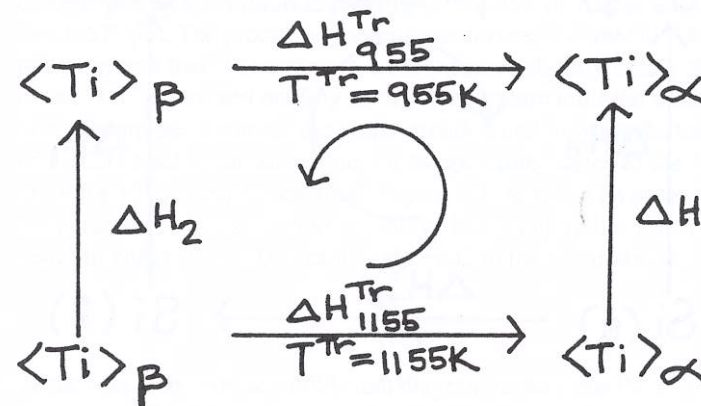## Chapter 2

[2.1] Calculate the transformation enthalpy for the isothermal transformation of Ti(β) to Ti(α) if the transformation occurs 200°C below the equilibrium transformation temperature during cooling.

Solution

(1) Set Up

$$\langle Ti \rangle_\beta \xrightarrow[T^{Tr}=955K]{\Delta H^{Tr}_{955}} \langle Ti \rangle_\alpha$$

$$\Delta H_2 \qquad \Delta H_1$$

$$\langle Ti \rangle_\beta \xrightarrow[T^{Tr}=1155K]{\Delta H^{Tr}_{1155}} \langle Ti \rangle_\alpha$$

(2) Sum

$$\sum \Delta H_{TL} = 0 = \Delta H^{Tr}_{1155} + \Delta H_1 - \Delta H^{Tr}_{955} - \Delta H_2$$

$$\Delta H^{Tr}_{955} = \Delta H^{Tr}_{1155} + \Delta H_1 - \Delta H_2$$

(3) Substitute

$$\Delta H^{Tr}_{1155} = -3473 \text{ J/mol}$$

$$\Delta H_1 = \int_{1155}^{955} (22.09 + 10.04 \times 10^{-3} T) dT = -6536 \text{ J/mol}$$

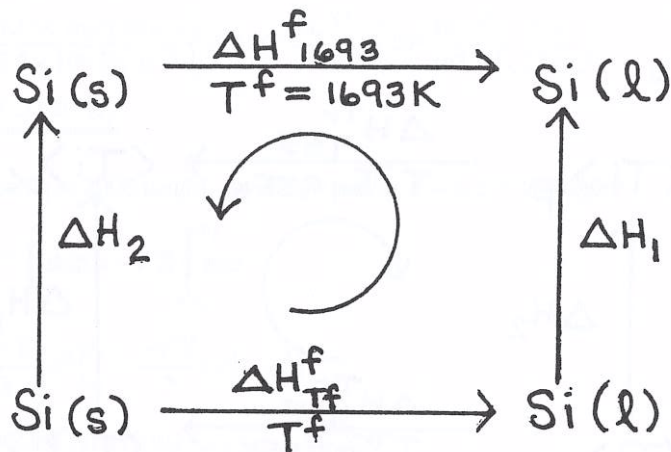$$\Delta H_2 = \int_{1155}^{955} 28.91 dT = -5782 \text{ J/mol}$$

(4) Solve

$$\Delta H^{Tr}_{955} = \underline{-4227 \text{ J/mol}} .$$

[2.2] Derive an expression for the heat of fusion of Si as a function of temperature at 1 atm pressure.

Solution

(1) Set Up

$$Si\,(s) \xrightarrow[\quad T^f = 1693K \quad]{\Delta H^f_{1693}} Si\,(\ell)$$

$$Si\,(s) \xrightarrow[\quad T^f \quad]{\Delta H^f_{Tf}} Si\,(\ell)$$

with vertical arrows ΔH_2 (left) and ΔH_1 (right).

(2) Sum

$$\sum \Delta H_{TL} = 0 = \Delta H^f_{Tf} + \Delta H_1 - \Delta H^f_{1693} - \Delta H_2$$

$$\Delta H^f_{Tf} = \Delta H^f_{1693} + \Delta H_2 - \Delta H_1$$

(3) Substitute

$$\Delta H_1 = \int_{T^f}^{1693} 25.61\,dT = 43{,}358 - 25.61T^f$$

$$\Delta H^f_{1693} = 50{,}630 \text{ J/mol}$$

$$\Delta H_2 = \int_{T^f}^{1693} (24.10 + 2.43\times10^{-3}T + 4.56\times10^5 T^{-2})\,dT$$

$$\Delta H_2 = 43{,}885 - 24.1T^f - 0.00117T^{f\,2} + \frac{4.56\times10^5}{T^f}$$

(4) Solve

$$\Delta H^f_{Tf} = 50{,}630 + 43{,}885 - 24.1T^f - 0.00117T^{f\,2} + \frac{4.56\times10^5}{T^f}$$

