

## Chapter 5. Chemical Bond Energy, Specific Heats, $C_p$ and $C_v$ for the Transition Elements

### 1. Chemical Bond Energy $\Phi_p(r_1)$

Continuing the mechanistic analysis of the solid mass atom begun in chapters three and four, the chemical bond energy, the specific heat at constant pressure  $C_p$  and the specific heat at constant volume  $C_v$  for the transition metals are derived in chapter five. 3.3 gives the field strength of an isolated atom at a distance  $r$  from the center of mass of the given atom where  $h_0^+ < r_1$ . At temperature  $T$  with no heat or electrical flow in the metal, replace  $h_0$  in 3.3 with the average radius of the atom  $r_0$  and using fig. 5.1:

$$5.1 \quad \Psi_p(R_1) \doteq \Psi_p(r_0^+) + \frac{\partial \Psi_p(r_0^+)}{\partial r} \cdot (R_1 - r_0^+) + \dots : r_0 < R_1 \lesssim 3r_0$$

$$|\Psi_p(r_0^+)| \ll |\Psi_p(r_0^-)|$$

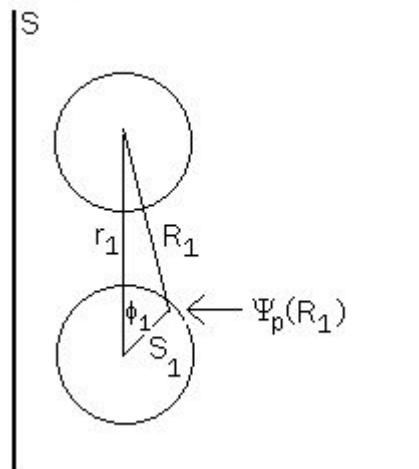
The potential energy  $\Phi_p$ , called the chemical bond energy, between two identical atoms whose center-to-center distance is  $r_1$  is:

$$5.2 \quad \Phi_p(r_1) = \int_V \rho(S_1) \Psi_p(R_1) S_1^2 \sin \phi_1 dS_1 d\phi_1 d\theta_1$$

Where  $R_1^2 = r_1^2 + S_1^2 - 2r_1 S_1 \cos \phi_1$ . The mass density is given by  $\rho(S_1) = a_p \left(\frac{S_1}{r_0}\right)^p$ ,

$a_p = \frac{(p+3)m}{4\pi r_0^3}$ , where for an isolated atom:  $-3.0 < p \leq 0$ . See figure 5.1

FIGURE 5.1



All measurements are taken from inertial frame S.

With  $r_1 = 2r_0 + R$ , expand  $\Phi_p(R)$  in a power series in R.  $2r_0 + R_0(T)$  is the average distance between the center of mass of two adjacent atoms at temperature T.

$$5.3 \quad \Phi_p(R) = a_0 + a_1 R + a_2 R^2 + \dots, \quad 0 \leq R \lesssim 10^{-10} \text{ cm}$$

$$\left(\frac{d\Phi_p}{dR}\right)_p = a_1 + 2a_2 R + 3a_3 R^2 + \dots = -F(R)$$

$$\left(\frac{d\Phi_p}{dT}\right)_p \Big|_{R_0(T)} = \left(\frac{d\Phi_p}{dR_0}\right)_p \left(\frac{dR_0}{dT}\right)_p = [a_1 + 2a_2 R_0 + 3a_3 R_0^2 + \dots] \left(\frac{dR_0}{dT}\right)_p = -F(R) \left(\frac{dR_0}{dT}\right)_p$$

$F(R)$  is the magnitude of the force between two adjacent atoms where  $2r_0 + R$  is the instantaneous distance between the center of mass of two adjacent atoms at temperature T.  $F(R_0)$  is the magnitude of the force between two adjacent atoms where  $2r_0 + R_0(T)$  is the average distance between the center of mass of two adjacent atoms at temperature T.

A rough evaluation of  $\Phi_p(R)$  follows.  $\Phi_p(0) = a_0 \approx -0.1 \text{ eV} \approx -10^{-13} \text{ erg}$  and  $F(0) = -a_1 \approx -10^{-4} \text{ dy}$ , See 5.3.

## 2. Specific Heat at Constant Pressure $C_p$

$C_p$  is the amount of heat energy  $\Delta Q$  per atom that must be supplied to a given atom to change its temperature by  $\Delta T$ , in the limit as  $\Delta T \rightarrow 0 \text{ K}^0$ , while maintaining the mass sample at constant external pressure. Experimentally, the external pressure on a transition metal is  $P_e = 1 \text{ atm} = 10^6 \text{ dy/cm}^2$ . For the transition metals  $C_p \approx 3K$  for  $T \approx 293 \text{ }^\circ\text{K}$ . The total energy of an atom in a solid is  $E_T = KE + PE + mC_1$  and equating the change per  $\text{K}^0$  of the total energy of the atom to the change in energy in, minus the change in energy out per  $\text{K}^0$  yields:

$$\left(\frac{dE_T}{dT}\right)_p = \left(\frac{dQ}{dT}\right)_p - P_e \left(\frac{dV}{dT}\right)_p - \frac{N}{N_T} S_u \left\{ \Omega_{Cr} \left(\frac{dN_{ph,out}}{dT}\right)_p + \frac{3}{2} K \Delta T'_{ph} \left(\frac{dN'_{ph,in}}{dT}\right)_p - \frac{3}{2} K T'_{ph} \left(\frac{dN''_{ph,in}}{dT}\right)_p \right\}$$

Each term to be described below. Solving for  $\left(\frac{dQ}{dT}\right)_p$  yields:

$$C_p = \left(\frac{dQ}{dT}\right)_p = \left(\frac{dE_T}{dT}\right)_p + P_e \left(\frac{dV}{dT}\right)_p + \frac{N}{N_T} S_u \left\{ \Omega_{Cr} \left(\frac{dN_{ph,out}}{dT}\right)_p + \frac{3}{2} K \Delta T'_{ph} \left(\frac{dN'_{ph,in}}{dT}\right)_p - \frac{3}{2} K T'_{ph} \left(\frac{dN''_{ph,in}}{dT}\right)_p \right\}$$

And

$$5.4 \quad C_p = \left(\frac{dKE}{dT}\right)_p + \left(\frac{dPE}{dT}\right)_p + m \left(\frac{dC_1}{dT}\right)_p + P_e \left(\frac{dV}{dT}\right)_p + \frac{N}{N_T} S_u \left\{ \Omega_{Cr} \left(\frac{dN_{ph,out}}{dT}\right)_p + \frac{3}{2} K \Delta T'_{ph} \left(\frac{dN'_{ph,in}}{dT}\right)_p - \frac{3}{2} K T'_{ph} \left(\frac{dN''_{ph,in}}{dT}\right)_p \right\}$$

KE is the kinetic energy of one atom and PE is the potential energy of one atom bonded to n atoms. In the case of the transition elements, n=6.  $(\frac{dKE}{dT})_p = \frac{3}{2}k$ , and

$(\frac{dPE}{dT})_p$  for a transition metal represents the change in potential energy wrt

temperature at constant external pressure of one atom coupled to six atoms.  $(\frac{d\Phi_p}{dT})_p$  represents the change in potential energy wrt temperature at constant pressure of two atoms coupled together.

