

Chapter 6


Heat capacity, enthalpy, & entropy

6.1 Introduction

In this lecture, we examine the heat capacity as a function of temperature, compute the enthalpy, entropy, and Gibbs free energy, as functions of temperature.

We then begin to assess phase equilibria constructing a phase diagram for a single component (unary) system.

- By eq. 2.6 & 2.7 $c_v = \left(\frac{\partial U}{\partial T}\right)_v$ (2.6) $c_p = \left(\frac{\partial H}{\partial T}\right)_p$ (2.7)

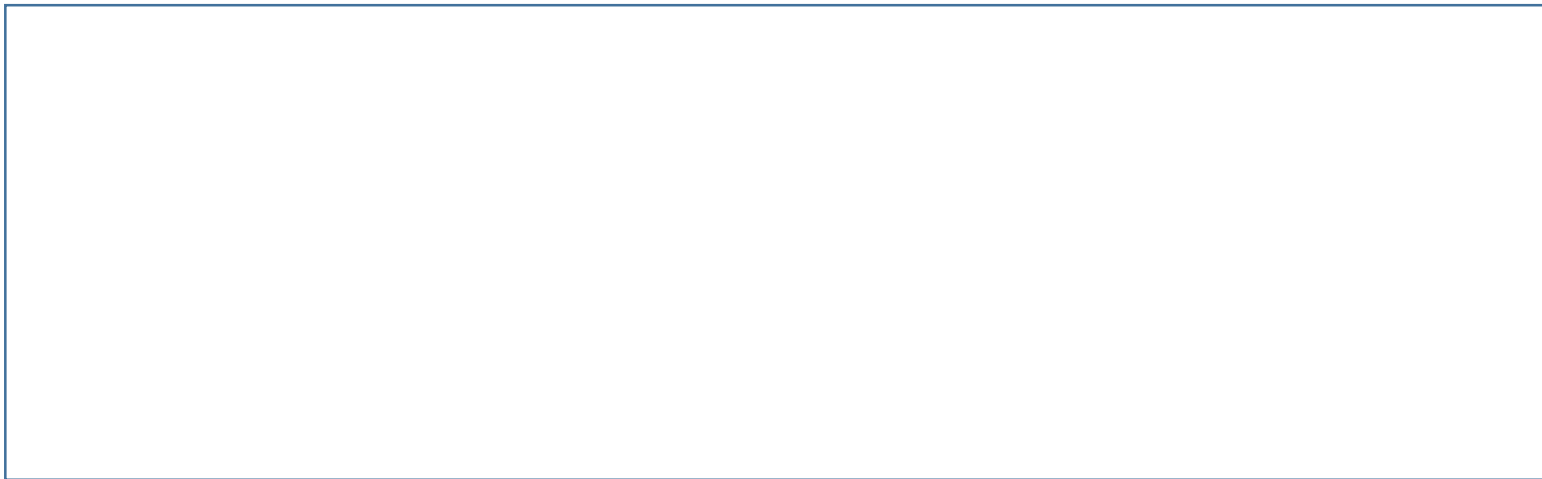

$$dU' = C_v dT = nc_v dT \quad \text{or} \quad dU = c_v dT \quad (2.6a)$$
$$dH' = C_p dT = nc_p dT \quad \text{or} \quad dH = c_p dT \quad (2.7a)$$

Integration of Eq. (2.7a) between the states (T_2, P) and (T_1, P) gives the difference between the molar enthalpies of the two states as

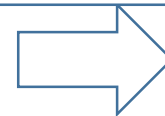
$$\Delta H = H(T_2, P) - H(T_1, P) = \int_{T_1}^{T_2} c_p dT \quad (6.1)$$

6.2 THEORETICAL CALCULATION OF THE HEAT CAPACITY

- Empirical rule by Dulong and Petit (1819) : $C_v \approx 3R$
(classical theory: avg. E for 1-D oscillator, $\varepsilon_i = kT$, $E = 3N_0kT = 3RT$)



- a system of 3n linear harmonic oscillators
(due to vibration in the x, y, and z directions)



$$U' = 3 \sum n_i \varepsilon_i \quad (6.3)$$

The Energy of Einstein crystal

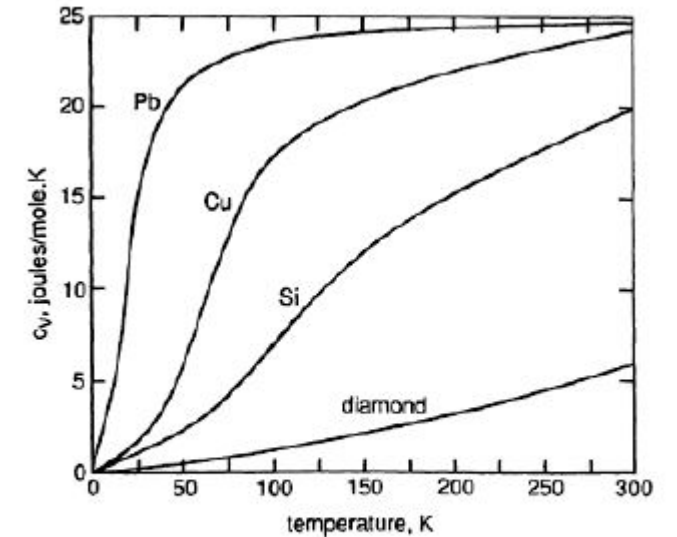


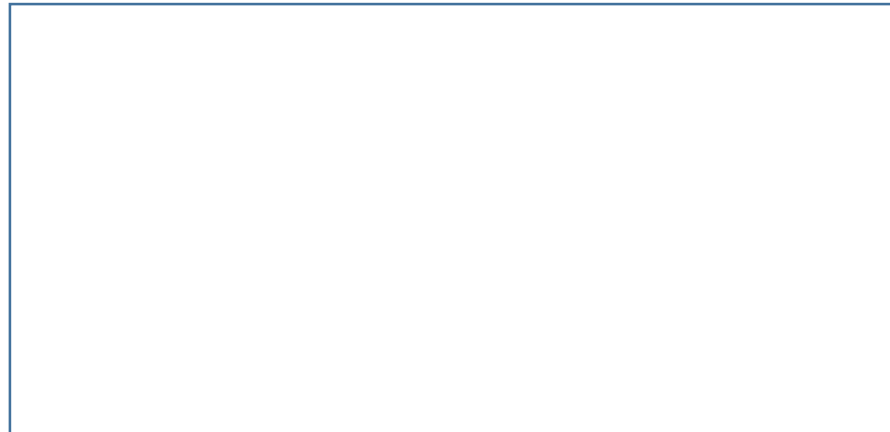
Figure 6.1 The constant-volume molar heat capacities of Pb, Cu, Si, and diamond as functions of temperature.

6.2 THEORETICAL CALCULATION OF THE HEAT CAPACITY

Using, $\varepsilon_i = \left(i + \frac{1}{2}\right) h\nu$ & eq. 4.13

$$n_i = \frac{ne^{-\beta\varepsilon_i}}{p} \quad \text{Into} \quad U' = 3 \sum n_i \varepsilon_i$$

$$\begin{aligned} U' &= 3 \sum \left(i + \frac{1}{2}\right) h\nu \left(\frac{ne^{-h\nu(i+\frac{1}{2})/kT}}{\sum e^{-h\nu(i+\frac{1}{2})/kT}} \right) \\ &= 3nh\nu \left(\frac{\sum i e^{-h\nu(i+\frac{1}{2})/kT}}{\sum e^{-h\nu(i+\frac{1}{2})/kT}} + \frac{\frac{1}{2} \sum e^{-h\nu(i+\frac{1}{2})/kT}}{\sum e^{-h\nu(i+\frac{1}{2})/kT}} \right) \end{aligned}$$



6.2 THEORETICAL CALCULATION OF THE HEAT CAPACITY

Taking $\sum i e^{-h\nu i/kT} = \sum i x^i$

$$\left[\text{Empty box for derivation} \right]$$

(6.4)

- Differentiation of eq. with respect to temperature at constant volume

$$C_v = \left(\frac{\partial U'}{\partial T} \right)_v = 3n h \nu (e^{h\nu/kT} - 1)^{-2} \frac{h\nu}{kT^2} e^{h\nu/kT} = 3nk \left(\frac{h\nu}{kT} \right)^2 \frac{e^{h\nu/kT}}{(e^{h\nu/kT} - 1)^2}$$

6.2 THEORETICAL CALCULATION OF THE HEAT CAPACITY

$$C_v = \left(\frac{\partial U'}{\partial T} \right)_v = 3nhv(e^{hv/kT} - 1)^{-2} \frac{hv}{kT^2} e^{hv/kT} = 3nk \left(\frac{hv}{kT} \right)^2 \frac{e^{hv/kT}}{(e^{hv/kT} - 1)^2}$$