$$- 43{,}385 + 25.61T^f$$

$$\underline{DH^f_{Tf}\ (J/mol) = 51{,}157 + 1.51T^f - 0.00117T^{f\,2} + \frac{4.56\times10^5}{T^f}}.$$
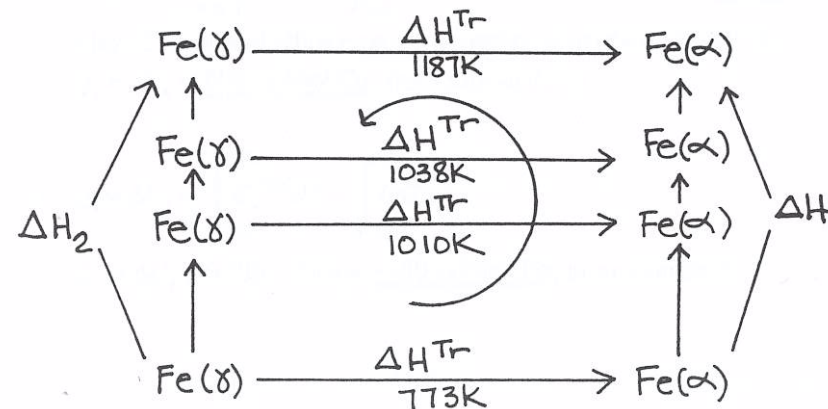
[2.3] Modified austempering is an isothermal transformation heat treatment used to produce bainite and pearlite (a mixture of ferrite (α) and cementite Fe_3C). The process involves austenitizing the steel to 100% austenite (γ) and then quenching to a temperature slightly below the nose of the "I-T" curve and holding at that temperature until the transformation is complete. Estimate the transformation enthalpy for the transition of a 1050 steel at the austempering temperature. Refer to the I-T diagram for 1050 steel, Appendix E, Figure E.1, to select an austempering temperature. Assume carbon solubility has a negligible effect on the result in either phase. Do not include Fe_3C in the calculations.

Solution

Review of the iron-iron carbide equilibrium diagram reveals that the $\delta \to \alpha$ transformation starts at ≈ 1038 K and ends at ≈ 1010 K, the eutectoid temperature. As a result of quenching, transformation is delayed and occurs isothermally at the quenching temperature. Based on the I-T diagram, a quenching temperature of 500°C is consistent with austempering.

(1) Set Up
Since the computation of $\Delta H^{Tr}_{773\,K}$ is path independent, any one of 3 loops might be selected. The outermost loop is selected because $\Delta H^{Tr}_{1187\,K}$ is known from Table A.2.

$$Fe(\gamma) \xrightarrow[\ 1187K\ ]{\Delta H^{Tr}} Fe(\alpha)$$

$$Fe(\gamma) \xrightarrow[\ 1038K\ ]{\Delta H^{Tr}} Fe(\alpha)$$

$$Fe(\gamma) \xrightarrow[\ 1010K\ ]{\Delta H^{Tr}} Fe(\alpha)$$

$$Fe(\gamma) \xrightarrow[\ 773K\ ]{\Delta H^{Tr}} Fe(\alpha)$$

with outer vertical arrows ΔH_2 (left) and ΔH_1 (right).

(2) Sum

$$\sum \Delta H_{TL} = 0 = \Delta H_{773}^{Tr} + \Delta H_1 - \Delta H_{1187}^{Tr} - \Delta H_2$$

$$\Delta H_{773}^{Tr} = \Delta H_{1187}^{Tr} + \Delta H_2 - \Delta H_1$$

(3) Substitute

$$\Delta H_{1187}^{Tr} = -669 \text{ J/mol}$$

$$\Delta H_2 = \int_{773}^{1187} (7.7 + 19.5 \times 10^{-3} T)\, dT$$

$$= 3188 + 7907 = 11{,}095 \text{ J/mol}$$

$$\Delta H_1 = \int_{773}^{1187} (17.49 + 24.77 \times 10^{-3} T)\, dT$$

$$= 7241 + 10{,}040 = 17{,}281 \text{ J/mol}$$

(4) Solve

$$\Delta H_{773}^{Tr} = -669 + 11{,}095 - 17{,}281$$

$$= \underline{6855 \text{ J/mol}}.$$

[2.4] The results of constant volume molar heat capacity calculations for several solids are illustrated in Figure 2.6. For each substance, C_v approaches zero as the absolute temperature approaches zero. In addition, C_v asymptotically approaches a constant value of 6 cal/(mol·°C) as temperature increases. This constant, known as the *Dulong and Petit value*, is best approximated for each solid in a different temperature range. For lead, this temperature range begins at about 180 K and for Cu, at about 500 K.
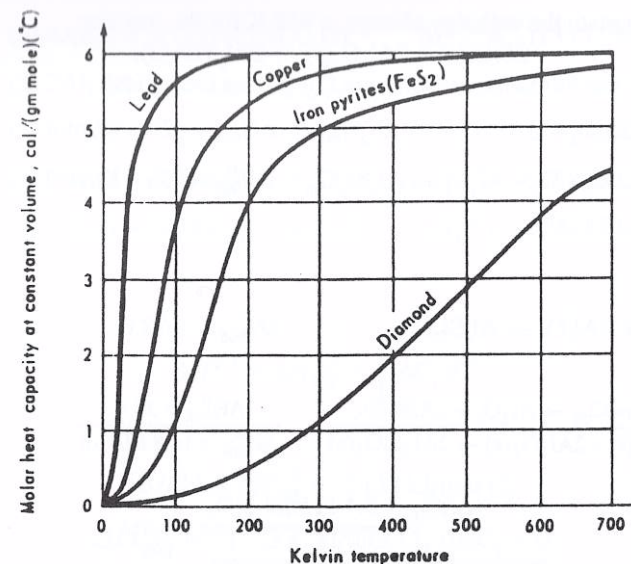

Figure 2.6 Variation of C_v of solids with Kelvin temperature. (From M.W. Zemansky and H.C. Van Ness, 1966, Basic Engineering Thermodynamics, Fig. 11.16. Reprinted by permission of McGraw Hill, Inc., New York.)

Calculate the molar heat transferred to or from the surroundings and the molar internal energy change occurring at constant volume when:
(a) Cu undergoes a temperature increase from 600 to 700 K.
(b) Pb undergoes a temperature decrease from 210 to 180 K.

Solution

(a) $\quad Q_v = \Delta U_v = \int_{600}^{700} C_v^{Cu(s)}\, dT = \int_{600}^{700} 6\, dT$

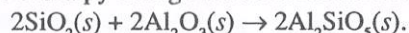where C_v asymptotically approaches a constant value of ≈ 6 cal/(mol · K).
$Q_v = \Delta U_v = \underline{600 \text{ cal/mol Cu}}$, from surroundings.

