta H_x}{\Delta H_m}$$



Example - Calculate the enthalpy of solidification for supercooled liquid zinc at 400 C. Find out the fraction of solid zinc if the supercooled liquid is allowed to solidify adiabatically

$$C_p(s) = 22.4 + 0.01005 \cdot T \text{ J/mol K}$$

$$C_p(l) = 31.4 \text{ J/mol K}$$

$$T_m = 693 \text{ K}$$

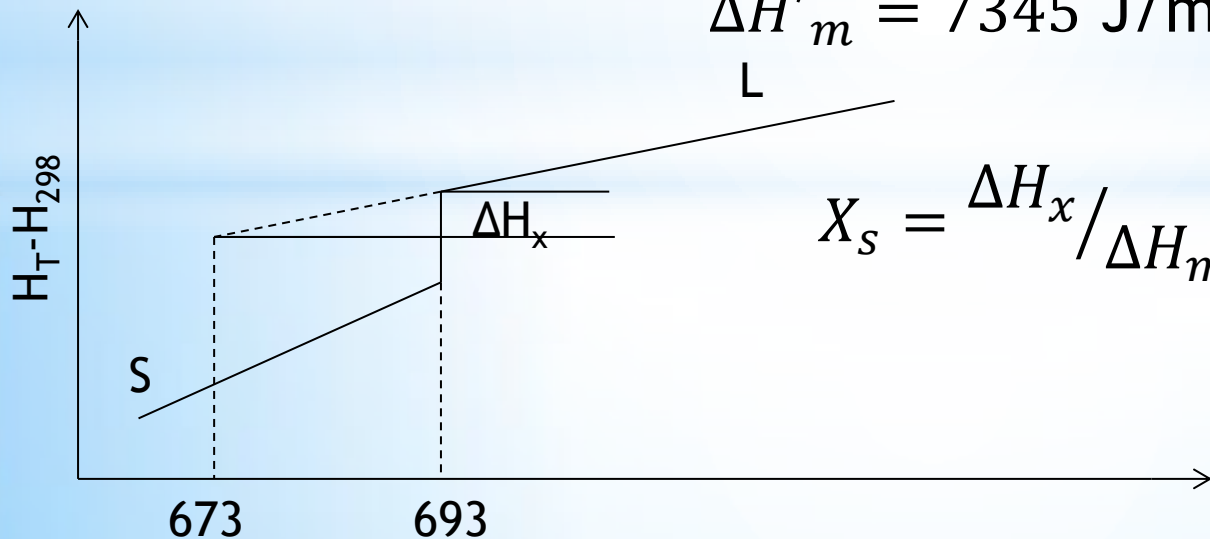
$$\Delta H_m = 7388 \text{ J/mole}$$

$$\Delta H'_m = \Delta H_m + \int_{T_m}^{T'_m} (C_p(l) - C_p(s)) dT$$

$$\Delta H'_m = 7388 + \int_{693}^{673} (C_p(l) - C_p(s)) dT$$

$$C_p(l) - C_p(s) = 9 - 0.01005 \cdot T$$

$$\Delta H'_m = 7345 \text{ J/mole}$$



$$X_s = \Delta H_x / \Delta H_m$$

Heat Effects of Chemical Reactions

So far change of state of a system through change in P,V or T by heat or work was considered

The state of a system can also change if chemical identity of constituents are altered by chemical reaction

Chemical reactions are accompanied either by the transfer of heat or by change in temperature during the process, in some cases by both

Heat and temperature changes are due to the differences in molecular structure of the products and reactants

A reaction is exothermic if it supplies heat to the surroundings ($-\Delta H$)

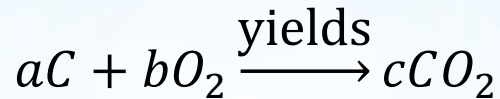
Reactions that require heat from the surroundings are endothermic ($+\Delta H$)

The reaction
$$aA + bB \xrightarrow{\text{yields}} cC + dD$$

may be carried out in many different conditions so each reaction carried out in a specific condition is accompanied by a different heat effect

Tabulation of all heat effects for all possible reactions is impossible
Calculation of all heat effects is possible from data for reactions carried out in a standard way

Example - Consider formation of CO_2 from C and O_2



The standard heat of reaction is defined as the enthalpy change when a moles of C and b moles of O_2 in their standard states at temperature T react to form c moles of CO_2 in its standard state at the same temperature T

Only enthalpy of formation of compounds can be measured, standard enthalpy of formation of pure elements in their standard states is zero

$$\Delta H_{\text{CO}_2} = f(P, T)$$

Enthalpy of formations are tabulated at 298 K under standard atmospheric pressure (101.33 kPa):

$$\Delta H_{298}^{\circ}(\text{CO}_2(\text{g})) = -393690 \text{ J/mole at 298 K} \quad \text{standard enthalpy of formation}$$