- Defining $hv/k = \theta_E$: Einstein characteristic temperature

$$c_v = 3R \left(\frac{\theta_E}{T} \right)^2 \frac{e^{\theta_E/T}}{(e^{\theta_E/T} - 1)^2} \quad (6.5)$$

$$C_V \approx R \text{ as } T \rightarrow \infty$$

$$C_V \approx 0 \text{ as } T \rightarrow 0$$

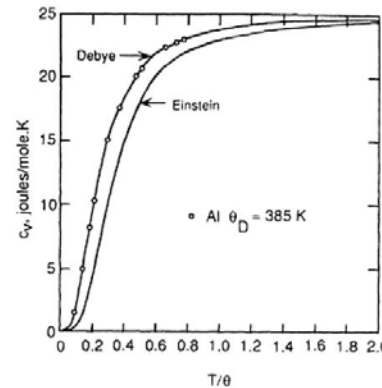
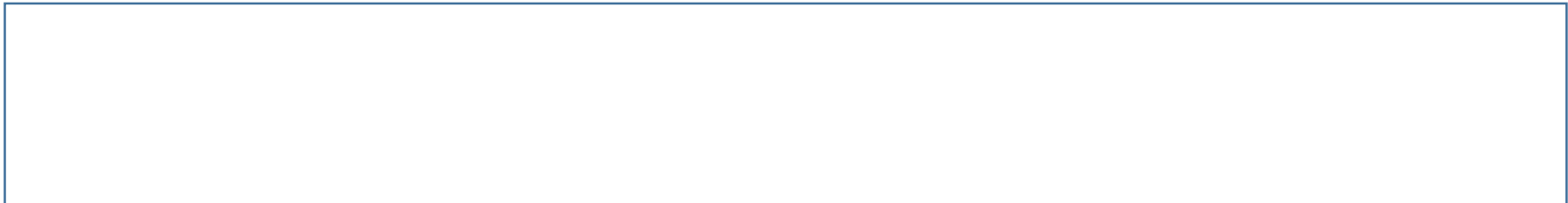


Figure 6.2 Comparison among the Debye heat capacity, the Einstein heat capacity, and the actual heat capacity of aluminum.



6.2 THEORETICAL CALCULATION OF THE HEAT CAPACITY

- In a crystal lattice as a harmonic oscillator, energy is expressed as

$$E_n = \frac{h\nu_E}{2} + nh\nu_E \quad (n = 0,1,2,\dots)$$

Einstein assumed that ν_E is const. for all the same atoms in the oscillator.

$$\nu_{\max} = \frac{v}{\lambda_{\min}} = \frac{5 \times 10^5}{5 \times 10^{-8}} = 10^{13} \text{ sec}^{-1} \quad : \text{ the maximum frequency of vibration of an oscillator}$$

6.2 THEORETICAL CALCULATION OF THE HEAT CAPACITY

- Integration Einstein's equation in the range, $0 \leq \nu \leq \nu_{max}$

obtained the heat capacity of the solid

which, with $x = h\nu/kT$, gives

(6.6)

- Defining $\theta_D = h\nu_{max}/k = h\nu_D/k$: Debye characteristic T

- ν_D (Debye frequency) = $\nu_{max} = \frac{\theta_D \cdot k}{h}$

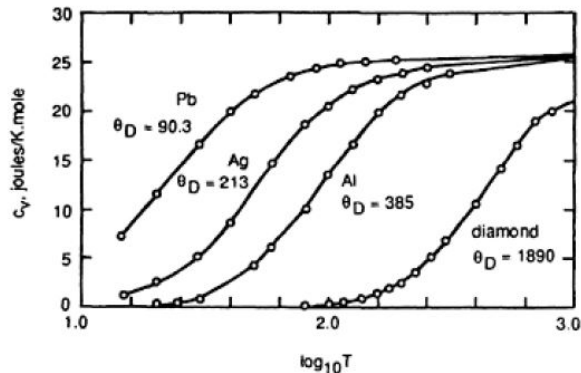


Figure 6.3 The constant-volume molar heat capacities of several solid elements. The curves are the Debye equation with the indicated values of θ_D .

6.2 THEORETICAL CALCULATION OF THE HEAT CAPACITY

- The value of the integral in Eq. (6.6) from 0 to infinity is 25.98, and thus, for very low temperatures, Eq. (6.6) becomes

$$\boxed{} \quad (6.7) \quad : \text{Debye } T^3 \text{ law for low-temperature heat capacities.}$$

Debye's theory: No consideration on the contribution made to the heat capacity by the uptake of energy by **electrons** (\propto absolute temperature)

- At high T, where the lattice contribution approaches the Dulong and Petit value, the molar C_v should vary with T as

$$c_v = 24.94 + bT \text{ J/K}\cdot\text{mole} \quad \text{in which } bT \text{ is the electronic contribution.}$$

6.3 THE EMPIRICAL REPRESENTATION OF HEAT CAPACITIES

- By experimental measurements,

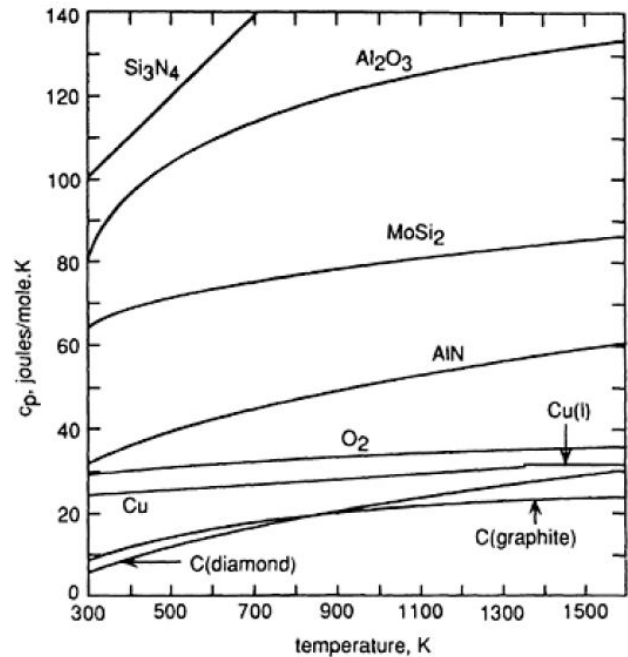
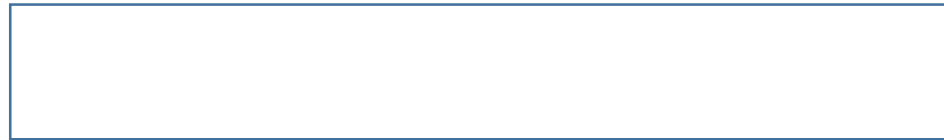


Figure 6.4 The variations, with temperature, of the constant-pressure heat capacities of several elements and compounds.

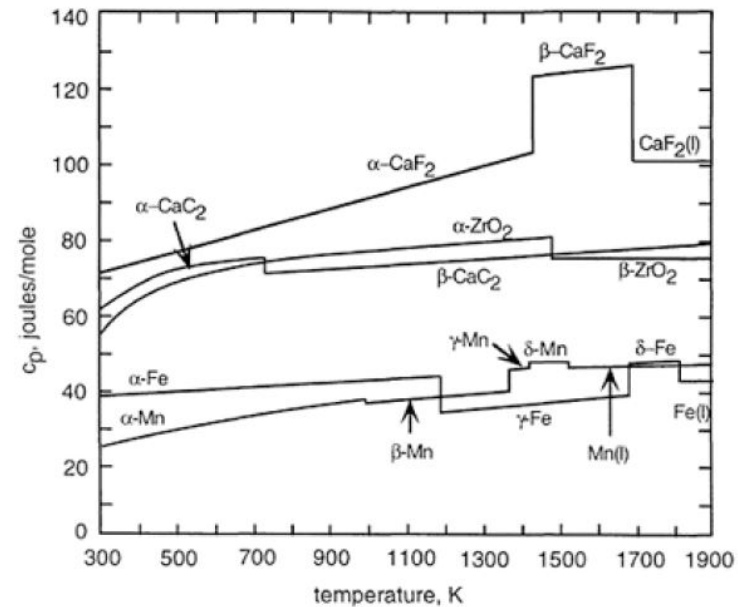


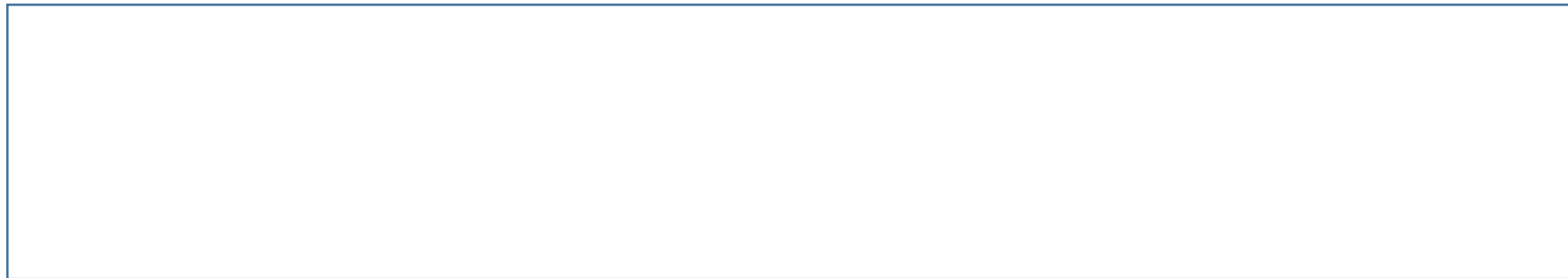
Figure 6.5 The variations, with temperature, of the constant-pressure molar heat capacities of some elements which exhibit allotropy and some compounds which exhibit polymorphism.