Using 5.3,  $(\frac{dPE}{dT})_p = 3(\frac{d\Phi_p}{dT})_p = 3[a_1 + 2a_2R + 3a_3R^2 + \dots](\frac{dR}{dT})_p$ . From 4.5;

$$(\frac{dR}{dT})_p = 2r_0 \left( \frac{d}{dT} \frac{\Delta L(T)}{L_0} \right)_p \equiv 2r_0 \alpha(T) \text{ and}$$

$$5.5 \quad \left( \frac{dPE}{dT} \right)_p = 6r_0 \alpha(T) \cdot [a_1 + 2a_2R + 3a_3R^2 + \dots]$$

$$\left( \frac{dPE}{dT} \right)_p \Bigg|_{\substack{T=293^{\circ}K \\ R=R_0(293)}} \doteq 6r_0 \alpha(293) \cdot [a_1 + 2a_2R_0(293)]$$

$\alpha(T)$  has been determined from experimental data and is listed in reference 1, chapter 4.

$\alpha(293)$  evaluated for Ag is,  $\alpha(293) = 1.9 \cdot 10^{-5} (\frac{1}{\theta_K})$  and from table 4.1,  $R_0(293)_{Ag} = 1.1 \cdot 10^{-11} \text{cm}$

$$\left( \frac{dPE}{dT} \right)_p \Bigg|_{\substack{T=293^{\circ}K \\ R=R_0(293)}} \text{ becomes: } \left( \frac{dPE}{dT} \right)_p \Bigg|_{\substack{T=293^{\circ}K \\ R=R_0(293)}} \doteq 1.5 \cdot 10^{-12} \cdot [a_1 + 2.2 \cdot 10^{-11} a_2],$$

$a_1 + 2.2 \cdot 10^{-11} a_2$  to be evaluated below.

From 3.28, the total internal energy  $mC_1$  of 1 atom is  $mC_1 = -\frac{m^2H}{r_0}$  and  $m \frac{dC_1}{dT} = \frac{m^2H}{r_0^2} \frac{dr_0}{dT}$ .

See Appendix 5A. Evaluating  $\frac{m^2H}{r_0^2}$  for Ag yields  $m \frac{dC_1}{dT} = 1.9 \cdot 10^2 \frac{dr_0}{dT}$

Note that using 4.6, the pressure  $P_{at}$  that two atoms in a transition metal exert on one

another is  $P_{at} = \frac{KT}{(2r_0)^2 R}$ . The average volume occupied by one atom in a transition metal is

$$V = (2r_0 + R)^3 \text{ and } \frac{dV}{dT} = 3(2r_0 + R)^2 \left( \frac{dR}{dT} \right) = 3(2r_0 + R)^2 (2r_0 \alpha) \doteq 3(2r_0)^2 (2r_0 \alpha). \quad P_{at} \frac{dV}{dT} \text{ becomes, } P_{at} \frac{dV}{dT} =$$

$$\frac{KT}{(2r_0)^2 R} \{ 3(2r_0)^2 (2r_0 \alpha) \} \text{ and treating } \alpha(293) \text{ as a constant (See reference 1, chapter 4) then}$$

$$R \doteq 2r_0 \alpha(293)T \text{ and } P_{at} \frac{dV}{dT} = 3K(2r_0 \alpha T) R^{-1} \doteq 3K. \text{ By direct contact, } P_{at} \frac{dV}{dT} \doteq \left( \frac{dKE}{dT} \right)_p + \left( \frac{dPE}{dT} \right)_p + m \left( \frac{dC_1}{dT} \right)_p \doteq 3K.$$

If  $\frac{dV}{dT} = 0$ , then  $(\frac{dKE}{dT})_p = 0$ ,  $(\frac{dPE}{dT})_p = 0$ , and  $m(\frac{dC_1}{dT})_p = 0$ . We however want a more accurate expression

$$\text{for } P_{at} \frac{dV}{dT} \text{ and will retain } \left( \frac{dKE}{dT} \right)_p + \left( \frac{dPE}{dT} \right)_p + m \left( \frac{dC_1}{dT} \right)_p = \frac{3}{2}K + 6r_0 \alpha(293) \cdot [a_1 + 2a_2R_0(293)] + \frac{m^2H}{r_0^2} \frac{dr_0}{dT}$$

The classical theory of specific heats for solids mistakenly calls  $C_p$ ,  $C_v$ . In the experimental setup under which specific heat is measured, the solid is unconstrained and for  $\Delta T \neq 0$ , the change in volume is  $\Delta V \neq 0$ . To measure  $C_v$ , the solid

must be constrained so as not to expand for  $\Delta T > 0$  and this takes  $P_{at} = \frac{KT}{(2r_0)^2 R} \sim 10^{12} \frac{dy}{cm^2}$  applied external pressure, which is order of magnitude, the pressure due to gravity at the center of the earth. Experimentally, pressures greater than  $\sim 10^{10} \frac{dy}{cm^2}$  for times  $> 1$ sec, have not been obtained.

Consideration of the  $P_e \left( \frac{dV}{dT} \right)_P$  term follows.

With  $P_e = 10^6 \frac{dy}{cm^2}$ ,  $P_e \left( \frac{dV}{dT} \right)_P = 3 \cdot 10^6 (2r_0)^3 \alpha(T) \approx 10^7 (r_0)^3 \alpha(T) \approx 10^{-17} \alpha(T) \approx 10^{-22} \approx 10^{-6} K \ll K$

The  $P_e \left( \frac{dV}{dT} \right)_P$  term is therefore dropped from 5.4. 5.4 becomes:

$$5.6 \quad C_p = \frac{3}{2}K + \left( \frac{dPE}{dT} \right)_P + \frac{m^2 H}{r_0^2} \frac{dr_0}{dT} + \frac{N}{N_T} S_u \left\{ \Omega_{Cr} \left( \frac{dN_{ph,out}}{dT} \right)_P + \frac{3}{2} K \Delta T'_{ph} \left( \frac{dN'_{ph,in}}{dT} \right)_P - \frac{3}{2} K T'_{ph} \left( \frac{dN''_{ph,in}}{dT} \right)_P \right\}$$

Consideration of the  $\frac{N}{N_T} S_u$  term follows.

