

Chap. 6.

6.1 Intro. 9/3/95

E', U' will be taken as denoting the value of the property for the sys. containing n moles, while E, U will be for the value / mole of the sys.

$$E' = nE, \quad dU' = C_v dT = n C_v dT \quad \text{or} \quad dU = C_v dT$$

$$\therefore \Delta U = \int C_v dT \quad \Delta H = \int C_p dT$$

6.2. Theo. Calculation of the Capacity.

First by Einstein using quantum theory. harm. the prop. of a xtal consisting of n atoms, behaving as n osc vibrating indep about its lattice pt., not affected by the h of its neighbors w/ a single fixed freq. ν . \rightarrow Einstein Xtl

Quantum theory: the E of the i th level of a harmonic oscill. showed $\rightarrow E_i = (i + \frac{1}{2}) h\nu$.

w/ 3 degrees of freedom. (x, y, z) $\rightarrow 3n$ linear harmonic osc

(6.3)
$$U' = 3 \sum n_i E_i$$

$$n_i = \frac{n e^{-\frac{E_i}{kT}}}{\sum e^{-\frac{E_i}{kT}}}$$

$$\therefore U' = 3 \sum (i + \frac{1}{2}) h\nu \left[\frac{n e^{-h\nu(i + \frac{1}{2})/kT}}{\sum e^{-h\nu(i + \frac{1}{2})/kT}} \right]$$

$$= \frac{3}{2} n h\nu \left[1 + \frac{2 \sum i e^{-h\nu i/kT}}{\sum e^{-h\nu i/kT}} \right]$$


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

(6.4)
$$U' = \frac{3}{2} n h\nu + \frac{3 n h\nu}{(e^{h\nu/kT} - 1)}$$
 \leftarrow relationship bet'n E_{trans} and E_{osc}

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

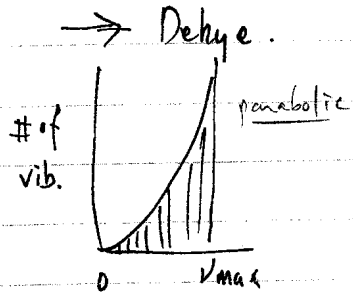
(6.5)
$$C_v = 3R \left(\frac{\theta_E}{T} \right)^2 \frac{e^{\theta_E/T}}{(e^{\theta_E/T} - 1)^2}$$

quantization of the energy level. remains const. at h.T. \rightarrow good agreement

- Debye theory - assumed that the range of ν is the same as that available to the elastic vibration of a continuous solid
- ① wave length: $\lambda_{min} = \text{interatomic}$ then all atoms in the same phase of vib.  $\therefore \lambda_{min} = 2 \times \text{inte} = 2a$
 - ② wave vel.: $U = 5 \times 10^5 \text{ cm/sec}$

$\nu_b = \nu_{max} = \frac{U}{\lambda_{min}} = 10^{13} / \text{sec}$ vel. of the shortest same

$0 \leq \nu \leq \nu_{max}$ # of vib / unit volume \uparrow pa



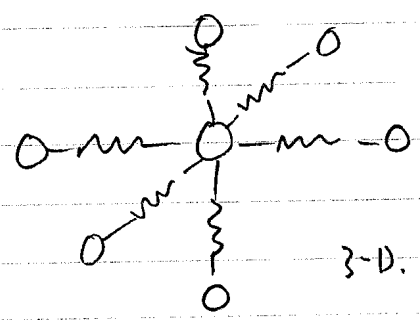
By integrating the Einsteins Expression in $0 \leq \nu \leq \nu_{max}$

$$C_v = 9R \left(\frac{T}{\theta_D} \right)^3 \int_0^{\theta_D/T} \frac{x^4 e^{-x}}{(1 - e^{-x})^2} dx$$

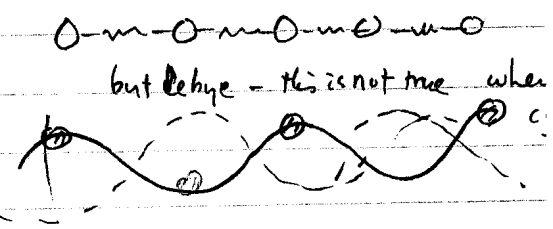
θ_D : Characteristic Debye temp.

where $x = \frac{h\nu}{k_B T} = \frac{\theta_D}{T}$ determi
measu
const. θ_D .

Debye Model



of possible harmonize ar



but Debye - this is not true when

- be assumed
- 1) the force bet'n a neighboring pair of atom. - equal v. to l of interacti
 - 2) parabolic distribution.