6.4 ENTHALPY AS A FUNCTION OF TEMPERATURE AND COMPOSITION

For a closed system of fixed composition, with a change in T from T_1 to T_2 at the const. P

i) $\Delta H = H(T_2, P) - H(T_1, P) = \int_{T_1}^{T_2} C_p dT$ (6.1) : ΔH is the area under a plot of C_p vs T

ii) $A + B = AB$ chem. rxn or phase change at const. T, P



6.4 ENTHALPY AS A FUNCTION OF TEMPERATURE AND COMPOSITION

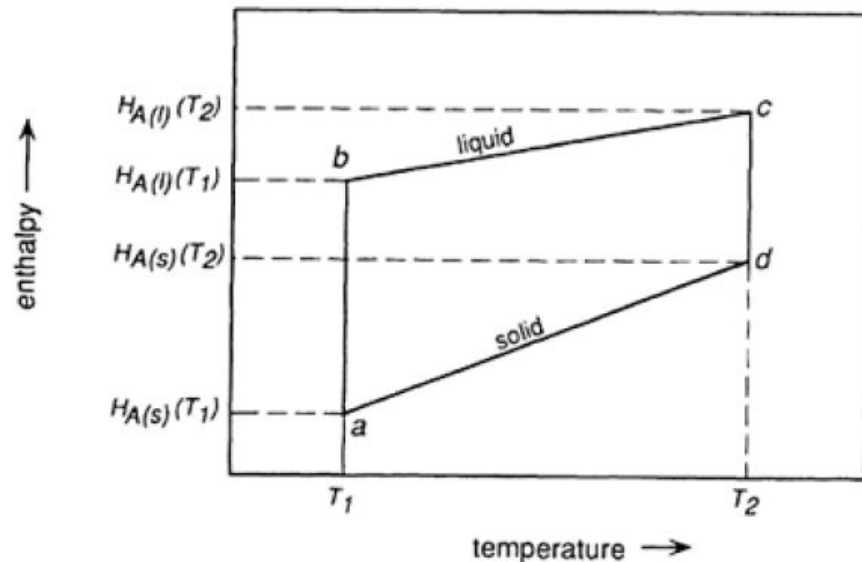


Figure 6.6 The variation, with temperature, of the molar enthalpies of the solid and liquid phases of a substance.

- **Enthalpy change**

Consider the change of state $A_{(s)} \rightarrow A_{(l)}$

$$\Delta H_{T_1} = H_{A(l)}(T_1) - H_{A(s)}(T_1)$$

where $\Delta H(a \rightarrow d)$ is the heat required to increase the temperature of one mole of solid A from T_1 to T_2 at constant pressure.

$$\Delta H(a \rightarrow b) = \Delta H(a \rightarrow d) + \Delta H(d \rightarrow c) + \Delta H(c \rightarrow b) \quad (i)$$

6.4 ENTHALPY AS A FUNCTION OF TEMPERATURE AND COMPOSITION

$$\therefore \Delta H(A_{(s)} \rightarrow A_{(l)} \text{ at } T_1) = \Delta H(A_{(s)} \rightarrow A_{(l)} \text{ at } T_2) + \int_{T_1}^{T_2} c_{pA(s)} dT - \int_{T_1}^{T_2} c_{pA(l)} dT \quad \text{or} \quad \Delta H_{T_2} = \Delta H_{T_1} + \int_{T_1}^{T_2} \Delta c_p dT \quad (6.9)$$

where $\Delta c_p = c_{pA(l)} - c_{pA(s)}$

ex) $M(s) + 1/2O_2(g) = MO(s)$ at 298K

$$\begin{aligned} \Delta H_{298} &= H_{MO(s),298} - H_{M(s),298} - \frac{1}{2}H_{O_2(g),298} \\ &= H_{MO(s),298} \text{ as } H_{M(s),298} \text{ \&} \end{aligned}$$

$H_{O_2(g),298} = 0$ by convention

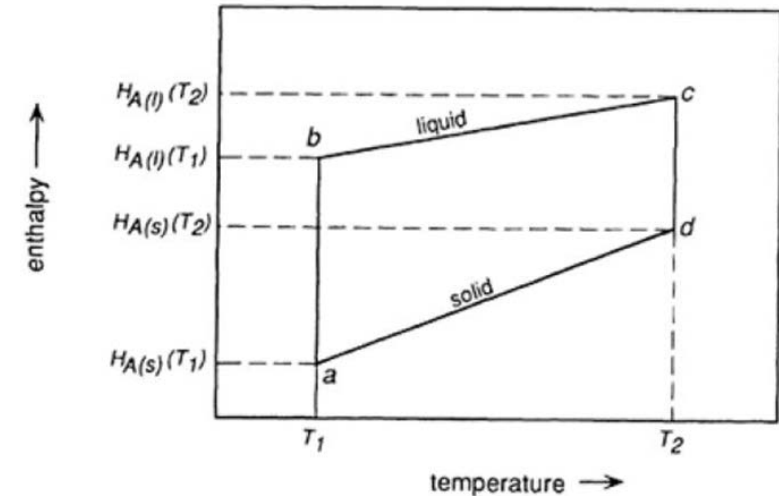


Figure 6.6 The variation, with temperature, of the molar enthalpies of the solid and liquid phases of a substance.

6.4 ENTHALPY AS A FUNCTION OF TEMPERATURE AND COMPOSITION

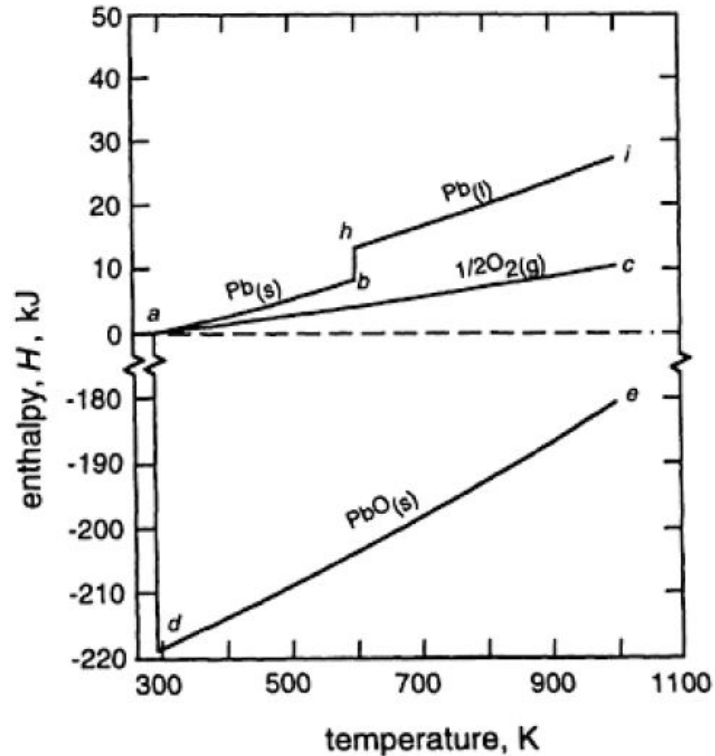


Fig 6.7 : For the oxidation $\text{Pb} + \frac{1}{2}\text{O}_2 = \text{PbO}$ with H of $\frac{1}{2}$ mole of O_2 gas, 1mole of $\text{Pb}(s)$ at 298K (=0 by convention)

Figure 6.7 (a) The variation, with temperature, of the enthalpies of $\text{Pb}(s)$, $\text{Pb}(l)$, $\frac{1}{2}\text{O}_2(g)$, and $\text{PbO}(s)$.