$\left( \frac{dN_{ph,out}}{dT} \right)_P$  is  $\left( \frac{dN_{ph,out}}{dT} \right)_P = \lim_{\Delta T \rightarrow 0} \left( \frac{\Delta N_{ph,out}}{\Delta T} \right)_P$ , and  $\frac{\Delta N_{ph,out}}{\Delta T}$  is the number of photons CREATED and emitted by a surface atom during the time interval at which the temperature of the transition metal changes from  $T$  to  $T + \Delta T$ . Similarly,  $\left( \frac{dN'_{ph,in}}{dT} \right)_P$  is the number of photons reflected by a surface atom during the time interval at which the temperature of the transition metal changes from  $T$  to  $T + \Delta T$ .  $\Delta T'_{ph} = T'_{ph,out} - T'_{ph,in}$  is the equivalent temperature of the photon out, minus the equivalent temperature of the photon in.  $\left( \frac{dN''_{ph,in}}{dT} \right)_P$  is the number of incoming photons that are adsorbed by a surface atom during the time interval at which the temperature of the transition metal changes from  $T$  to  $T + \Delta T$ . Note that we are assuming that  $\Delta T > 0$  and therefore  $\Delta T'_{ph} < 0$ . As hypothesized in chapter six, a photon is a solid mass particle created by collision of two solid mass atoms. Let  $\Omega_{ph} = \Omega(T)_{ph}$  represent the average energy it takes to create a photon with 0 photon kinetic energy from a given atom, as measured from an inertial frame at rest w.r.t. the center of mass of the photon. As shown in chapter 6, section 5:  $\Omega(T)_{ph} = -BE(T)_{ph}$  where  $BE(T)_{ph} < 0$  is the binding energy of the photon. The total average energy it takes to create one photon at temperature  $T$  is:

$$5.7 \quad \Omega_{Cr} \doteq -BE_{ph} + \frac{3}{2}KT$$

The photons under consideration are in the infrared and with  $BE_{ph} \approx 0.1 \text{ eV}$  and  $\frac{3}{2}k(293) = 6.1 \cdot 10^{-14} \text{ erg} = 0.038 \text{ eV}$ ,  $\Omega_{Cr}$  becomes  $\Omega_{Cr} = 0.14 \text{ eV} = 2.2 \cdot 10^{-13} \text{ erg}$ . In order to experimentally determine 5.6, consider a calorimeter filled with water at  $373^\circ \text{K}$  into which is placed a cube of a transition metal  $L \text{ cm}$  on a side. Initially the temperature difference  $\Delta T$  between the cube and the water is  $80 \text{ K}^0$ . Given  $N_{Su}$  is the number of atoms on the surface of the cube and  $N_T$  is the total number of atoms in the

$$\text{cube: } \frac{N_{Su}}{N_T} = \frac{12r_0}{L} \approx \frac{10^{-7}}{L}.$$

The power density,  $PD_{tm}$ , emitted by the surface atoms of a transition metal due to the KE of emitted photons is 1.0 to 0.01 that of a black body. At  $293^\circ \text{K}$  a black body emits  $4.2 \cdot 10^5 \frac{\text{erg}}{\text{sec cm}^2}$  and using Ag with  $r_0 = 1.3 \cdot 10^{-8}$  and emissivity  $\epsilon = 0.03$  as an example:  $4.2 \cdot 10^5 (1.3)^2 \cdot 10^{-16} (0.03) = 2.1 \cdot 10^{-12} \frac{\text{erg}}{\text{sec atom}}$ .

Let  $T$  represent the temperature of the transition metal cube and let the water reservoir be large enough so that the water temperature remains constant.

With  $\frac{3}{2}k(293) = 6.1 \cdot 10^{-14} \text{ erg}$ , solve for  $\frac{dN_{ph,out}}{dT}$  this yields  $\frac{dN_{ph,out}}{dT} = 34 \frac{\text{photons}}{\text{sec atom}}$  and with  $\frac{dN_{ph,out}}{dT} = \frac{dN_{ph,out}}{dt} \cdot \frac{dt}{dT} = 34 \cdot \frac{dt}{dT} \cdot \frac{N_{Su} \Omega_{Cr} (\frac{dN_{ph,out}}{dT})_P}{N_T}$  becomes:  $\frac{N_{Su} \Omega_{Cr} (\frac{dN_{ph,out}}{dT})_P}{N_T} = \frac{10^{-7}}{L} (2.2 \cdot 10^{-13}) 34 \cdot \frac{dt}{dT} = 7.5 \cdot 10^{-19} (\frac{1}{L}) \frac{dt}{dT} (\frac{\text{erg}}{\text{K}^0})$ .

For specificity consider a cube,  $1 \text{ cm}$  on a side. The number of atoms on the surface of the cube is  $N_{Su} = \frac{6}{(2r_0)^2} = 9.0 \cdot 10^{15}$  Ag atoms and the cube emits  $N_{Su} (\frac{dN_{ph,out}}{dT})_P = 9.0 \cdot 10^{15} \cdot 34 = 3.1 \cdot 10^{17} \frac{\text{photons}}{\text{cube sec}}$ . The total power given up by the cube in order to emit  $3.1 \cdot 10^{17} \frac{\text{photons}}{\text{cube sec}}$  is  $(\Omega_{Cr}) N_{Su} (\frac{dN_{ph,out}}{dT})_P = (2.2 \cdot 10^{-13}) (3.1 \cdot 10^{17}) = 6.8 \cdot 10^4 \frac{\text{erg}}{\text{cube sec}}$ . The total number of atoms in the cube is  $\frac{1}{(2r_0)^3} = 5.8 \cdot 10^{22}$  Ag atoms and the power given up by the cube per atom in the cube is  $P_{at} = (6.8 \cdot 10^4) (5.8 \cdot 10^{22})^{-1} = 1.2 \cdot 10^{-18} \frac{\text{erg}}{\text{atom sec}}$ .

Given that  $T = 0.485 \cdot 10^{16} \text{ KE(erg)}$  and  $\frac{dT}{dt} = 0.485 \cdot 10^{16} \frac{dKE}{dt} = 0.485 \cdot 10^{16} (\frac{1}{2}) P_{at} = 2.9 \cdot 10^{-3} (\frac{\text{K}^0}{\text{sec}})$ .

Evaluating  $\frac{N_{Su} \Omega_{Cr} (\frac{dN_{ph,out}}{dT})_P}{N_T}$  for  $T = 293^\circ \text{K}$  yields,  $\frac{N_{Su} \Omega_{Cr} (\frac{dN_{ph,out}}{dT})_P}{N_T} = 2.6 \cdot 10^{-16} (\frac{\text{erg}}{\text{K}^0}) = 1.9 \text{ K}$ .

Evaluating  $\frac{N_{Su} \Omega_{Cr} (\frac{dN_{ph,out}}{dT})_P}{N_T}$  for  $T = 373^\circ \text{K}$  yields,  $\frac{N_{Su} \Omega_{Cr} (\frac{dN_{ph,out}}{dT})_P}{N_T} = 2.8 \cdot 10^{-16} (\frac{\text{erg}}{\text{K}^0}) = 2.0 \text{ K}$ .

For thin films, the  $\frac{1}{L}$  term will strongly influence  $C_P$  for calorimeters using water as a heat source. See Appendix 5B.

The emissivity of water is  $\epsilon=.93$  and at  $373^{\circ}\text{K}$  a black body emits  $1.1 \cdot 10^6 \frac{\text{erg}}{\text{sec cm}^2}$  and water with  $r_0=1.25 \cdot 10^{-8}\text{cm}$  emits  $1.1 \cdot 10^6 (1.25)^2 \cdot 10^{-16} (.93) = 1.7 \cdot 10^{-10} \frac{\text{erg}}{\text{sec atom}}$ .