6.3. Empirical Representation of Heat Capacities

experimental expression of C_p : $C_p = a + bT + cT^{-2}$
only applicable in a stated temp. range.

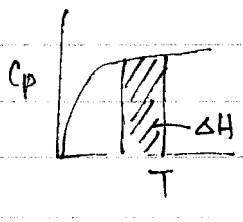
normally $C_p = a + bT$.
liquid $C_p = a = \text{const.}$

Ionic compounds. heat capacity of a solid "compound"
Copp's Rule = $\sum C_p$ of its constituent elements.

6.4 Enthalpy as a fnc of temp and composition.

For a sys. of fixed composition. (at const P) undergoing a temp change T_1 to T_2 .

$$(2.7a) \quad \Delta H = H(T_2, P) - H(T_1, P) = \int_{T_1}^{T_2} C_p dT.$$



$$\int dH = \int T ds + \int v dp = \int d\delta_P = \int C_p dT$$

$$= dU(-T ds - p dv) + p dv + v dp$$

For a chemical reaction at const P & T . ($A+B = AB$).

"Hess's law" (6.8) $\Delta H(T, P) = H_{AB}(T, P) - H_A(T, P) - H_B(T, P).$

$\Delta H > 0$ endothermic. rxn occurs w/ an absorptiv

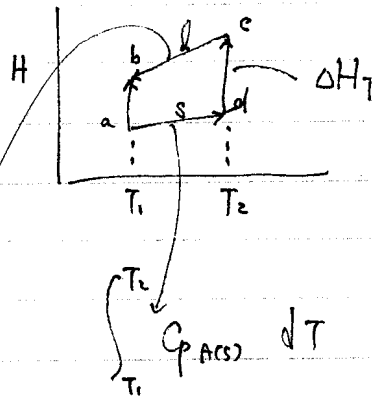
$\Delta H < 0$ exothermic. rxn occurs w/ a evolution.

① H₂O(l) → H₂O(s) ΔH = -6.0 kJ/mol
 ② H₂O(l) → H₂O(g) ΔH = +44.0 kJ/mol
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For the phase change $A(s) = A(c)$ $\Delta H_{T_1}, \Delta H_{T_2}$.

\vec{ab} $\Delta H_{T_1} = H_{A(c)}(T_1) - H_{A(s)}(T_1)$

\vec{cd} $\Delta H_{T_2} = H_{A(c)}(T_2) - H_{A(s)}(T_2)$



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

$$-\int_{T_1}^{T_2} C_{p(A(c))} dT$$

$$\int_{T_1}^{T_2} C_{p(A(s))} dT$$

$$\Delta H_{T_1} = \int_{T_1}^{T_2} C_{p(A(s))} dT + \Delta H_{T_2}(s \rightarrow l) - \int_{T_1}^{T_2} C_{p(A(c))} dT$$

$$\therefore \Delta H_{T_2}(s \rightarrow l) = \Delta H_{T_1}(s \rightarrow l) + \int_{T_1}^{T_2} [C_{p(A(c))} - C_{p(A(s))}] dT$$

$$= \Delta H_{T_1} + \int_{T_1}^{T_2} \Delta C_p dT$$

the absolute value of H for any state is unknown. //
 (only ΔH. change!! can be measured) //

Convention !! zero = the enthalpy of elemental substances in their stable states at 25°C. (formation energy)

① $\text{Mg} + \frac{1}{2} \text{O}_2 \rightarrow \text{MgO}$
 $\Delta H_{298} = H_{\text{MgO}(s)}(298) - H_{\text{Mg}(s)}(298) - \frac{1}{2} H_{\text{O}_2(g)}(298)$

$$\Delta H_{298} = H_{\text{MgO}(s)}(298) - H_{\text{Mg}(s)}(298) - \frac{1}{2} H_{\text{O}_2(g)}(298)$$

= $H_{\text{MgO}(s)}(298)$ = the heat of formation of the compound at 298

look at Examples in the text!!

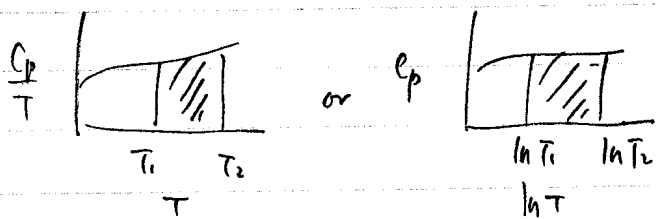
6.5. Temp. Dependence of Entropy + the 3rd law of Thermo.