6.4 ENTHALPY AS A FUNCTION OF TEMPERATURE AND COMPOSITION

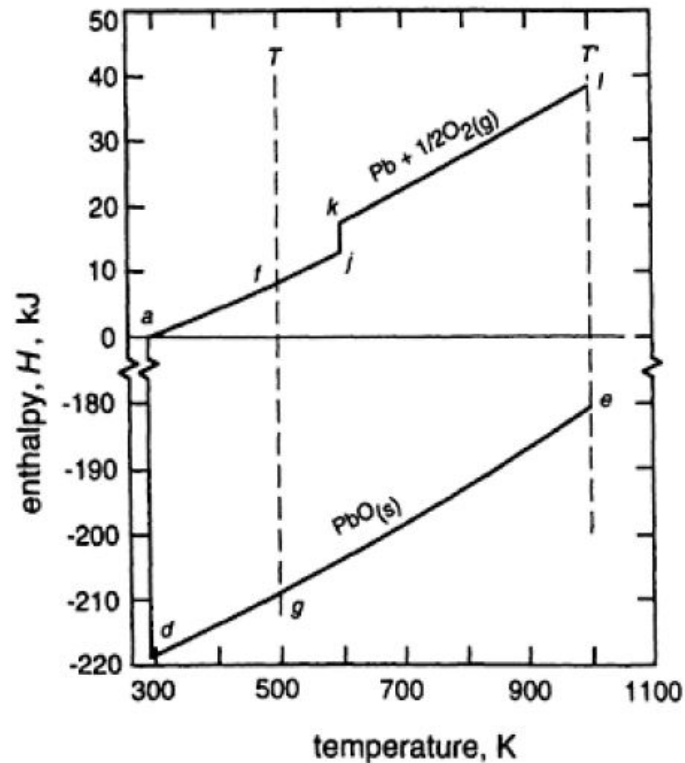


Figure 6.7 (b) The variation, with temperature, of the enthalpies of $(\text{Pb} + \frac{1}{2}\text{O}_2)$ and PbO .

With H of $\frac{1}{2}$ mole of $\text{O}_2(\text{g})$ and 1 mole of $\text{Pb}(\text{s})$ at $298\text{K}(=0$ by convention)



$$\begin{aligned} \text{Thus } \Delta H_{\text{PbO}, 298 \text{ K}} &= \Delta H(a \rightarrow f) + \Delta H(f \rightarrow g) + \Delta H(g \rightarrow d) \\ &= \int_{298}^T \left(\frac{1}{2} c_{p, \text{O}_2(\text{g})} + c_{p, \text{Pb}(\text{s})} \right) dT + \Delta H_{\text{PbO}, T} + \int_T^{298} c_{p, \text{PbO}(\text{s})} dT \end{aligned}$$

$$\Delta H_T = \Delta H_{298} + \int_{298}^T \Delta c_p dT$$

$$\text{where } \Delta c_p = c_{p, \text{PbO}(\text{s})} - c_{p, \text{Pb}(\text{s})} - \frac{1}{2} c_{p, \text{O}_2(\text{g})}$$

6.4 ENTHALPY AS A FUNCTION OF TEMPERATURE AND COMPOSITION

Table 6.1 Thermochemical data for Pb, PbO, and O₂.

$$H_{\text{PbO}(298)} = -219,000 \text{ J/K}$$

$$C_{p,\text{Pb}(s)} = 23.6 + 9.75 \times 10^{-3} T \text{ J/K from } 298 \text{ K to } T_{m,\text{Pb}}$$

$$C_{p,\text{Pb}(l)} = 32.4 - 3.1 \times 10^{-3} T \text{ J/K from } T_{m,\text{Pb}} \text{ to } 1200 \text{ K}$$

$$C_{p,\text{PbO}(s)} = 37.9 + 26.8 \times 10^{-3} T \text{ J/K from } 298 \text{ K to } T_{m,\text{PbO}}$$

$$C_{p,\text{O}_2(g)} = 29.96 + 4.18 \times 10^{-3} T - 1.67 \times 10^5 T^{-2} \text{ J/K from } 298 \text{ K to } 3000 \text{ K}$$

$$\Delta H_{m,\text{Pb}} = 4810 \text{ J at } T_{m,\text{Pb}} = 600 \text{ K}$$

$$T_{m,\text{PbO}} = 1159 \text{ K}$$

From the data in Table 6.1,

$$\Delta c_p = -0.7 + 14.96 \times 10^{-3} T + 0.85 \times 10^5 T^{-2}$$

and, thus, from 298 to 600 K ($T_{m,\text{Pb}}$)

$$\begin{aligned} \Delta H_T &= -219,000 + \int_{298}^T (-0.7 + 14.96 \times 10^{-3} T + 0.85 \times 10^5 T^{-2}) dT \\ &= -219,000 - 0.7(T - 298) + 7.48 \times 10^{-3}(T^2 - 298^2) \\ &\quad - 0.85 \times 10^5 \left(\frac{1}{T} - \frac{1}{298} \right) \end{aligned}$$

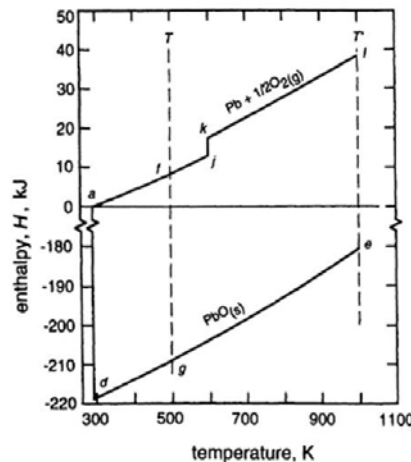


Figure 6.7 (b) The variation, with temperature, of the enthalpies of ($\text{Pb} + \frac{1}{2}\text{O}_2$) and PbO.

6.4 ENTHALPY AS A FUNCTION OF TEMPERATURE AND COMPOSITION

- In Fig. 6.7b, \overline{ajkl} : H of 1 mole of Pb and 1 mole of $O_{2(g)}$, and hence ΔH_T is calculated from the cycle

$$\Delta H_{298\text{ K}} = \Delta H(a \rightarrow d) = \Delta H(a \rightarrow j) + \Delta H(j \rightarrow k) + \Delta H(k \rightarrow l) + \Delta H(l \rightarrow e) + \Delta H(e \rightarrow g) + \Delta H(g \rightarrow d)$$

where $\Delta H(a \rightarrow j) = \int_{298}^{T_{m,Pb}} \left(c_{p,Pb(s)} + \frac{1}{2}c_{p,O_2(g)} \right) dT$

$\Delta H(j \rightarrow k)$ = the latent heat of melting of Pb at $T_{m,Pb} = 4810\text{ J}$

$$\Delta H(k \rightarrow l) = \int_{T_{m,Pb}}^T \left(c_{p,Pb(l)} + \frac{1}{2}c_{p,O_2(g)} \right) dT$$

$$\Delta H(l \rightarrow e) = \Delta H_T$$

$$\Delta H(e \rightarrow g) = \int_T^{T_{m,Pb}} c_{p,PbO(s)} dT$$

$$\Delta H(g \rightarrow d) = \int_{T_{m,Pb}}^{298} c_{p,PbO(s)} dT$$

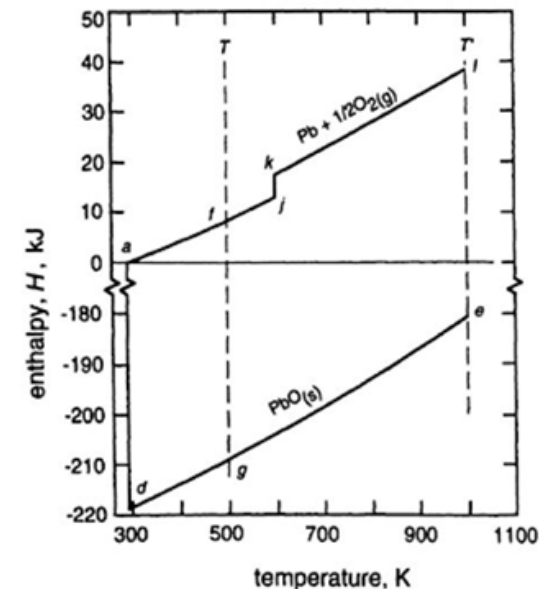


Figure 6.7 (b) The variation, with temperature, of the enthalpies of $(Pb + \frac{1}{2}O_2)$ and PbO.