(b) $\quad Q_v = \Delta U_v = \int_{210}^{180} C_v^{Pb(s)}\, dT = \int_{210}^{180} 6\, dT$
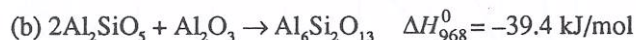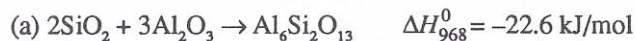
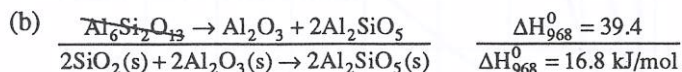$Q_v = \Delta U_v = 6(180 - 210) = \underline{-180 \text{ cal/mol Pb}}$, to surroundings.

[2.5] Calculate the enthalpy change at 968 K for the reaction
$$2SiO_2(s) + 2Al_2O_3(s) \rightarrow 2Al_2SiO_5(s).$$
Use the following information (all phases are solids):

(a) $2SiO_2 + 3Al_2O_3 \rightarrow Al_6Si_2O_{13}$ $\quad \Delta H^0_{968} = -22.6 \text{ kJ/mol}$

(b) $2Al_2SiO_5 + Al_2O_3 \rightarrow Al_6Si_2O_{13}$ $\quad \Delta H^0_{968} = -39.4 \text{ kJ/mol}$

Solution

(a) $2SiO_2 + 3Al_2O_3 \rightarrow \cancel{Al_6Si_2O_{13}}$ $\qquad \Delta H^0_{968} = -22.6$

(b) $\dfrac{\cancel{Al_6Si_2O_{13}} \rightarrow Al_2O_3 + 2Al_2SiO_5 \qquad \Delta H^0_{968} = 39.4}{2SiO_2(s) + 2Al_2O_3(s) \rightarrow 2Al_2SiO_5(s) \qquad \Delta H^0_{968} = 16.8 \text{ kJ/mol}}$
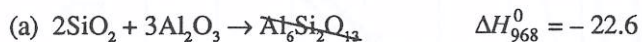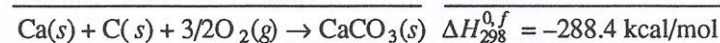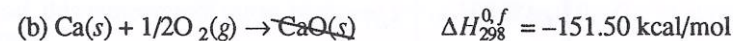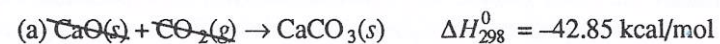
$$\Delta H^0_{968} = \underline{8.4 \text{ kJ/mol } SiO_2}$$

[2.6] Calculate the standard enthalpy of formation of $CaCO_3$ at 298 K in kcal/mol and kJ/mol from the following data:
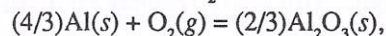
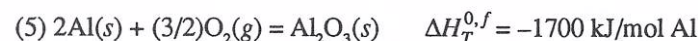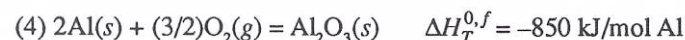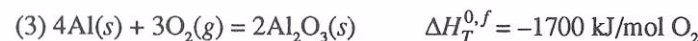(a) $CaO(s) + CO_2(g) \rightarrow CaCO_3(s)$ $\quad \Delta H^0_{298} = -42.85 \text{ kcal/mol}$

(b) $Ca(s) + 1/2O_2(g) \rightarrow CaO(s)$ $\quad \Delta H^{0,f}_{298} = -151.50 \text{ kcal/mol}$

(c) $C(s) + O_2(g) \rightarrow CO_2(g)$ $\quad \Delta H^{0,f}_{298} = -94.05 \text{ kcal/mol}$

Solution

(a) $\cancel{CaO(s)} + \cancel{CO_2(g)} \rightarrow CaCO_3(s)$ $\quad \Delta H^0_{298} = -42.85 \text{ kcal/mol}$

(b) $Ca(s) + 1/2O_2(g) \rightarrow \cancel{CaO(s)}$ $\quad \Delta H^{0,f}_{298} = -151.50 \text{ kcal/mol}$

(c) $\dfrac{C(s) + O_2(g) \rightarrow \cancel{CO_2(g)} \qquad \Delta H^{0,f}_{298} = -94.05 \text{ kcal/mol}}{Ca(s) + C(s) + 3/2O_2(g) \rightarrow CaCO_3(s) \quad \Delta H^{0,f}_{298} = -288.4 \text{ kcal/mol}}$
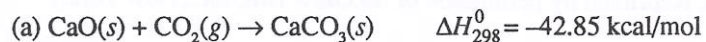
$$\Delta H^{0,f}_{298} = \underline{-288.4 \text{ kcal/mol}} = -1207 \text{ kJ/mol}.$$

[2.7] Given $\Delta H^{0,f}_T = -1133 \text{ kJ/mol } O_2$ for the reaction
$$(4/3)Al(s) + O_2(g) = (2/3)Al_2O_3(s),$$

(a) Show $\Delta H^{0,f}_{298} = -1133 \text{ kJ/mol if } \Delta C_p \approx 0.$

(b) Select the correct alternatives below for $\Delta H^{0,f}_T$.

(1) $4Al(s) + 3O_2(g) = 2Al_2O_3(s)$ $\quad \Delta H^{0,f}_T = -1133 \text{ kJ/mol } O_2$

(2) $2Al(s) + (3/2)O_2(g) = Al_2O_3(s)$ $\quad \Delta H^{0,f}_T = -3399 \text{ kJ/mol Al}$

(3) $4Al(s) + 3O_2(g) = 2Al_2O_3(s)$ $\quad \Delta H^{0,f}_T = -1700 \text{ kJ/mol } O_2$

(4) $2Al(s) + (3/2)O_2(g) = Al_2O_3(s)$ $\quad \Delta H^{0,f}_T = -850 \text{ kJ/mol Al}$

(5) $2Al(s) + (3/2)O_2(g) = Al_2O_3(s)$ $\quad \Delta H^{0,f}_T = -1700 \text{ kJ/mol Al}$