From the 2nd law $ds = \frac{\delta q}{T}$ (3.8)

if reversible process at const P. $dS = \left(\frac{\delta q}{T}\right)_p = \left(\frac{dH}{T}\right)_p = C_p \frac{dT}{T}$.

∴ if Temp ↑ of a closed sys. of fixed comp., the increase in the entro per mole of the sys.

$\Delta S = S(T_2, P) - S(T_1, P) = \int_{T_1}^{T_2} C_p \frac{dT}{T} = \int_{T_1}^{T_2} C_p d \ln T$

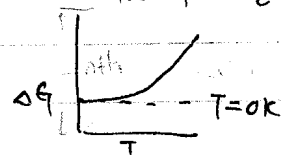


The entropy / mole of the sys. at T.

$S_T = S_0 + \int_0^T C_p d \ln T$

the 3rd law (∴ $S_{0K} = 0$)

for a rxns w/ Nernst $\rightarrow \Delta S_0$



Nernst postulated. $\left(\frac{\partial \Delta G}{\partial T}\right)_p$ & $\left(\frac{\partial \Delta H}{\partial T}\right)_p \rightarrow 0$ as $T \rightarrow 0$.

as $T \rightarrow 0$, the slope ($\Delta S \rightarrow 0$) and the variation of the intercept $\left(\frac{\partial \Delta H}{\partial T} \rightarrow 0, = \Delta C_p\right)$

a chemical rxn at const T.

(5.2) $\rightarrow G = H - TS \rightarrow \Delta G_T = \Delta H_T - T \Delta S_T$

then. At temp. T slope $\left(\frac{\partial \Delta G_T}{\partial T}\right) = \left(\frac{\partial \Delta H_T}{\partial T}\right) - \Delta S_T - T \left(\frac{\partial \Delta S_T}{\partial T}\right)$
 $\rightarrow -\Delta S_T$, intercept = ΔH_T at $T=0$

As $T \rightarrow 0$ slope $\rightarrow 0 \Rightarrow \Delta S_{0K} = 0 \therefore \Delta C_p = 0$.

can be shown this way

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

(S.12) with $\left(\frac{\partial \Delta G}{\partial p}\right)_p = -\Delta S$. $\therefore \left(\frac{\partial \Delta H}{\partial T}\right)_p = T \left(\frac{\partial \Delta S}{\partial T}\right)_p = \Delta C_p$.

$dg = -sdT + vdp$ \therefore if $\left(\frac{\partial \Delta G}{\partial T}\right)_p$ and $\left(\frac{\partial \Delta H}{\partial T}\right)_p \rightarrow 0$ as $T \rightarrow 0$.

It Analytically means then (S.12) $\Delta S, \Delta C_p \rightarrow 0$ as $T \rightarrow 0$.

Nerst stated. Substance in condensed state $\Delta S = 0$ at $T=0$ for $A+B=AB$

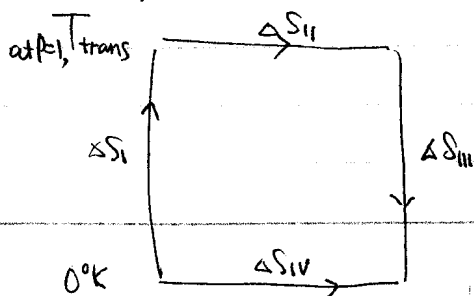
$\Delta S = S_{AB} - S_A - S_B = 0$ if $S_A = S_B = 0, S_{AB} = 0$.

Planck the entropy of any homo. substance, which is in internal equil^m, may be taken at 0°K.

- 1. Glass: undercooled non equil^m state $S_{0°K} \neq 0$ (degree of disorder)
- 2. Mixture: a non equil^m degree of order can be frozen into the solid solution $\Delta S > 0$ → kinetic frozen
- 3. mixture of isotopes. $Cl^{35} - Cl^{35}, Cl^{35} - Cl^{37}, Cl^{37} - Cl^{37}$ $\Delta S > 0$ but allow
- 4. no equil^m defects frozen

b.b. Experimental Verification of the 3rd law ($S_{0°K} = 0$)

for a phase transformation of an element $\alpha \rightarrow \beta$. α, β solid allotrope of the el



entropy is state prop.