6.4 ENTHALPY AS A FUNCTION OF TEMPERATURE AND COMPOSITION

Thus

$$\Delta H_T = \Delta H_{298 \text{ K}} + \int_{298}^{T_{m,\text{Pb}}} \left(c_{p,\text{PbO}(s)} - c_{p,\text{Pb}(s)} - \frac{1}{2}c_{p,\text{O}_2(g)} \right) dT - \Delta H_{m,\text{Pb}} + \int_{T_{m,\text{Pb}}}^T \left(c_{p,\text{PbO}(s)} - c_{p,\text{Pb}(l)} - \frac{1}{2}c_{p,\text{O}_2(g)} \right) dT$$

$$= -219,000 + \int_{298}^{600} (-0.7 + 14.96 \times 10^{-3}T + 0.85 \times 10^5 T^{-2}) dT - 4810 + \int_{600}^T (-9.3 + 27.8 \times 10^{-3}T + 0.85 \times 10^5 T^{-2}) dT$$

This gives $\Delta H_{1000} = -216,700 \text{ J}$ at $T'=1000\text{K}$

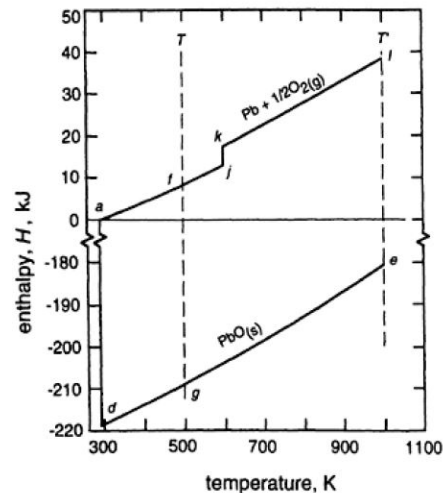


Figure 6.7 (b) The variation, with temperature, of the enthalpies of $(\text{Pb} + \frac{1}{2}\text{O}_2)$ and PbO .

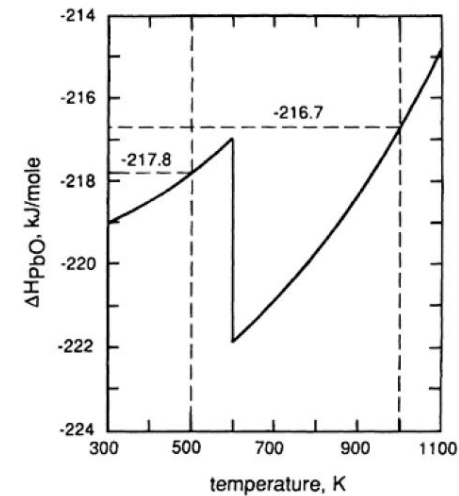


Figure 6.8 The variation, with temperature, of the enthalpy change for the reaction $\text{Pb} + \frac{1}{2}\text{O}_2 = \text{PbO}$.

6.4 ENTHALPY AS A FUNCTION OF TEMPERATURE AND COMPOSITION

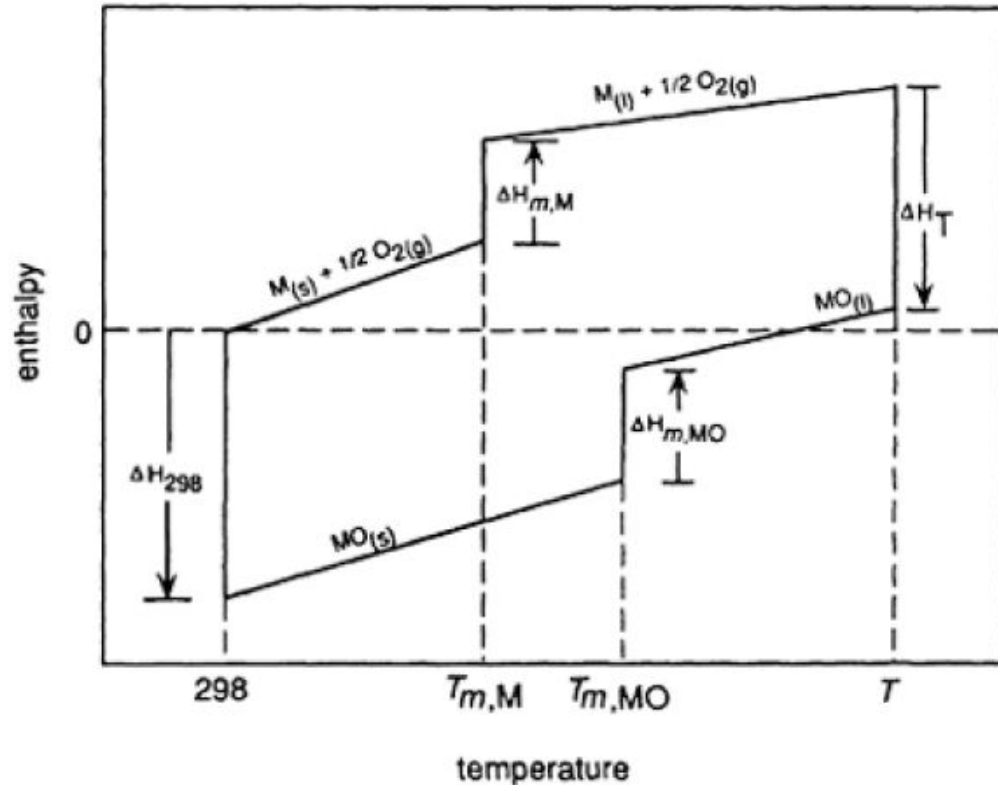


Figure 6.9 The effect of phase changes on ΔH for a chemical reaction.

If the T of interest is higher than the T_m of both the metal and its oxide, then both latent heats of melting must be considered.

$$\begin{aligned}
 & \text{M} + \frac{1}{2} \text{O}_2 = \text{MO} \\
 \Delta H_T = & \Delta H_{298} + \int_{298}^{T_{m,M}} \left(c_{p,\text{MO}(s)} - c_{p,\text{M}(s)} - \frac{1}{2} c_{p,\text{O}_2(g)} \right) dT \\
 & - \Delta H_{m,M} + \int_{T_{m,M}}^{T_{m,MO}} \left(c_{p,\text{MO}(s)} - c_{p,\text{M}(l)} - \frac{1}{2} c_{p,\text{O}_2(g)} \right) dT \\
 & + \Delta H_{m,MO} + \int_{T_{m,MO}}^T \left(c_{p,\text{MO}(l)} - c_{p,\text{M}(l)} - \frac{1}{2} c_{p,\text{O}_2(g)} \right) dT
 \end{aligned}$$

6.4 ENTHALPY AS A FUNCTION OF TEMPERATURE AND COMPOSITION

- If the system contains a low-temperature phase in equilibrium with a high-temperature phase at the equilibrium phase transition temperature then introduction of heat to the system (the external influence) would be expected to increase the temperature of the system (the effect) by Le Chatelier's principle.
- However, the system undergoes an endothermic change, which absorbs the heat introduced at constant temperature, and hence nullifies the effect of the external influence. The endothermic process is the melting of some of the solid. A phase change from a low- to a high-temperature phase is always endothermic, and hence ΔH for the change is always a positive quantity. Thus ΔH_m is always positive. The general Eq. (6.9) can be obtained as follows:

$$\text{For the state 1 } \left(\frac{\partial H_1}{\partial T} \right)_P = c_{p(1)}$$

$$\text{For the state 2 } \left(\frac{\partial H_2}{\partial T} \right)_P = c_{p(2)}$$

6.4 ENTHALPY AS A FUNCTION OF TEMPERATURE AND COMPOSITION

Subtraction gives

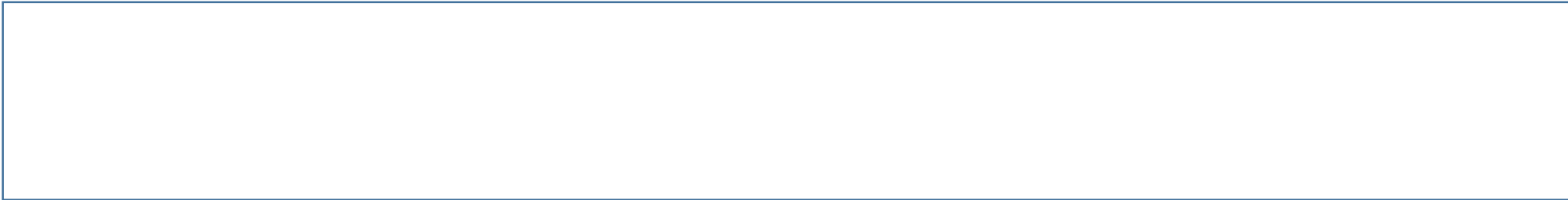
$$\left(\frac{\partial H_2}{\partial T}\right)_P - \left(\frac{\partial H_1}{\partial T}\right)_P = c_{p(2)} - c_{p(1)} \quad \text{or} \quad \left(\frac{\partial \Delta H}{\partial T}\right)_P = \Delta c_p \quad (6.10)$$
$$\left[\frac{\partial(H_2 - H_1)}{\partial T}\right]_P = \Delta c_p$$

and integrating from state 1 to state 2 gives

$$\Delta H_{T_2} - \Delta H_{T_1} = \int_{T_1}^{T_2} \Delta c_p dT \quad (6.11)$$

Equations (6.10) and (6.11) are expressions of **Kirchhoff's Law**.