At  $373^{\circ}\text{K}$ , the average kinetic energy of a photon is  $7.7 \cdot 10^{-14}\text{erg}$  and the water

surface emits  $\frac{dN_{\text{ph,out,w}}}{dt} = 2.2 \cdot 10^3 \frac{\text{photons}}{\text{sec atom}}$ . The reflectance of Ag in the thermal infrared is  $R=.97$  and  $\frac{dN_{\text{ph,out,w}}}{dt} \cdot R = \frac{dN'_{\text{ph,in}}}{dt} = 2.1 \cdot 10^3 \frac{\text{photons}}{\text{sec atom}}$  and  $\frac{dN'_{\text{ph,in}}}{dT} = \frac{dN'_{\text{ph,in}}}{dt} \cdot \frac{dt}{dT} = 2.1 \cdot 10^3 \cdot \frac{dt}{dT}$ .

With  $N_{\text{Su}} = 9.0 \cdot 10^{15}$ , the total number of  $\frac{\text{photons}}{\text{sec}}$  reflected from the surface of the cube is  $9.0 \cdot 10^{15} (2.1 \cdot 10^3) = 1.9 \cdot 10^{19} \frac{\text{photons}}{\text{sec}}$ .

The total power in, due to photons that will reflect from the Ag cube is,  $7.7 \cdot 10^{-14} (1.9 \cdot 10^{19}) = 1.5 \cdot 10^6 \left(\frac{\text{erg}}{\text{sec}}\right)$ . The total number of atoms in the cube is  $N_T = \frac{1}{(2r_0)^3} = 5.8 \cdot 10^{22}$  Ag atoms

and the power in per atom is  $(1.5 \cdot 10^6) (5.8 \cdot 10^{22})^{-1} = 2.6 \cdot 10^{-17} \frac{\text{erg}}{\text{sec atom}}$ . The total power in retained by the cube per atom is,  $\frac{dE}{dt} = -2.6 \cdot 10^{-17} \left(\frac{\Delta T'_{\text{ph}}}{80}\right) = -3.3 \cdot 10^{-19} \Delta T'_{\text{ph}} \frac{\text{erg}}{\text{sec atom}}$ .

Given that  $T = 0.485 \cdot 10^{16} \text{KE}(\text{erg})$  and  $\frac{dT}{dt} = 0.485 \cdot 10^{16} \frac{d\text{KE}}{dt} = 0.485 \cdot 10^{16} \left(\frac{1}{2}\right) \frac{dE}{dt} = -8.0 \cdot 10^{-4} \Delta T'_{\text{ph}} \left(\frac{\text{K}^0}{\text{sec}}\right)$ .

$\frac{N_{\text{Su}}}{N_T} \left(\frac{3}{2} K \Delta T'_{\text{ph}}\right) \left(\frac{dN'_{\text{ph,in}}}{dT}\right)_P$  becomes:  $\frac{N_{\text{Su}}}{N_T} \left(\frac{3}{2} K \Delta T'_{\text{ph}}\right) \left(\frac{dN'_{\text{ph,in}}}{dT}\right)_P = -5.5 \cdot 10^{-17} \left(\frac{\text{erg}}{\text{K}^0}\right) = -0.39\text{K}$ .

The absorbance of Ag is  $A = 1 - .97 = .03$  and  $\frac{dN_{\text{ph,out,w}}}{dt} \cdot A = \frac{dN''_{\text{ph,in}}}{dt} = 66 \frac{\text{photons}}{\text{sec atom}}$  and

$\frac{dN''_{\text{ph,in}}}{dT} = \frac{dN''_{\text{ph,in}}}{dt} \cdot \frac{dt}{dT} = 66 \cdot \frac{dt}{dT}$ . With  $N_{\text{Su}} = 9.0 \cdot 10^{15}$ , the total number of  $\frac{\text{photons}}{\text{sec}}$

absorbed by the surface of the cube is  $9.0 \cdot 10^{15} (66) = 5.9 \cdot 10^{17} \frac{\text{photons}}{\text{sec}}$ . The

total power in, due to photons that will be adsorbed by the Ag cube is,  $7.7 \cdot 10^{-14} (5.9 \cdot 10^{17}) = 4.5 \cdot 10^4 \left(\frac{\text{erg}}{\text{sec}}\right)$ . The total power in per atom retained by the cube is  $\frac{dE}{dt} = 4.5 \cdot 10^4 (N_T)^{-1} =$

$4.5 \cdot 10^4 (5.8 \cdot 10^{22})^{-1} = 7.8 \cdot 10^{-19} \left(\frac{\text{erg}}{\text{sec atom}}\right)$ .

Given that  $T = 0.485 \cdot 10^{16} \text{KE}(\text{erg})$  and  $\frac{dT}{dt} = 0.485 \cdot 10^{16} \frac{d\text{KE}}{dt} = 0.485 \cdot 10^{16} \left(\frac{1}{2}\right) \frac{dE}{dt} = 1.9 \cdot 10^{-3} \left(\frac{\text{K}^0}{\text{sec}}\right)$

$-\frac{N_{\text{Su}}}{N_T} \frac{3}{2} K T'_{\text{ph}} \left(\frac{dN''_{\text{ph,in}}}{dT}\right)_P$  becomes:  $-\frac{N_{\text{Su}}}{N_T} \frac{3}{2} K T'_{\text{ph}} \left(\frac{dN''_{\text{ph,in}}}{dT}\right)_P = -2.7 \cdot 10^{-16} \left(\frac{\text{erg}}{\text{K}^0}\right) = -1.9\text{K}$

Summing up results:

5.8  $\frac{dN_{\text{ph,out}}}{dT} = 34 \frac{\text{photons}}{\text{sec atom}}$  emitted by each atom on the surface of the cube at  $293^{\circ}\text{K}$

$\frac{dN_{\text{ph,out}}}{dT} = 93 \frac{\text{photons}}{\text{sec atom}}$  emitted by each atom on the surface of the cube at  $373^{\circ}\text{K}$

$\frac{dN_{\text{ph,out,w}}}{dt} = 2.2 \cdot 10^3 \frac{\text{photons}}{\text{sec atom}}$  emitted by each atom on a water surface at  $373^{\circ}\text{K}$

And

$$5.9 \quad \frac{N_s}{N_T} \Omega_{Cr} \left( \frac{dN_{ph,out}}{dT} \right)_P = 1.9K \text{ at } 293^{\circ}K \text{ emitted by the cube}$$

$$\frac{N_s}{N_T} \Omega_{Cr} \left( \frac{dN_{ph,out}}{dT} \right)_P = 2K \text{ at } 373^{\circ}K \text{ emitted by the cube}$$

$$\frac{N_s}{N_T} \Omega_{Cr} \left( \frac{3}{2} K \Delta T'_{ph} \right) \left( \frac{dN'_{ph,in}}{dT} \right)_P = -0.39K \text{ reflected from the cube}$$

$$-\frac{N_s}{N_T} \Omega_{Cr} \left( \frac{3}{2} K T'_{ph} \right) \left( \frac{dN''_{ph,in}}{dT} \right)_P = -1.9K \text{ adsorbed by the cube, } T'_{ph} = 373^{\circ}K$$