Solution

(a)
$$\Delta H^{0,f}_T = \Delta H^{0,f}_{298} + \int_{298}^{T} \Delta C_p dT$$

If $\Delta C_p \approx 0$,

$$\Delta H^{0,f}_T = \Delta H^{0,f}_{298} = -1133 \text{ kJ/mol } O_2$$
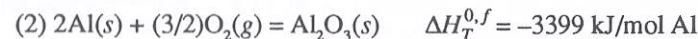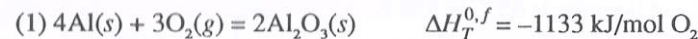
$$\Delta H^{0,f}_{298} = \underline{-1133 \text{ kcal/mol } O_2 \text{ if} \Delta C_p \approx 0}.$$

(b) Reaction (1) = $3 \times [4/3Al(s) + O_2(g) = 2/3Al_2O_3(s)]$ so for reaction (1), $\Delta H^{0,f}_T = 3(-1133 \text{ kJ}/3 \text{ mol } O_2) = -1133 \text{ kJ /mol } O_2$. Reaction (4) = $3/2[4/3Al(s) + O_2(g) = 2/3Al_2O_3(s)]$ so for reaction (4), $\Delta H^{0,f}_T = 3/2(-1133 \text{ kJ}/2 \text{ mol Al}) = -850 \text{ kJ/mol Al}$. Correct alternatives: $\underline{(1)}$ and $\underline{(4)}$.

[2.8] Fifty grams of the mineral ilmenite, $FeTiO_3$, are heated in an insulated furnace and then quenched in a 500 gm copper vessel containing 200 gm of water. The temperature of the water and vessel both rise from 30°C to 65°C. To what temperature was the ilmenite heated prior to quenching?

Solution

$$50 \text{ gm ilmenite} = 50 \text{ gm} \left(\frac{1 \text{ mol}}{151.75 \text{ gm}}\right) = 0.33 \text{ mol ilmenite}$$

$$200 \text{ gm } H_2O(l) = 200 \text{ gm} \left(\frac{1 \text{ mol}}{18.02 \text{ gm}}\right) = 11.10 \text{ mol } H_2O(l)$$

$$500 \text{ gm Cu} = 500 \text{ gm} \left(\frac{1 \text{ mol}}{63.55 \text{ gm}}\right) = 7.87 \text{ mol/Cu}$$

The initial temperature of the water and Cu vessel is 30°C = 303 K. T = the initial temperature of the ilmenite. The final temperature of the water, Cu

vessel, and ilmenite is 65°C = 338 K.

The heat lost by ilmenite = heat gained by H_2O and Cu vessel.

$$\left| Q'_{\text{ilm}} \right| = Q'_{H_2O} + Q'_{Cu}$$

$$\left| Q'_{\text{ilm}} \right| (J) = - \int_{T}^{338} (0.33)(116.61 + 18.24 \times 10^{-3} T - 20.04 \times 10^5 T^{-2}) dT$$

$$= -15{,}307.08 + (38.48T + 0.003T^2 + 661{,}320.0/T)$$

$$Q'_{H_2O}(J) = \int_{303}^{398} (11.10)(75.44) dT = 29{,}308.30$$

$$Q'_{Cu}(J) = \int_{303}^{338} (7.87)(27.964 + 1.6124 \times 10^{-3} T + 3.411 \times 10^{-7} T^2$$

$$- 1.0067 \times 10^2 T^{-0.5}) dT$$

$$= 6{,}305.21$$

Equating $\left| Q'_{\text{ilm}} \right|$ with Q'_{H_2O} and Q'_{Cu},
$-15{,}307.08 + (38.48T + 0.003T^2 + 661{,}320.0/T) = (29{,}308.30 + 6{,}305.21)$.
Solving for T,
$T = \underline{1197\ K} = \underline{924°C}$.

[2.9] Calculate the final temperature and enthalpy change of the mineral galena, Pbs, when 253.62 gm of the mineral at 80°C are placed into 58.73 gm of adiabatically contained water initially at a temperature of 27°C. Express the enthalpy change in cal/mol PbS.

Solution

$$253.62\ \text{gm galena} = 253.62\ \text{gm} \left(\frac{1\ \text{mol}}{239.26\ \text{gm}} \right) = 1.06\ \text{mol Pbs}$$

$$58.73\ \text{gm } H_2O(l) = 58.73\ \text{gm} \left(\frac{1\ \text{mol}}{18.02\ \text{gm}} \right) = 3.26\ \text{mol } H_2O(l)$$

The initial temperature of galena is 80°C (353 K) and of H_2O is 27°C (300K).
Let T_f = the final temperature of galena and H_2O,

$$-Q'_{\text{galena}} = Q'_{H_2O}.$$

Since for a constant pressure process $Q' = \Delta H'_p$,

$$-\Delta H'_{PbS(s)} = \Delta H'_{H_2O(l)}.$$

$$-\int_{353}^{T_f} (1.06\ \text{mol}) C_p^{PbS(s)} dT = \int_{300}^{T_f} (3.26\ \text{mol}) C_p^{H_2O(l)} dT.$$ Expanding,

$$-\int_{353}^{T_f} (1.06)(44.60 + 16.40 \times 10^{-3} T) dT = \int_{300}^{T_f} (3.26)(75.44) dT$$

or
$276.61 T_f + 8.20 \times 10^{-3} T_f^2 = 86{,}369.67$

Solving for T_f,
$T_f = \underline{309\ K} = \underline{36°C}$

$$\Delta H'_{PbS(s)} = -\Delta H'_{H_2O(l)} = \int_{300}^{309} (3.26)(75.44) dT$$

$$\Delta H_{PbS(s)} = \frac{\Delta H'_{PbS(s)}}{1.06\ \text{mol}} = \frac{-529.02\ \text{cal}}{1.06\ \text{mol}} = \underline{-499\ \text{cal/mol}}.$$