6.5 THE DEPENDENCE OF ENTROPY ON TEMPERATURE AND THE THIRD LAW OF THERMODYNAMICS



For a closed system undergoing a reversible process,

$$dS = \frac{\delta q}{T} \quad (3.8)$$

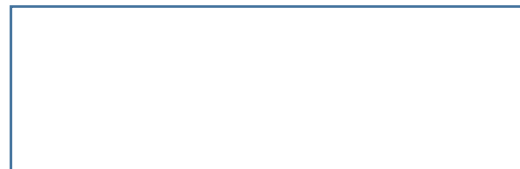
At const. P,

$$dS = \left(\frac{\delta q}{T} \right)_P = \left(\frac{dH}{T} \right)_P = c_p \frac{dT}{T}$$

As T increased,

$$\Delta S = S(T_2, P) - S(T_1, P) = \int_{T_1}^{T_2} \frac{c_p}{T} dT \quad (6.12)$$

the molar S of the system at any T is given by



(6.13)

6.5 THE DEPENDENCE OF ENTROPY ON TEMPERATURE AND THE THIRD LAW OF THERMODYNAMICS

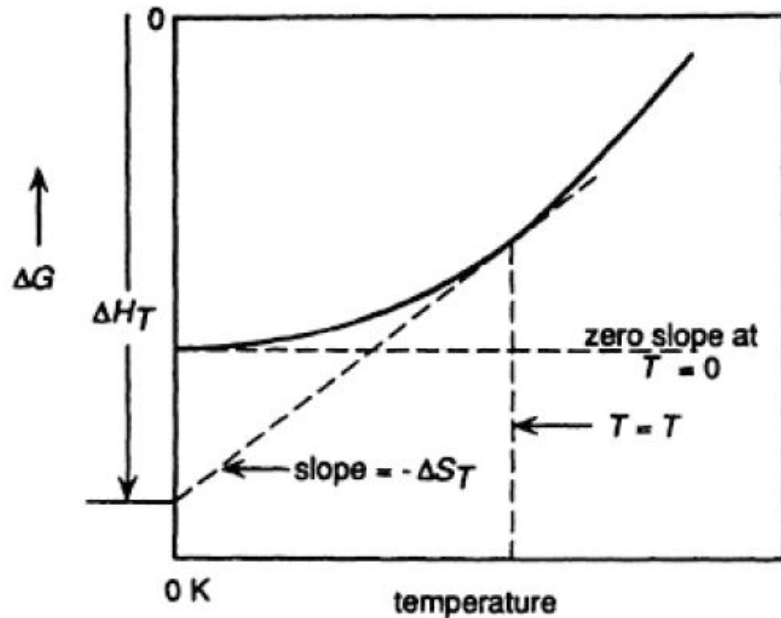


Figure 6.10 The variation of the change in the Gibbs free energy for a reaction with temperature as the temperature approaches absolute zero.

$$\Delta G_T = \Delta H_T - T\Delta S_T$$

$$\Rightarrow \left(\frac{\partial \Delta G}{\partial T}\right)_P = \left(\frac{\partial \Delta H}{\partial T}\right)_P - T\left(\frac{\partial \Delta S}{\partial T}\right)_P - \Delta S$$

From Eq. (5.12) $dG = -SdT + VdP$

$$\left(\frac{\partial \Delta G}{\partial T}\right)_P = -\Delta S$$

6.5 THE DEPENDENCE OF ENTROPY ON TEMPERATURE AND THE THIRD LAW OF THERMODYNAMICS

- (i) $\Delta C_p = \sum v_i C_{pi} \rightarrow 0$ means that each $C_{pi} \rightarrow 0$ (solutions)
by Einstein & Debye ($T \rightarrow 0, C_v \rightarrow 0$)
- (ii) $\Delta S = \sum v_i S_i \rightarrow 0$ means that each $S_i \rightarrow 0$

$$\begin{aligned} S_{\text{total}} &= S_{\text{th}} + S_{\text{conf}} \\ &= k \ln \Omega_{\text{th}} + k \ln \Omega_{\text{conf}} \\ &= k \ln \Omega_{\text{th}} \Omega_{\text{conf}} \end{aligned}$$

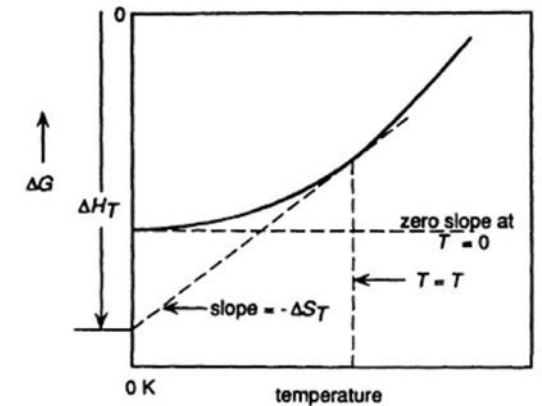


Figure 6.10 The variation of the change in the Gibbs free energy for a reaction with temperature as the temperature approaches absolute zero.

6.5 THE DEPENDENCE OF ENTROPY ON TEMPERATURE AND THE THIRD LAW OF THERMODYNAMICS

- If $(\partial\Delta G/\partial T)_P$ and $(\partial\Delta H/\partial T)_P \rightarrow 0$ as $T \rightarrow 0$, ΔS & $\Delta C_p \rightarrow 0$ as $T \rightarrow 0$
- Nernst's heat theorem states that "for all reactions involving substances in the condensed state, ΔS is zero at the absolute zero of temperature"

6.5 THE DEPENDENCE OF ENTROPY ON TEMPERATURE AND THE THIRD LAW OF THERMODYNAMICS

the substance be in complete internal equilibrium:

① Glasses

- noncrystalline, supercooled liquids
liquid-like disordered atom arrangements
→ frozen into solid glassy state → metastable
- $S_0 \neq 0$, depending on degree of atomic order

② Solutions

- mixture of atoms, ions or molecules
- entropy of mixing
- atomic randomness of a mixture determines its degree of order
 - : complete ordering : every A is coordinated only by B atoms and vice versa
 - : complete randomness : 50% of the neighbors of every atom are A atoms and 50% are B atoms.

6.5 THE DEPENDENCE OF ENTROPY ON TEMPERATURE AND THE THIRD LAW OF THERMODYNAMICS

③ Even chemically pure elements

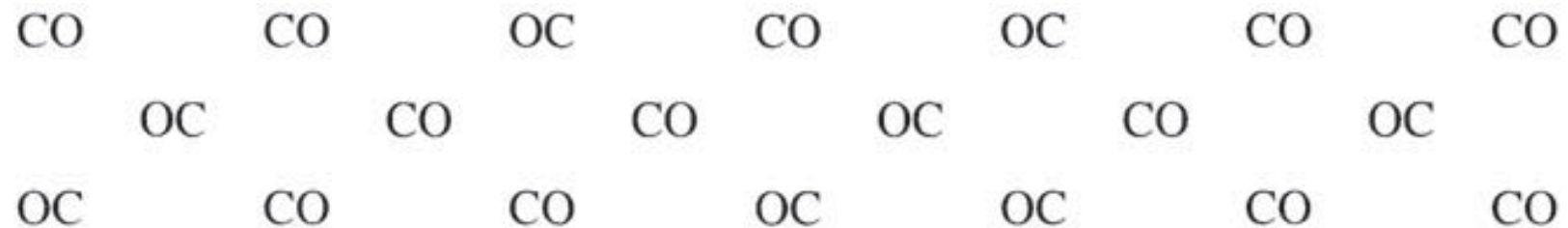
- mixtures of isotopes → entropy of mixing