With average value  $\text{Avg} \frac{N_s}{N_T} \Omega_{Cr} \left( \frac{dN_{ph,out}}{dT} \right)_P = 2K$  as  $T$  of the cube goes from  $T=293^{\circ}K$  to  $T=373^{\circ}K$ , 5.6 evaluated for Ag becomes:

$$5.10 \quad C_p = \frac{3}{2}K + 1.1 \cdot 10^4 [a_1 + 2.2 \cdot 10^{-11} a_2] K + 1.9 \cdot 10^2 \frac{dr_0}{dT} - 0.29K = 3.1K$$

If  $\frac{dr_0}{dT}$  is small enough so that  $1.9 \cdot 10^2 \frac{dr_0}{dT}$  may be dropped from 5.10, then  $[a_1 + 2.2 \cdot 10^{-11} a_2] = 1.7 \cdot 10^{-4}$  and  $C_p = \frac{3}{2}K + 1.9K - 0.29K = 3.1K$ . If  $1.9 \cdot 10^2 \frac{dr_0}{dT}$  must be retained in 5.10, then  $1.1 \cdot 10^4 [a_1 + 2.2 \cdot 10^{-11} a_2] K + 1.9 \cdot 10^2 \frac{dr_0}{dT} = (1.9) \cdot K$  and 5.10 holds as written. Further, if it should turn out that  $1.1 \cdot 10^4 [a_1 + 2.2 \cdot 10^{-11} a_2] K = 1.5K$ , then  $\frac{dr_0}{dT} = 2.9 \cdot 10^{-19} \left( \frac{cm}{K^0} \right)$ .

At  $T > 0^{\circ}K$  infra red photons are constantly being produced and lost at the surface of the mass sample even in vacuum with no photon input. There is an energy loss from the sample due to the energy,  $(-BE_{ph})$ , it takes to compress a CREATED photon from its parent atom plus the kinetic energy of the photon; for a total energy loss of  $-Be_{ph} + \frac{3}{2}KT$  per photon.

For macroscopic transition metal mass samples, experimentally, the photon energy lost per second per  $cm^2$  is independent of the volume of the material and therefore as used above, only atoms on the surface of the metal produce photons. Unless the energy lost by photon creation and emission is provided by an external source, the temperature  $T$  of the sample will go to  $0^{\circ}K$  as  $t \rightarrow \infty$ :  $\lim_{t \rightarrow \infty} T = 0^{\circ}K$ . THERE IS NO EQUILIBRIUM GROUND STATE FOR THE SOLID MASS ATOM FOR  $T > 0^{\circ}K$ .

In the above computations leading to 5.10, it was assumed that the emissivity  $\epsilon$  is measured in an environment with negligible  $\Delta Q$  and negligible incident photon energy (Photons in).

With  $r_{ph} \ll r_{atom}$ , (Chapter 6. sec. 3), and using 5.1,  $|\Psi_p(r_0^+)| \ll |\Psi_p(r_0^-)| \doteq \frac{mH}{r_0}$ ,

$\Phi(r_0^+)_{\text{ph,atom}}$  becomes:  $|\Phi(r_0^+)_{\text{ph,atom}}| \ll \frac{m_{\text{ph}} m_{\text{atom}} H}{r_0} \approx 10^{-34} \cdot 10^{-22} \cdot 10^{30} \cdot 10^8 = 10^{-18} \text{erg} \approx 10^{-6} \text{ev}$  with temperature equivalence  $\approx 10^{-2} (^{\circ}\text{K})$ . A photon with  $\text{KE}_{\text{ph}} \ll 10^{-6} \text{ev}$ . and concomitant temperature equivalence  $T \ll 10^{-2} (^{\circ}\text{K})$  will escape from the atom.

### 3. Specific Heat at Constant Pressure $C_p$ as $T \rightarrow 0^+ \text{ } ^{\circ}\text{K}$

From 5.6,

$$C_p = \frac{3}{2}K + \left(\frac{dPE}{dT}\right)_P + \frac{m^2 H}{r_0^2} \frac{dr_0}{dT} + \frac{N}{N_T} \text{Su} \left\{ \Omega_{Cr} \left(\frac{dN_{\text{ph,out}}}{dT}\right)_P + \frac{3}{2}K \Delta T_{\text{ph}}' \left(\frac{dN_{\text{ph,in}}'}{dT}\right)_P - \frac{3}{2}K T_{\text{ph}}'' \left(\frac{dN_{\text{ph,in}}''}{dT}\right)_P \right\}.$$

The first 3 terms are positive and the sum of the last 3 terms is negative. Taking the limit as  $T$  approaches 0:

$$\lim_{T \rightarrow 0^+} \left\{ \frac{3}{2}K + \left(\frac{dPE}{dT}\right)_P + \frac{m^2 H}{r_0^2} \frac{dr_0}{dT} \right\} \doteq 3K \text{ and setting}$$

$$\lim_{T \rightarrow 0^+} \frac{N}{N_T} \text{Su} \left\{ \Omega_{Cr} \left(\frac{dN_{\text{ph,out}}}{dT}\right)_P + \frac{3}{2}K \Delta T_{\text{ph}}' \left(\frac{dN_{\text{ph,in}}'}{dT}\right)_P - \frac{3}{2}K T_{\text{ph}}'' \left(\frac{dN_{\text{ph,in}}''}{dT}\right)_P \right\} = 0 \text{ with result}$$

$$5.11a \quad \lim_{T \rightarrow 0^+} C_p \doteq 3K$$

In 1906 Einstein derived the expression  $C_p = 3K \left(\frac{T}{T_0}\right)^3$  for  $T < 300^{\circ}\text{K}$  and  $T_0 \geq T \geq 0^{\circ}\text{K}$ .

Einstein's theory however is based on the assumption that the force between two atoms is a Hook's Law force  $f_H(R) = -k_1 R$  and  $\overline{f_H(R(T))} = -k_1 \overline{R(T)}$  with  $\lim_{T \rightarrow 0^+} \overline{R(T)} = 0^+$  and

if no external forces are applied,  $\lim_{T \rightarrow 0^+} R = 0^+$ .  $2r_0 + R$  is the center-to-center distance

between two like atoms. Evaluate  $k_1$  where  $f_H = -k_1 10^{-10} \doteq -10^{-4} \text{dy}$  and therefore

$$k_1 \doteq 10^6 \frac{\text{dy}}{\text{cm}}.$$

Consider a transition metal bar of length  $L$  and uniform cross section  $A_0$  at  $0 < T_1 < 1^{\circ}\text{K}$ . With no external force acting on the ends of the bar, the average atomic force that two atoms exert on one another is  $\overline{f_H(R(T_1))}$ .