**[2.10]** Calculate the heat absorbed and standard enthalpy change at (a) 373 K and (b) 373 K < T < 800 K resulting from the dehydration of the mineral serpentine, $Mg_3Si_2O_5(OH)_4$, in the presence of quartz to form talc, $Mg_3Si_4O_{10}(OH)_2$. Use the heat capacity for $H_2O(l)$ in Appendix A, Table A.3A and the heat capacity for $H_2O(g)$ in Appendix A, Table A.3B. The reaction is:
$Mg_3Si_2O_5(OH)_4(s) + 2SiO_2(s) \rightarrow Mg_3Si_4O_{10}(OH)_2(s) + H_2O(g)$.
    Serpentine   α-Quartz   Talc
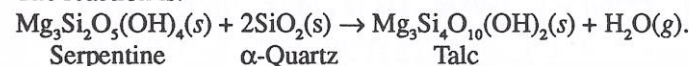
Solution

(a) Incorporating the H_2O phase change in an isobaric TL:

(1) <u>Set Up</u>
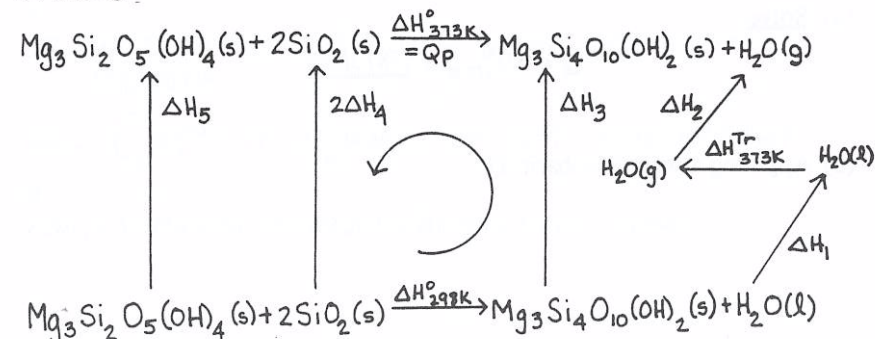
(2) Sum

$$\Sigma \Delta H_{TL} = 0 = \Delta H_{298}^0 + \Delta H_1 + \Delta H_{373}^{Tr} + \Delta H_2 + \Delta H_3 - \Delta H_{373}^0 - 2\Delta H_4 - \Delta H_5$$

(3) Substitute

$$\Delta H_{298 \ K}^0 = \sum n\Delta H_{298 \ K}^{0,f} (\text{Products}) - \sum n\Delta H_{298 \ K}^{0,f} (\text{Reactants})$$

$$\Delta H_{298}^0 \ (\text{kJ/mol}) = (1)(-5915.9) + 1(-285.90) - 1(-4361.66) - 2(-910.7) =$$
$$-18.74 \ \text{kJ/mol}$$

$$\Delta H_1 = \int_{298}^{373} C_p^{H_2O(l)} dT = \int_{298}^{373} 75.44 \, dT = 5658 \ \text{J/mol}$$

$$\Delta H_{373}^{Tr} = 41.09 \times 10^3 \ \text{J/mol}$$

$$\Delta H_2 = \int_{373}^{373} C_p^{H_2O(g)} dT \Rightarrow \Delta H_2 = 0$$

$$\Delta H_3 = \int_{298}^{373} C_p^{Talc} dT = \int_{298}^{373} (5653.6 - 5271.7 \times 10^{-3}T + 27.291 \times 10^{-7}T^2$$
$$-769.26 \times 10^2 T^{-\frac{1}{2}} + 4021.1 \times 10^4 T^{-2}) dT$$
$$= 3047.6 \ \text{J/mol}$$

$$2\Delta H_4 = 2\int_{298}^{373} C_p^{SiO_2(s)} dT = 2\int_{298}^{373} (44.60 + 37.754 \times 10^{-3}T - 10.018 \times 10^5 T^{-2}) dT$$
$$= 7238.1 \ \text{J}$$

$$\Delta H_5 = \int_{298}^{373} C_p^{Serp} dT = \int_{298}^{373} (899.60 - 144.76 \times 10^{-3}T - 109.32 \times 10^2 T^{-\frac{1}{2}}$$
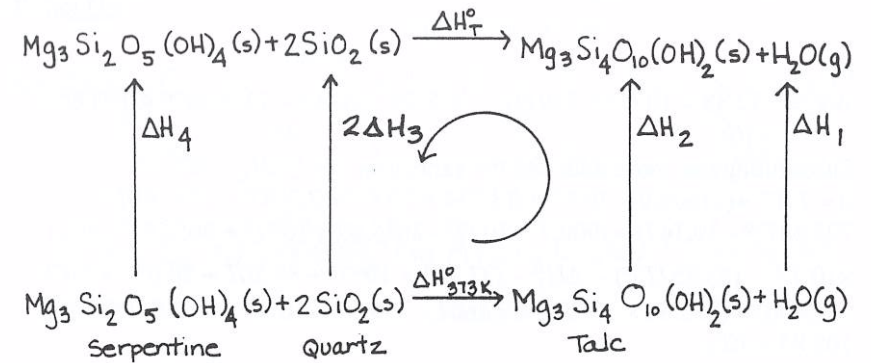$$+ 449.99 \times 10^4 T^{-2}) dT$$
$$= 22,031 \ \text{J/mol}$$

Substituting the previous data into $\Sigma \Delta H_{TL} = 0$,

$$0 = -18.74 \times 10^3 + 5658 + 41.09 \times 10^3 + 0 + 3047.6 - \Delta H_{373}^0 - 7238.1 -$$
$$22,031$$

(4) Solve

$$Q = \Delta H_{373 \ K}^0 = \underline{1787 \ \text{J/mol}}$$

(b) Applying a second isobaric TL:

---

(1) Set Up

(2) Sum

$$\Sigma \Delta H_{TL} = 0 = \Delta H_{373}^0 + \Delta H_1 + \Delta H_2 - \Delta H_T^0 - 2\Delta H_3 - \Delta H_4$$