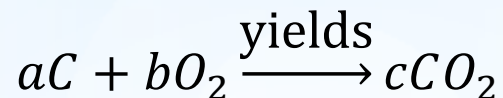
Standard state for gases: The pure substance in the ideal gas state at 1 atm

For Liquids and solids: The real pure liquid or solid at 1 atm pressure

Enthalpy change of any reaction can be calculated using Hess' law

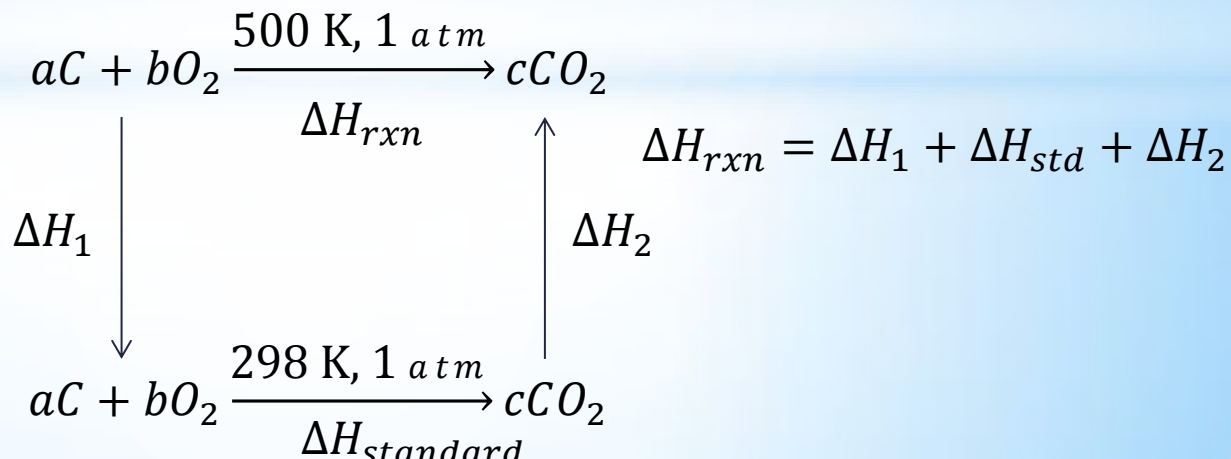
$$\Delta H_{rxn} = \sum \Delta H_{products} - \sum \Delta H_{reactants}$$

Example - Compound formation from elements



Hess' law states that enthalpy change accompanying a chemical reaction is the same whether it takes place in one or several stages since enthalpy is a state function

It is useful in calculating the unknown enthalpy change of a reaction using known enthalpy change at standard conditions



Example - What is the change in internal energy and enthalpy for the decomposition of CaCO_3 to CaO and CO_2 at 25°C and 1 atm.?



$$\begin{aligned}\Delta H_{\text{rxn}} &= \sum \Delta H_{\text{products}} - \sum \Delta H_{\text{reactants}} \\ \Delta H_{\text{rxn}} &= ((-635.5) + (-394)) - (-1207) = +571 \text{ KJ}\end{aligned}$$

$$\Delta H = \Delta U + P\Delta V, \quad P\Delta V = \Delta n RT,$$

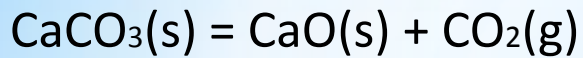
Therefore

$$\begin{aligned}\Delta H &= \Delta U + \Delta n RT \\ \Delta U &= \Delta H - \Delta n RT\end{aligned}$$

$$\begin{aligned}\Delta n &= \text{moles of gaseous products} - \text{moles of gaseous reactants} (n = 1 - 0) = 1 \\ \Delta U &= (+571) - ((1) \times 0.00831 \times (25 + 273)) = +571 - 2.48 = 569 \text{ KJ}\end{aligned}$$

Example -

1 ton of limestone (CaCO_3) is calcined at 727 C according to reaction



180 kg of coke containing 100% C was used as fuel. If limestone, coke and air enter the furnace at room temperature, calculate

a) The heat required for calcination

b) The heat available when coke is burned with air (21% O_2 , 79% N_2) to yield an exhaust gas (CO_2 - N_2) at 727 C

c) Thermal efficiency (ratio of the required heat to available heat of the process)

$$\text{CaCO}_3(\text{s}) \Delta H_{298} = -1207 \text{ kJ/mole } C_p = 104.57 + 0.02193T - 2595000/T^2 \text{ J/molK}$$

$$\text{C}(\text{s}) C_p = 16.87 + 0.00477T - 854000/T^2 \text{ J/molK}$$

$$\text{CaO} \Delta H_{298} = -635.5 \text{ kJ/mole}, C_p = 49.95 + 0.00489T - 352000/T^2 \text{ J/molK}$$

$$\text{O}_2(\text{g}) C_p = 29.97 + 0.00419T - 167000/T^2 \text{ J/moleK}$$

$$\text{N}_2(\text{g}) C_p = 27.88 + 0.00427T \text{ J/molK } (H_T - H_{298}) = -8502 + 27.88T + 0.00213T^2$$

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