At  $t=0$  equal and opposite forces of magnitude  $F = |f_0| \left(\frac{A_0}{2}\right) \doteq 10^6 R_H \left(\frac{A_0}{2}\right)$  are

applied on either end of the bar tending to elongate the bar  $0 < \overline{R(T_1)} < R_H$

Let  $T_1$  be small enough so that the average atomic force  $\overline{f_H(R(T_1))}$  that two atoms exert on one another with out arbitrary applied force  $F > 0$  is  $|\overline{f_H(R(T_1))}| \ll 10^{-4} \text{dy}$  and  $T_1$  small enough so that  $0 < \overline{R(T_1)} \ll R_H$ .



L contains  $\sim 5 \cdot 10^7 L$  atoms and when subjected to force F, the bar elongates by an amount  $\Delta L_H \doteq (R_H - \overline{R(T_1)})(5 \cdot 10^7 L) \doteq \{10^{-6} |f_0| = \overline{R(T_1)}\}(5 \cdot 10^7 L) \doteq \{10^{-6} |f_0|\}(5 \cdot 10^7 L)$ .

With  $|f_0| = 10^{-5} \text{ dy}$ , it follows that  $R \approx 10^{-11} \text{ cm}$ , and with  $L = 10^1 \text{ cm}$ ;  $\lim_{T \rightarrow 0^+} \Delta L_H \doteq 5 \cdot 10^{-3} \text{ cm}$ .

With  $|f_0| = 10^{-5} \text{ dy}$ :  $\frac{F}{A_0} \doteq 10^{10} \frac{\text{dy}}{\text{cm}^2}$  which is close to the upper limit of the value for a laboratory applied expansive force.

Using 4.6, the average force  $f(T)_{sm}$  between two transition metal solid mass atoms with no external force  $|f_0|$  applied to the ends of the metal bar is  $f_{sm} = \frac{KT}{R(T)}$  and using

table 4.1:  $2.0 \cdot 10^{-11} < \overline{R(293)} < 2.2 \cdot 10^{-10} \text{ cm}$ . Consequently  $1.8 \cdot 10^{-4} < f(293)_{sm} < 2.010^{-3} \text{ dy}$ .

Equating  $f(T)_{sm}$  with the field force exerted by two atoms at center to center distance

$2r_0 + \overline{R(T)}$  cm apart, and as  $|\overline{f(R, 0^+)}|_{sm} > |\overline{f(R, 293)}|_{sm}$ , it follows that  $|\overline{f(R, 0^+)}|_{sm} > 1.8 \cdot 10^{-4} \text{ dy}$ .

Consequently with  $|f_0| = 10^{-5} \text{ dy}$ ;  $\lim_{T \rightarrow 0^+} \Delta L_{sm} = 0 \text{ cm}$ .

Summing up results:

$$5.11b \quad |f_0| = 10^{-5} \text{ dy}, L = 10^1 \text{ cm}, \frac{F}{A_0} \approx 10^{10} \frac{\text{dy}}{\text{cm}^2}$$

$$a. \quad \lim_{T \rightarrow 0^+} \Delta L_H \approx 5 \cdot 10^{-3} \text{ cm}$$

$$b. \quad \lim_{T \rightarrow 0^+} \Delta L_{sm} = 0 \text{ cm}$$

Which result is correct, a or b, can be determined by direct measurement.

Einstein's 1906 formulation that  $C_p = 3K \left(\frac{T}{T_0}\right)^3$  for small enough T provided a target formula for experimentalists to aim for. If the author of this text is correct, the experimentalists that found that  $C_p = 3K \left(\frac{T}{T_0}\right)^3$  for small enough T, accomplished the task by placing the temperature measuring thermocouples close to the heating elements used to raise the temperature of the transition metal under experimental scrutiny. Hence 5.11a is considered to be correct.

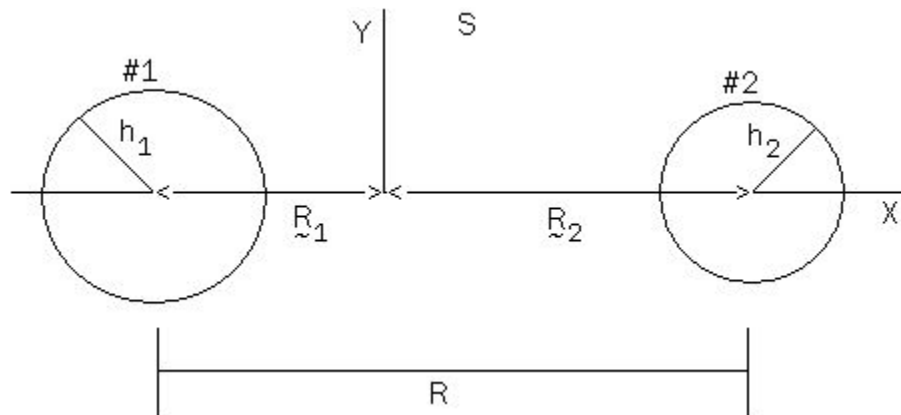
#### 4. Resonant Chemical Bonding

Consider an inertial frame S at rest w.r.t. the center of mass of two isolated atoms bonded together with potential energy  $\Phi(R)$ ; See 5.3. As the two atoms move toward, collide and move away from one another, the center of mass of the two atoms remains at the origin of S. (Center on center collision, fig. 5.2).

Atom #1 has radius  $h(t)_1 = \chi_1(t)$  with  $\chi_1(0) = \bar{r}_1$  where  $\bar{r}_1$  is the average radius of atom #1 and  $A_1 \ll \bar{r}_1$  where  $A_1$  is the oscillation amplitude of atom #1 and  $\tau_1$  is the oscillation period with  $\chi_1(t + \tau_1) = \chi_1(t)$ .  $h(t)_1$  and  $A_1$  are measured from a frame of reference at rest w.r.t. the center of mass of atom #1.

Atom #2 has radius  $h(t)_2 = \chi_2(t)$  with  $\chi_2(0) = \bar{r}_2 + b_0$  where  $\bar{r}_2$  is the average radius of atom #2 and  $A_2 \ll \bar{r}_2$  where  $A_2$  is the oscillation amplitude of atom #2 and  $\tau_2$  is the oscillation period with  $\chi_2(t + \tau_2) = \chi_2(t)$ .  $b_0$  is determined below.  $h(t)_2$  and  $A_2$  are measured from a frame of reference at rest w.r.t. the center of mass of atom #2. In what follows,  $\chi_1(t)$  and  $\chi_2(t)$  will be determined. Atom #1 has mass  $m_1$  and atom #2 has mass  $m_2$ .

FIGURE 5.2



For the present, it is assumed that no photons are produced in the collision process. See chapter 6, section 5.