(3) Substitute

$$\Delta H_{373}^0 = 1787 \ \text{J/mol} \ (\text{from Part (a)})$$

$$\Delta H_1 = \int_{373}^{T} C_p^{H_2O(g)} dT = \int_{373}^{T} (7.368 + 27.468 \times 10^{-3}T - 48.117 \times 10^{-7}T^2$$
$$+ 3.6174 \times 10^2 T^{-0.5} - 22.316 \times 10^4 T^{-2}) dT$$

or

$$\Delta H_1 = -1603.9 \times 10^{-9}T^3 + 13,734 \times 10^{-6}T^2 + 7.368T + 223,160T^{-1} +$$
$$723.48T^{1/2} - 19,147$$

$$\Delta H_2 = \int_{373}^{T} C_p^{Talc} = \int_{373}^{T} (5653.6 - 5271.7 \times 10^{-3}T + 27.291 \times 10^{-7}T^2$$
$$-769.26 \times 10^2 T^{-1/2} + 4021.1 \times 10^4 T^{-2}) dT$$

or

$$\Delta H_2 = 909.7 \times 10^{-9}T^3 - 2635.85 \times 10^{-3}T^2 + 5653.6T - 4021.1 \times 10^4 T^{-1} -$$
$$153,852T^{1/2}$$

$$2\Delta H_3 = \int_{373}^{T} 2C_p^{SiO_2(s)} dT = 2\int_{373}^{T} (44.60 + 37.754 \times 10^{-3}T - 10.018 \times 10^5 T^{-2}) dT$$

or

$$2\Delta H_3 = 37.754 \times 10^{-3}T^2 + 89.20T + 20,036 \times 10^2 T^{-1} - 43,896$$

$$\Delta H_4 = \int_{373}^{T} C_p^{Serp} dT = \int_{373}^{T} (899.60 - 144.76 \times 10^{-3}T - 109.32 \times 10^2 T^{-1/2}$$
$$+ 449.99 \times 10^4 T^{-2}) dT$$

or
$$\Delta H_4 = -72.38 \times 10^{-3}T^2 + 899.60T - 499.99 \times 10^4 T^{-1} - 21{,}864T^{1/2} + 108.85 \times 10^3$$

Substituting the above data into the expression for $\Sigma\Delta H_{TL} = 0$,
$0 = 1787 + (-1603.9 \times 10^{-9}T^3 + 13{,}734 \times 10^{-6}T^2 + 7.368T + 223{,}160T^{-1} + 723.48T^{1/2} - 19{,}147) + (909.7 \times 10^{-9}T^3 - 2635.85 \times 10^{-3}T^2 + 5653.6T - 4021.1 \times 10^4 T^{-1} - 153{,}852T^{1/2}) - \Delta H_T^0 - (37.754 \times 10^{-3}T^2 + 89.20T + 20{,}036 \times 10^2 T^{-1} - 43{,}896) - (-72.38 \times 10^{-3}T^2 + 899.60T - 499.99 \times 10^4 T^{-1} - 21{,}864T^{1/2} + 108.85 \times 10^3)$

(4) Solve

Solving the expression above for ΔH_T^0,

$\underline{\Delta H_T^0}$ (J/mol) $= -69.42 \times 10^{-8}T^3 - 2.59T^2 + 4672.2T - 3.70 \times 10^7 T^{-1} - 131{,}264T^{0.5} - 82{,}315$ for 373 K < T < 800 K.
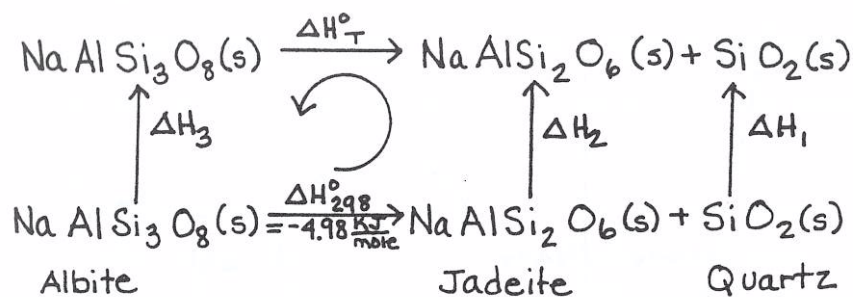
[2.11] A high pressure mineral reaction occurring in some rocks buried to depths of 30 km or more within the earth involves the decomposition of the mineral albite (Ab) to form the minerals jadeite (Jd) and quartz (Qz). Calculate the standard enthalpy change at 298 K for the albite decomposition reaction:

$$NaAlSi_3O_8(s) \rightarrow NaAlSi_2O_6(s) + SiO_2(s).$$
$$\quad Ab \qquad\qquad Jd \qquad\qquad \alpha\text{-Qz}$$
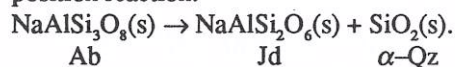
Solution

$$\Delta H_{298}^0 = \sum n\Delta H_{298}^{0,f}(\text{Products}) - \sum n\Delta H_{298}^{0,f}(\text{Reactants})$$

ΔH_{298}^0 (kJ/mol) $= 1(-910.7) + (1)(-3029.4) - (1)(-3935.12)$
$$\qquad\qquad = \underline{-5 \text{ kJ/mol}}.$$

[2.12] Using the standard enthalpy change computed for the reaction in Exercise Problem [2.11], calculate the standard enthalpy change of this reaction at T where 298 K < T < 844 K. No phase changes occur.