ex) $\text{Cl}^{35} - \text{Cl}^{37}$

④ Point defects

- entropy of mixing with vacancy

Ex) Solid CO Structure



6.5 THE DEPENDENCE OF ENTROPY ON TEMPERATURE AND THE THIRD LAW OF THERMODYNAMICS

using Stirling's approximation,

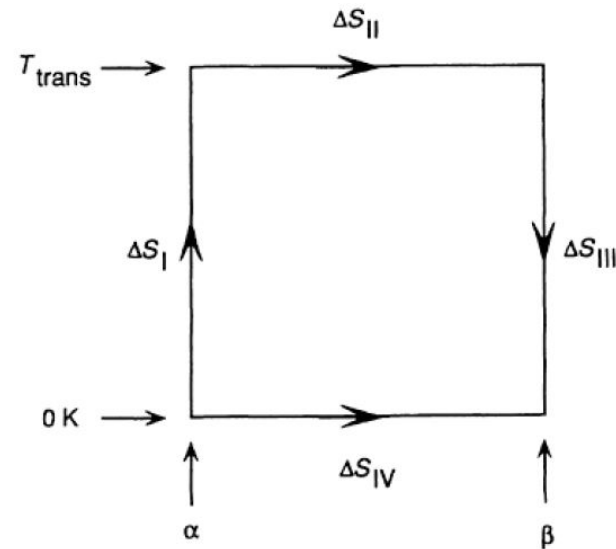
$$\begin{aligned}\Delta S_{\text{conf}} &= k \left[N_O \ln N_O - \frac{1}{2}N_O \ln \left(\frac{1}{2}N_O \right) - \frac{1}{2}N_O \ln \left(\frac{1}{2}N_O \right) \right] \\ &= k \times 4.175 \times 10^{23} \\ &= 1.38054 \times 10^{-23} \times 4.175 \times 10^{23} \\ &= 5.76 \text{ J/mole}\cdot\text{K}\end{aligned}$$

measured value: 4.2 J/mole K : requires complete internal equilibrium

6.6 EXPERIMENTAL VERIFICATION OF THE THIRD LAW

- The Third Law can be verified by considering a phase transition in an element such as $\alpha \rightarrow \beta$ where α & β are allotropes of the element and this **for the case of sulfur**:

For the cycle shown in Fig. 6.11



$$\Delta S_{IV} = \Delta S_I + \Delta S_{II} + \Delta S_{III}$$

For the Third Law to be obeyed, $S_{IV} = 0$, which requires that

$$\Delta S_{II} = -(\Delta S_I + \Delta S_{III})$$

where

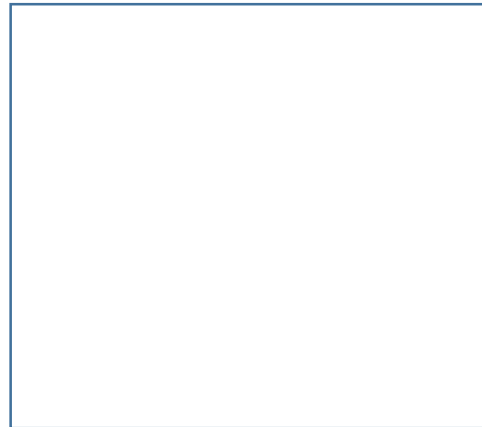


Figure 6.11 The cycle used for the experimental verification of the Third Law of Thermodynamics.

6.6 EXPERIMENTAL VERIFICATION OF THE THIRD LAW

- In Fig 6.11, a monoclinic form which is stable above 368.5 K and an orthorhombic form which is stable below 368.5 K
- The measured heat capacities give

$$\Delta S_{\text{I}} = \int_0^{368.5} \frac{c_{p(\text{rhombic})}}{T} dT = 36.86 \text{ J/K}$$

$$\Delta S_{\text{II}} = \frac{\Delta H_{\text{trans}}}{T_{\text{trans}}} = \frac{400}{368.5} = 1.09 \text{ J/K}$$

$$\Delta S_{\text{III}} = \int_{368.5}^0 \frac{c_{p(\text{monoclinic})}}{T} dT = -37.8 \text{ J/K}$$



$$-(\Delta S_{\text{I}} + \Delta S_{\text{III}}) = -(36.86 - 37.8) = 0.94 \text{ J/K}$$

$$\Delta S_{\text{II}} = 1.09 \text{ J/K}$$

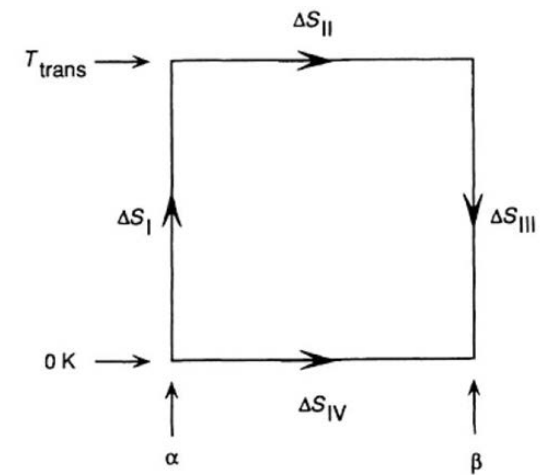


Figure 6.11 The cycle used for the experimental verification of the Third Law of Thermodynamics.

6.6 EXPERIMENTAL VERIFICATION OF THE THIRD LAW

Assigning a value of zero to S_0 allows the absolute value of the entropy of any material to be determined as

$$S_T = \int_0^T \frac{c_p}{T} dT \text{ J/K}$$

and molar entropies are normally tabulated at 298 K, where

$$S_{298} = \int_0^{298} \frac{c_p}{T} dT \text{ J/K}$$

With the constant-pressure molar heat capacity of the solid expressed in the form

$$c_{p(s)} = a + bT + cT^{-2}$$

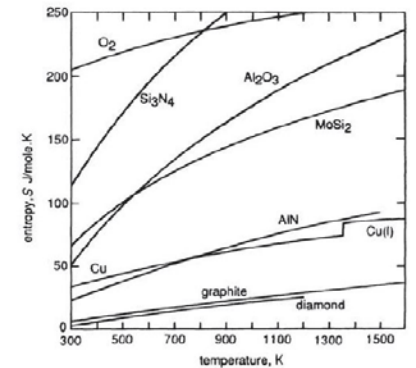


Figure 6.12 The variation, with temperature, of the molar entropies of several elements and compounds.

6.6 EXPERIMENTAL VERIFICATION OF THE THIRD LAW

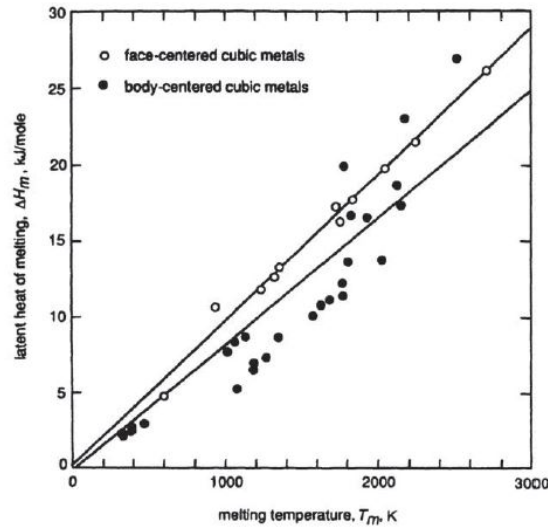


Figure 6.13 An illustration of Richard's rule.

Richard's rule (generally metal)

$$\frac{\Delta H_m}{T_m} \approx \Delta S_m \approx 9.6 \text{ J/K (FCC)},$$

$$8.3 \text{ J/K (BCC)}$$

$$\Delta H_m = 9.61 T_m + 0.01 \text{ J/K} \quad \text{From FCC}$$

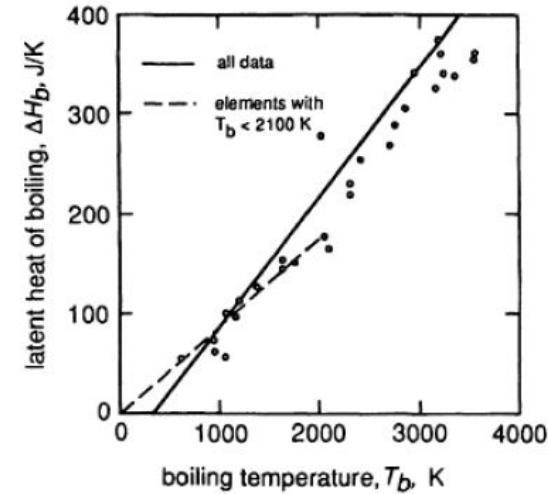


Figure 6.14 An illustration of Trouton's rule.