Let  $\Delta m$  be the mass of a spherical shell at  $h_1$  of atom #1, with  $h_1 = \chi_1(t)$ ,  $\chi_1(0) = \bar{r}_1$ , and  $\Delta m \ll m_1$ . The force acting on  $\Delta m$   $f_1 = \Delta m \ddot{h}(t)_1 = \Delta m \ddot{\chi}_1(t) = -\left(\frac{m_1 \Delta m H}{(\chi_1)^2} - \frac{m_1 \Delta m H}{(\bar{r}_1)^2}\right)$

Write  $(\chi_1(t))^2 = (\bar{r}_1 + \chi_1(t) - \bar{r}_1)^2 \doteq (\bar{r}_1)^2 \left(1 + \frac{2}{\bar{r}_1} [\chi_1(t) - \bar{r}_1]\right)$  and  $-\left(\frac{m_1 \Delta m H}{(\chi_1)^2} - \frac{m_1 \Delta m H}{(\bar{r}_1)^2}\right)$  becomes:

$-\left(\frac{m_1 \Delta m H}{(\chi_1)^2} - \frac{m_1 \Delta m H}{(\bar{r}_1)^2}\right) \doteq -m_1 \Delta m H \left(\frac{2}{\bar{r}_1^3}\right) [\chi_1(t) - \bar{r}_1]$ . Solve the resultant  $\ddot{\chi}_1(t) \doteq -m_1 H \left(\frac{2}{\bar{r}_1^3}\right) [\chi_1(t) - \bar{r}_1]$

to yield:  $\chi_1(t) = A_1 \sin \omega_0 t + \bar{r}_1$  and:

$$5.12a \quad \ddot{h}(t)_1 = -A_1 \omega_1^2 \sin \omega_1 t$$

$$5.12b \quad \dot{h}(t)_1 = A_1 \omega_1 \cos \omega_1 t$$

$$5.12c \quad h(t)_1 = A_1 \sin \omega_1 t + \bar{r}_1$$

$$5.12d \quad \omega_1 = \left( \frac{2m_1 H}{\bar{r}_1^3} \right)^{\frac{1}{2}}$$

With similar results for atom #2.

$$5.13a \quad \ddot{h}(t)_2 = -A_2 \omega_2^2 \sin(\omega_2 t + \varphi_0)$$

$$5.13b \quad \dot{h}(t)_2 = A_2 \omega_2 \cos(\omega_2 t + \varphi_0)$$

$$5.13c \quad h(t)_2 = A_2 \sin(\omega_2 t + \varphi_0) + \bar{r}_2$$

$$5.13d \quad \omega_2 = \left( \frac{2m_2 H}{\bar{r}_2^3} \right)^{\frac{1}{2}}$$

The phase factor  $\varphi_0$  is set at  $\varphi_0 = \frac{3}{2}\pi(1 - \frac{\omega_2}{\omega_1})$  so that at time  $t_0 = \frac{3\pi}{2\omega_1}$ :  $h(t_0)_1 = \bar{r}_1 - A_1$ ,  $h(t_0)_2 = \bar{r}_2 - A_2$ ,  $\dot{h}(t_0)_1 = 0$ ,  $\dot{h}(t_0)_2 = 0$ ,  $\ddot{h}(t_0)_1 = A_1 \omega_1^2$ ,  $\ddot{h}(t_0)_2 = A_2 \omega_2^2$ .

In order to form a chemical bond it is hypothesized that at a given pressure, temperature and incident electromagnetic radiation that at  $t=t_0$ ,  $m_1$  and  $m_2$  are in contact collision. Further, there exists 2 integers  $n_1$  and  $n_2$  such that:

$$5.14a \quad n_1 \tau_1 = n_2 \tau_2 = \Delta t_1$$

Where  $\omega_1 = \frac{2\pi}{\tau_1}$  and  $\omega_2 = \frac{2\pi}{\tau_2}$  and  $\Delta t_1 = (t_1 - t_0)$  where as above  $t_0$  is the instant at which  $m_1$  and  $m_2$  collide and  $t_1$  is the instant at which the center of mass of  $m_1$  and the center of mass of  $m_2$  are at rest with respect to one another in inertial frame S. Using 5.12d, 5.13d and 5.14a yields:

$$5.14b \quad n_1 = \left( \frac{2m_1 H}{\bar{r}_1^3} \right)^{\frac{1}{2}} \left( \frac{\Delta t_1}{2\pi} \right), \quad n_2 = \left( \frac{2m_2 H}{\bar{r}_2^3} \right)^{\frac{1}{2}} \left( \frac{\Delta t_1}{2\pi} \right),$$

Let  $\Delta T_1$  represents the time interval between initial contact time  $t_0$  and the next contact time  $T_1$  where  $\Delta T_1 = T_1 - t_0$ . It is required that for some integer  $p$ ,

$$5.14c: \Delta T_1 = p \Delta t_1$$

As above:

- a. At  $t_0 = \frac{3\pi}{2\omega_1}$ : both atoms are in initial contact.
- b. At  $t_1 = 2\pi\frac{n_1}{\omega_1} + \frac{3\pi}{2\omega_1} = 2\pi\frac{n_2}{\omega_2} + \frac{3\pi}{2\omega_1}$  the center of mass of  $m_1$  and the center of mass of  $m_2$  are at rest with respect to one another.
- c. At  $t_1 + \Delta t_1 = 2t_1 - t_0$ ,  $m_1$  and  $m_2$  separate and:

$$5.14d: \quad R(t_0) = h(t_0)_1 + h(t_0)_2 = \bar{r}_1 - A_1 + \bar{r}_2 - A_2,$$

$$h(t_0)_1 = \bar{r}_1 - A_1, \quad h(t_0)_2 = \bar{r}_2 - A_2, \quad \dot{h}(t_0)_1 = \dot{h}(t_0)_2 = 0, \quad \ddot{h}(t_0)_1 = A_1\omega_1^2, \quad \ddot{h}(t_0)_2 = A_2\omega_2^2$$

$$h(t_1)_1 = \bar{r}_1 - A_1, \quad h(t_1)_2 = \bar{r}_2 - A_2, \quad \dot{h}(t_1)_1 = \dot{h}(t_1)_2 = 0, \quad \ddot{h}(t_1)_1 = A_1\omega_1^2, \quad \ddot{h}(t_1)_2 = A_2\omega_2^2$$

$$h(t_1 + \Delta t_1)_1 = \bar{r}_1 - A_1, \quad h(t_1 + \Delta t_1)_2 = \bar{r}_2 - A_2, \quad \dot{h}(t_1 + \Delta t_1)_1 = \dot{h}(t_1 + \Delta t_1)_2 = 0,$$

$$\ddot{h}(t_1 + \Delta t_1)_1 = A_1\omega_1^2, \quad \ddot{h}(t_1 + \Delta t_1)_2 = A_2\omega_2^2$$

Using figure 5.2; for any two atoms chemically bonded together, the initial conditions, total energy  $E_T$  and momentum are given by:

$$5.15a \quad E_T = \frac{1}{2}m_1 V_1^2(t) + \frac{1}{2}m_2 V_2^2(t) + \Phi(R(t)) + m_1 C(t)_1 + m_2 C(t)_2 = \text{const.} < 0$$

$$m_1 V_1(t) + m_2 V_2(t) = m_1 V_1(0) + m_2 V_2(0)$$

$$V_1(t) = \dot{R}_1(t) \hat{x}, \quad V_2(t) = \dot{R}_2(t) \hat{x}, \quad V_1(0^+) = \dot{R}_1(0^+) > 0, \quad V_2(0^+) = \dot{R}_2(0^+) < 0$$

$$R(t) = R_1(t) + R_2(t), \quad R(0) = h_1(0) + h_2(0) = \bar{r}_1 - A_1 + \bar{r}_2 - A_2,$$