Solution

(1) Set Up

$$NaAlSi_3O_8(s) \xrightarrow{\Delta H_T^\circ} NaAlSi_2O_6(s) + SiO_2(s)$$
$$\uparrow \Delta H_3 \qquad \circlearrowleft \qquad \uparrow \Delta H_2 \qquad \uparrow \Delta H_1$$
$$NaAlSi_3O_8(s) \xrightarrow[= -4.98 \frac{kJ}{mole}]{\Delta H_{298}^\circ} NaAlSi_2O_6(s) + SiO_2(s)$$
$$\text{Albite} \qquad\qquad \text{Jadeite} \qquad\qquad \text{Quartz}$$

(2) Sum

$$\Sigma\Delta H_{TL} = \Delta H_{298}^0 + \Delta H_1 + \Delta H_2 - \Delta H_T^0 - \Delta H_3 = 0$$

$\Delta H_T^0 = \Delta H_1 + \Delta H_2 + \Delta H_{298}^0 - \Delta H_3$
Collecting terms and applying [2-16] and [2-17]:
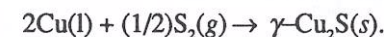
(3) Substitute

$$\Delta H_T^0 \text{ (J/mol)} = \Delta H_{298}^0 + \int_{298}^{T} (-238.21 + 140.749 \times 10^{-3}T - 49.191 \times 10^5 T^{-2}$$
$$-227.22 \times 10^{-7}T^2 + 43.692 \times 10^2 T^{-0.5}) dT$$
$$= 4{,}980 - 238.21T + 70{,}986.58 + 70.37 \times 10^{-3}T^2 - 6249.54 + 49.191 \times 10^5 T^{-1}$$
$$- 16507.05 - 75.74 \times 10^{-7}T^3 + 8738.4T^{1/2}$$

(4) Solve

$\underline{\Delta H_T^0 (J/mol)} = 53.21 \times 10^3 - 238.21T + 7.04 \times 10^{-2}T^2 - 7.57 \times 10^{-6}T^3 + 4.92 \times 10^6 T^{-1} + 8.74 \times 10^3 T^{0.5}.$

[2.13] At 1356 K and 1 atm pressure, the following exothermic reaction occurs:

$$2Cu(l) + (1/2)S_2(g) \rightarrow \gamma\text{-}Cu_2S(s).$$
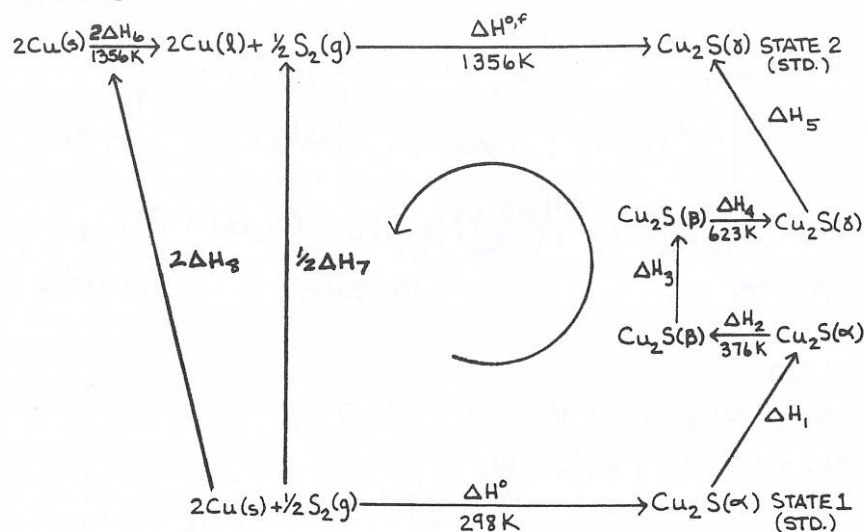
Calculate the heat evolved and enthalpy of formation of γ-$Cu_2S(s)$ at 1356 K and 1 atm pressure. Use the heat capacity for $S_2(g)$ in Appendix A, Table A.3B. Hint: begin with the reaction

$$2Cu(s) + (1/2)S_2(g) \rightarrow Cu_2S(\alpha).$$
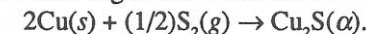
Solution

(1) Set Up

(2) Sum

$$\Sigma\Delta H_{TL} = 0 = \Delta H_{298}^{0} + \Delta H_1 + \Delta H_2 + \Delta H_3 + \Delta H_4 + \Delta H_5 - \Delta H_{1356}^{0,f} - 2\Delta H_6 - 1/2\Delta H_7 - 2\Delta H_8$$

which upon rearranging gives

$$\Delta H_{1356}^{0,f} = \Delta H_{298}^{0} + \Delta H_1 + \Delta H_2 + \Delta H_3 + \Delta H_4 + \Delta H_5 - 2\Delta H_6 - 1/2\Delta H_7 - 2\Delta H_8.$$

(3) Substitute

The data from Appendix A, Tables A.1, A.2, A.3A, and A.3B is substituted in $\Delta H_{1356}^{0,f}$ above:
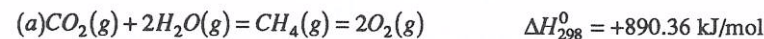
$$\Delta H_{1356}^{0,f} = [1 \text{ mol}(-80.115 \text{ kJ/mol}) - 0.5 \text{ mol}(128.49 \text{ kJ/mol})]$$

$$+ \int_{298}^{376} 1 \, C_p^{Cu_2S(\alpha)} dT + 1 \, (3849 \text{ J/mol}) + \int_{376}^{623} 1 \, C_p^{Cu_2S(\beta)} dT$$

$$+ 1 \, (836.8 \text{ J/mol}) + \int_{623}^{1356} 1 \, C_p^{Cu_2S(\gamma)} dT - 2 \, (13.054 \text{ kJ/mol})$$

$$- \int_{298}^{1356} 0.5 \, C_p^{S_2(g)} dT - \int_{298}^{1356} 2 \, C_p^{Cu(s)} dT.$$

(4) Solve

Upon intergrating and completing calculations,

$$Q_{1 \text{ atm}} = \Delta H_{1356}^{0,f} = -108 \text{ kJ/mol}.$$

[2.14] Calculate the standard enthalpy of formation of methane, $CH_4(g)$, at 298 K in kJ/mol and kcal/mol from the following information:

(a) $CH_4(g) + 2O_2(g) = CO_2(g) + 2H_2O(g)$ $\Delta H_{298}^{0} = -890.36$ kJ/mol