Trouton's rule (generally metal)-**more useful!!**

$$\frac{\Delta H_v}{T_b} \approx \Delta S_b \approx 88 \text{ J/K (for both FCC and BCC)}$$

$$\Delta H_m = 8.25 T_m - 0.19 \text{ J/K} \quad \text{From BCC}$$

6.6 EXPERIMENTAL VERIFICATION OF THE THIRD LAW

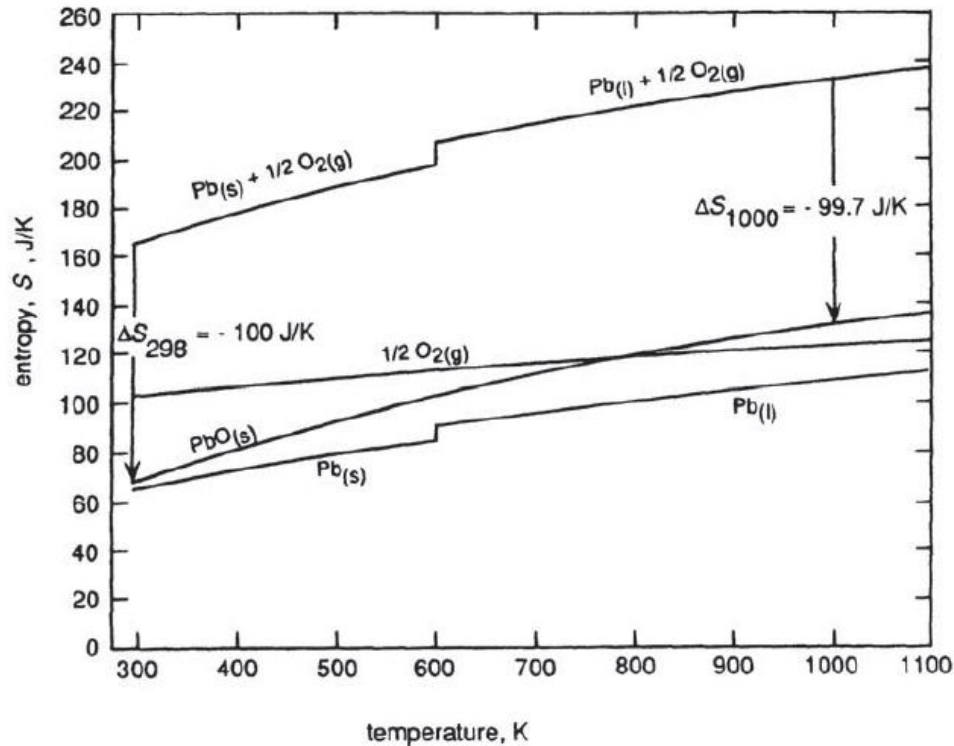


Figure 6.15 The variation, with temperature, of the entropies of $\text{Pb}_{(s)}$, $\text{Pb}_{(l)}$, $\text{PbO}_{(s)}$, $\frac{1}{2} \text{O}_{2(g)}$, and the entropy change for the reaction $\text{Pb} + \frac{1}{2} \text{O}_2 = \text{PbO}$.

Because of the similar molar S of the condensed phases Pb and PbO , it is seen that ΔS for the reaction,

$$\Delta S_T = S_{T,\text{PbO}} - S_{T,\text{Pb}} - \frac{1}{2} S_{T,\text{O}_2}$$

is very nearly equal to $-\frac{1}{2} S_{T,\text{O}_2}$ at 298K

$$\begin{aligned} \Delta S_{298} &= S_{298,\text{PbO}} - S_{298,\text{Pb}} - \frac{1}{2} S_{298,\text{O}_2} \\ &= 67.4 - 64.9 - \frac{1}{2} \times 205 \\ &= -100 \text{ J/K} \end{aligned}$$

6.7 THE INFLUENCE OF PRESSURE ON ENTHALPY AND ENTROPY

(i) For a closed system of fixed composition, with a change of P at const. T ,

$$dH = \left(\frac{\partial H}{\partial P} \right)_T dP \quad (dH = TdS + VdP)$$

$$\left(\frac{\partial H}{\partial P} \right)_T = T \left(\frac{\partial S}{\partial P} \right)_T + V \quad \alpha = \frac{1}{V} \left(\frac{\partial V}{\partial T} \right)_P$$

Maxwell's equation (5.34) gives $(\partial S / \partial P)_T = -(\partial V / \partial T)_P$

6.7 THE INFLUENCE OF PRESSURE ON ENTHALPY AND ENTROPY

The change in molar enthalpy caused by the change in state from (P_1, T) to (P_2, T) is thus

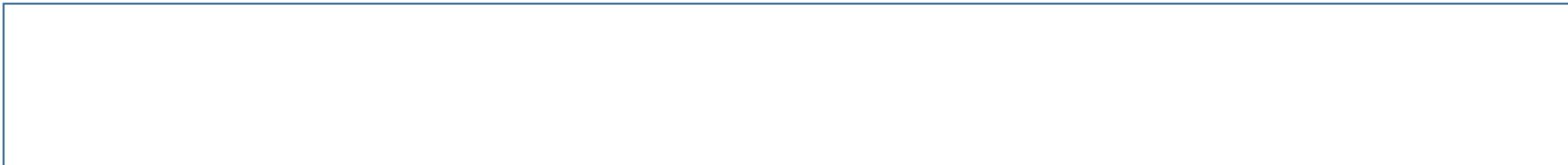
$$\Delta H = H(P_2, T) - H(P_1, T) = \int_{P_1}^{P_2} V(1 - \alpha T) dP \quad (6.14)$$

For an ideal gas, $\alpha = 1/T$ an Eq. (6.14) = 0, H of an ideal gas is independent of P.

- The molar V and α of Fe are, respectively, 7.1 cm^3 and $0.3 \times 10^{-4} \text{ K}^{-1}$.

the P increase on Fe from 1 to 100 atm at 298 K causes the H to increase by

$$\begin{aligned} 7.1 \times 10^{-3} \times (1 - 0.3 \times 10^{-4} \times 298) \times (100 - 1) &= 0.696 \text{ liter}\cdot\text{atm} \\ &= 0.696 \times 101.3 = 71 \text{ J} \end{aligned}$$



6.7 THE INFLUENCE OF PRESSURE ON ENTHALPY AND ENTROPY

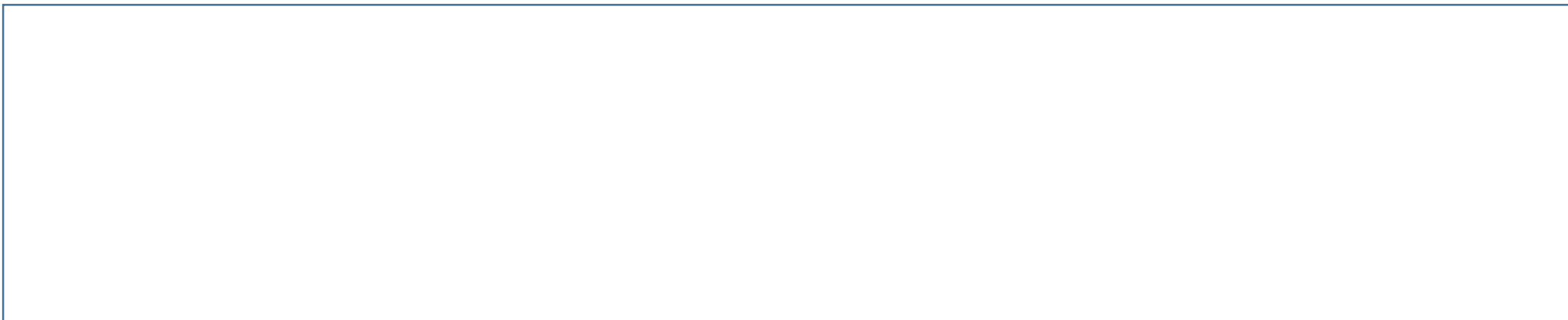
(ii) For a closed system of fixed composition, with a change of P at const. T ,

$$dS = \left(\frac{\partial S}{\partial P} \right)_T dP$$

Maxwell's equation (5.34) gives $(\partial S / \partial P)_T = -(\partial V / \partial T)_P$ & $\alpha = \frac{1}{V} \left(\frac{\partial V}{\partial T} \right)_P$

$$\Rightarrow \left(\frac{\partial S}{\partial P} \right)_T = -\alpha V$$

Thus, for the change of state from (P_1, T) to (P_2, T)



6.7 THE INFLUENCE OF PRESSURE ON ENTHALPY AND ENTROPY

- Solid : An increase in the pressure exerted on Fe

Fe: from 1 to 100 atm at 298K

$$\Rightarrow \Delta S = -0.0022 \text{ J/K}$$

Al: from 1 to 100 atm at 298K

$$\Rightarrow \Delta S = -0.007 \text{ J/K}$$

- For same ΔS , how much is the temperature change?

Fe \rightarrow 0.29K required

Al \rightarrow 0.09K required

\therefore very insignificant effect

6.7 THE INFLUENCE OF PRESSURE ON ENTHALPY AND ENTROPY

(iii) For a closed system of fixed composition with changes in both P and T , combination of Eqs. (6.1) and (6.14) gives

$$\boxed{\hspace{15em}} \quad (6.16)$$

and combination of Eqs. (6.12) and (6.15) gives

$$\boxed{\hspace{15em}} \quad (6.17)$$

For condensed phases over small ranges of P , these P dependencies can be ignored.