$\therefore \Delta S_{IV} = \Delta S_I + \Delta S_{II} + \Delta S_{III} = 0$

By the 3rd law $\therefore \Delta S_{II} = -(\Delta S)$

$$\Delta S_i = \int_0^{T_{trans}} C_p(\alpha) d \ln T, \quad \Delta S_{ii} = \frac{\Delta H_{trans}}{T_{trans}}$$

$$\Delta S_{iii} = \int_{T_{trans}}^0 C_p(\beta) d \ln T.$$

|| $\Delta S_{ii} \rightarrow$ experimental entropy change. } the same
 $-(\Delta S_i + \Delta S_{iii}) \rightarrow$ 3rd law entropy change. } if the 3rd law

Using sulfur as an example, the diff. bet'n ΔS_{ii} and $-(\Delta S_i + \Delta S_{iii})$

$$\boxed{S_T = S_{298} + \int_{298}^T C_p d \ln T} \leftarrow \begin{aligned} \therefore S_T &= S_{0^\circ K} + \int_0^T C_p d \ln T \text{ joules/degree.} \\ S_{298} &= \int_0^{298} C_p d \ln T \end{aligned}$$

\hookrightarrow w/ $C_p = a + bT + cT^{-2}$

$$S_T = S_{298} + a \ln \left(\frac{T}{298} \right) + b(T - 298) - \frac{1}{2}c \left(\frac{1}{T^2} - \frac{1}{298^2} \right)$$

In the temp. range over which liquid exists

$$\left(= \frac{\Delta H_m}{T_m} \right)$$

$$S_T = S_{298} + \int_{298}^{T_m} C_p(s) d \ln T + \Delta S_m + \int_{T_m}^T C_p(l) d \ln T$$

Richard's Rule $\frac{\Delta H_m}{T_m} = \Delta S_m \sim 8 \text{ to } 16 \text{ Joules/}^\circ K.$

\hookrightarrow more applicable
 Trouton's Rule $\frac{\Delta H_v}{T_b} = \Delta S_b \sim 88 \text{ J/degree}$; if know T_b , can

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6.7. H & S as Ans of P.

i) For a closed sys. of fixed comp. at const T. $dH = \left(\frac{\partial H}{\partial P} \right)_T dP.$

$$dH = T ds + v dp \rightarrow \left(\frac{\partial H}{\partial p} \right)_T = T \left(\frac{\partial s}{\partial p} \right)_T + v.$$

from Maxwell's relation.

$$(5.34) \quad dG = -SdT + Vdp \rightarrow \left(\frac{\partial S}{\partial p}\right)_T = -\left(\frac{\partial V}{\partial T}\right)_p$$

$$\therefore \left(\frac{\partial H}{\partial p}\right)_T = -T\left(\frac{\partial V}{\partial T}\right)_p + V = -T\alpha V + V = \frac{V(1-\alpha T)}{\dots}$$

Since α at $p = \text{const} = \frac{1}{V}\left(\frac{\partial V}{\partial T}\right)_p$ ideal gas $\left(\frac{\partial H}{\partial p}\right)_T =$

\therefore for the change of state (P_1, T) to (P_2, T) .

$$(6.14) \quad \Delta H = H(P_2, T) - H(P_1, T) = \int_{P_1}^{P_2} \left(\frac{\partial H}{\partial p}\right)_T dp \quad \text{for ideal gas } \alpha = \frac{1}{T}$$

≈ 0 even for real case

ii) for a closed sys. of fixed comp. undergoing a change of P at const

$$dS = \left(\frac{\partial S}{\partial p}\right)_T dp$$

Maxwell eq. (5.34) \implies $\left(\frac{\partial S}{\partial p}\right)_T = -\left(\frac{\partial V}{\partial T}\right)_p = -\alpha V$

\therefore for the change of state (P_1, T) to (P_2, T) .

$$(6.15) \quad \Delta S = S(P_2, T) - S(P_1, T) = - \int_{P_1}^{P_2} \alpha V dp \quad \left(\frac{1}{T} \text{ for an ideal gas}\right)$$

$$\Delta S = - \int_{P_1}^{P_2} R \ln P = -R \ln \left(\frac{P_2}{P_1}\right) = -R \ln \left(\frac{V_1}{V_2}\right)$$

✓ 例, Fe, Al pressure increase 1 to 100 atm (entropy 0.0022 J/K , 0.007 equivalent to lowering the temp. of Fe, Al by $0.2-0.09$ degree. from 298°K .)

The molar enthalpies and entropies of condensed phase are relatively insensitive to pressure change.

⑧

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(ii) For a close sys. of fixed comp. undergoing both temp & pressure change.

$$\Delta H = H(P_2, T_2) - H(P_1, T_1) = \int_{T_1}^{T_2} C_p dT + \int_{P_1}^{P_2} v dp \text{ for conds}$$
$$\Delta S = S(P_2, T_2) - S(P_1, T_1) = \int_{T_1}^{T_2} C_p d \ln T - \int_{P_1}^{P_2} \frac{v}{T} dp \text{ ph}$$