$V_1(t_0)$ ,  $V_1(t_1 + \Delta t_1)$  represent the initial and final speed of the center of mass of atom #1 at collision and at separation and  $V_2(t_0)$ ,  $V_2(t_1 + \Delta t_1)$  represent the initial and final speed of the center of mass of atom #2 at collision and at separation as measured from inertial frame S, where  $V_1(t_0) > 0$  and  $V_2(t_0) < 0$ . Using the conservation of translational kinetic energy and momentum equations yields:

$$5.15b \quad V_1(t_1 + \Delta t_1) = \frac{(m_1 - m_2)V_1(t_0) + 2m_2 V_2(t_0)}{(m_1 + m_2)}$$

$$V_2(t_1 + \Delta t_1) = \frac{2m_1 V_1(t_0) - (m_1 - m_2)V_2(t_0)}{(m_1 + m_2)}$$

The computed linear speeds will be modified however by the creation of solid mass photons. The physical process whereby photons with total energy  $\frac{3}{2}KT + m_{ph}C_1$  (3.29), are created, is described in chapter 6.

## 5. Exothermic and Endothermic Chemical Reactions

Consider the exothermic reaction  $2\text{H}_2 + \text{O}_2 \rightarrow 2\text{H}_2\text{O} + 5.7\text{eV}$  where the binding energy of  $2\text{H}_2$  is  $-9.0\text{eV}$ , that of  $\text{O}_2$  is  $-5.2\text{eV}$  and that of  $2\text{H}_2\text{O}$  is  $-19.9\text{eV}$  as determined from spectroscopic data.

On the other hand the disassociation of water occurs at  $\sim 2.5 \cdot 10^3 \text{ }^\circ\text{K}$  with energy equivalent  $0.32\text{eV}$ . The binding energy of  $2\text{H}_2\text{O}$  is therefore  $-0.64\text{eV}$ . The spectroscopic based disassociation of water binding energy is  $-19.9\text{eV}$ . This value is based on Bragg's Law, the wave nature of light and  $E=h\nu$ , all of which are false as discussed in chapter 6. Consequently the disassociation of water binding energy is NOT  $-19.9\text{eV}$ .

As regards exothermic reactions, the energy for the observed increase in temperature of the reactants comes from a decrease in the internal energy  $\Delta mC_1$  of the involved atoms with resultant decrease in radius of the involved atoms.

In endothermic reactions the energy for the observed decrease in temperature of the reactants goes into increasing the internal energy  $\Delta mC_1$  of the involved atoms with resultant increase in radius of the involved atoms.

## 6. Appendix 5A

It is possible that instead of  $r_0=r_0(T)$ ,  $r_0=r_0(T,t)=r_0(T)+a_0(T)\sin[\omega(T)t]$  with  $a_0(T) \ll r_0(T)$ . In this case, the  $a_0(T)\sin[\omega(T)t]$  is passed on by direct contact to neighbor atoms where the neighbor atoms initially have  $r_0=r_0(T)$ . In this way the oscillation energy is passed from atoms of the transition element to the atoms surrounding the transition element. This represents a further way in which energy will be lost by the transition element.

## 7. Appendix 5B

The following applies for calorimeters using water as a constant heat source.

Consider a rectangular solid of constant cross section  $x^2$  and volume  $x^2L$  with surface area  $2x^2+4xL$ .  $\frac{N_{Su}}{N_T}$  becomes,  $\frac{N_{Su}}{N_T} = (2x^2+4xL)(2r_0)^{-2}(x^2L)^{-1}(2r_0)^3 = 2r_0(2x^2+4xL)(x^2L)^{-1}$

and with  $L \ll x$  (Thin film limit)  $\frac{N_{Su}}{N_T} \approx 4r_0(L)^{-1}$  and with  $L=2nr_0$ ,  $\frac{N_{Su}}{N_T}$  becomes:

$$\frac{N_{Su}}{N_T} = 2(n)^{-1}, n=1,2,3,..N$$

For small enough  $n$ , the photons are not adsorbed by the thin film but punch their way through the atoms of the thin film. See chapter 6 section 7. For such films, the absorbance term  $-\frac{N_{Su}}{N_T} \frac{3}{2} kT'_{ph} \left( \frac{dN''}{dT} \right)_{ph,in} P$  goes to 0. See 5.9.

Let  $M(n)$  be the transmittance of the foil for infrared photons produced by water at  $373^{\circ}\text{K}$  where  $0 \leq M(n) \leq 1$ . For  $M=1$ , all of the infrared photons incident to the foil go through the foil with no loss of energy and for  $M=0$  all of the photons incident to the foil are stopped by the foil.

Using 5.6, evaluated for Ag,  $C_p$  becomes:

$$5.15 \quad C_p = \frac{3}{2}K + 1.1 \cdot 10^4 [a_1 + 2.2 \cdot 10^{-11} a_2] K + 1.4 \cdot 10^{18} \frac{dr_0}{dT} \cdot K + 2 \cdot 10^7 (n)^{-1} \left\{ \Omega_{Cr} \left( \frac{dN_{ph,out}}{dT} \right)_P + \frac{3}{2} K \Delta T'_{ph} \left( \frac{dN'_{ph,in}}{dT} \right)_P - \frac{3}{2} K T'_{ph} \left( \frac{dN''_{ph,in}}{dT} \right)_P [1 - M(n)] \right\}$$

And using 5.15, 5.9, and  $1.1 \cdot 10^4 [a_1 + 2.2 \cdot 10^{-11} a_2] K = 1.5K$

$$5.16 \quad C_p = \left\{ \frac{3}{2} + \frac{3}{2} + 1.4 \cdot 10^{18} \frac{dr_0}{dT} + 2 \cdot 10^7 (n)^{-1} (1.6 - 1.9[1 - M(n)]) \right\} K$$

For thin films, i.e.  $n=1,2,3,\dots \approx 10^4$ ;  $1.4 \cdot 10^{18} \frac{dr_0}{dT} + 2 \cdot 10^7 (n)^{-1} (1.6 - 1.9[1 - M(n)])$  are predicted to satisfy:  $1.4 \cdot 10^{18} \frac{dr_0}{dT} + 2 \cdot 10^7 (n)^{-1} (1.6 - 1.9[1 - M(n)]) = K^{-1.5} C_{p,ex}$  where  $C_{p,ex}$  is the experimentally determined specific heat of Ag.

For  $n = n_0, n_0 + 1, n_0 + 2, \dots$

where  $n_0 \approx 10^4$ , and for the special case  $1.1 \cdot 10^4 [a_1 + 2.2 \cdot 10^{-11} a_2] K = 1.5K$  and using 5.10: 5.16 reverts to:

$$5.17 \quad C_p = 3K + 1.9 \cdot 10^2 \frac{dr_0}{dT} - 0.29K = 3.1K$$