(b) $C(s) + O_2(g) = CO_2(g)$ $\Delta H_{298}^{0,f} = -393.51$ kJ/mol

(c) $H_2(g) + (1/2)O_2(g) = H_2O(g)$ $\Delta H_{298}^{0,f} = -241.814$ kJ/mol

Solution

$$(a) CO_2(g) + 2H_2O(g) = CH_4(g) = 2O_2(g) \qquad \Delta H_{298}^{0} = +890.36 \text{ kJ/mol}$$

$$(b) C(s) + O_2(g) = CO_2(g) \qquad \Delta H_{298}^{0,f} = -393.51 \text{ kJ/mol}$$

$$2 \times (c) 2H_2(g) + O_2(g) = 2H_2O(g) \qquad \Delta H_{298}^{0,f} = -483.628 \text{ kJ/mol}$$

―――――――――――――――――――――――――――

$$C(s) + 2H_2(g) = CH_4(g) \qquad \Delta H_{CH_4,298}^{0,f} = 13.22 \text{ kJ/mol}$$

$$\Delta H_{CH_4,298}^{0,f} = 13.22 \frac{\text{kJ}}{\text{mol}} \times \frac{1 \text{ cal}}{4.184 \text{ J}} = 3.12 \frac{\text{kcal}}{\text{mol}}$$

$$\Delta H_{298}^{0,f} = \underline{13.22 \text{ kJ/mol}} = \underline{3.12 \text{ kcal/mol}}.$$

[2.15] The enthalpy increment for element A at two temperatures is given as follows:

T(K)	$H_T^0 - H_{500}^0 (J/mol)$
1000	1750
700	640

Determine the heat capacity of A which most accurately reflects the data given.

Solution

$$\text{Eqn 1} \qquad 1750 = \int_{500}^{1000} (a + bT) dT \left. \right\}$$

$$\text{Eqn 2} \qquad 640 = \int_{500}^{700} (a + bT) dT \left. \right\} \text{Simultaneous Solution}$$

$$1750 = a(1000 - 500) + (b/2)[(1000)^2 - (500)^2]$$

$$640 = a(700 - 500) + (b/2)[(700)^2 - (500)^2]$$

and expanding:

$$a = 2.0$$
$$b = 2 \times 10^{-3}$$
$$C_p^A \text{ (J/mol)} = \underline{2.0 + 2 \times 10^{-3}T}.$$
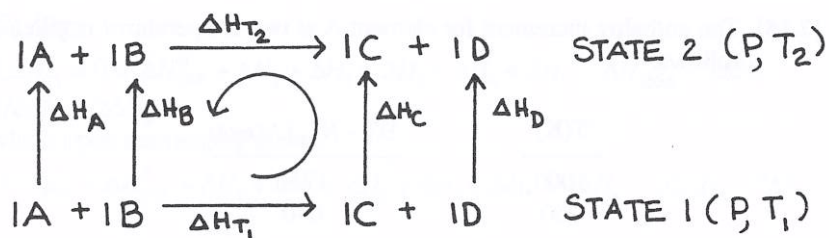
[2.16] Derive the formula

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

where

(a) ΔH_{T_1} and ΔH_{T_2} are the constant pressure molar enthalpy changes of a reaction in states 1 and 2 respectively.

(b) No phase changes occur between states 1 and 2.

(c) All reaction components exist as one mole in the balanced reaction.

Solution

(1) Set Up

(2) Sum

$$\Sigma \Delta H_{TL} = 0 = \Delta H_{T_1} + \Delta H_C + \Delta H_D - \Delta H_{T_2} - \Delta H_A - \Delta H_B$$

$$\Delta H_{T_2} = \Delta H_{T_1} + \Delta H_C + \Delta H_D - \Delta H_A - \Delta H_B$$

(3) Substitute

$$\Delta H_{T_2} = \Delta H_{T_1} + \int_{T_1}^{T_2} C_p^C dT + \int_{T_1}^{T_2} C_p^D dT - \int_{T_1}^{T_2} C_p^A dT - \int_{T_1}^{T_2} C_p^B dT$$

or

$$\Delta H_{T_2} = \Delta H_{T_1} + \int_{T_1}^{T_2} (C_p^C + C_p^D - C_p^A - C_p^B) dT$$

Let $\Delta C_p = \Sigma n_i C_p^i \text{ (Products)} - \Sigma n_i C_p^i \text{ (Reactants)}$

Hence,

$$\Delta C_p = (1)C_p^C + (1)C_p^D - (1)C_p^A - (1)C_p^B$$

(4) Solve

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

[2.17] Confirm the internal energy change for the transformation of potassium from liquid to vapor phase at 1000 K and 0.753 bar.

Solution

From [2-4] and Table D.2,
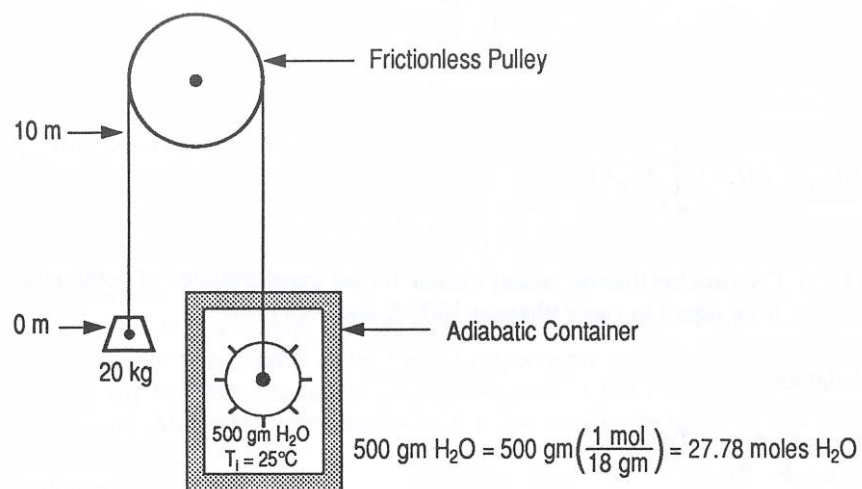$$u = h - Pv$$

Differentiating at constant pressure,

$$du = dh - Pdv - \cancel{vdP}^{\,0}$$

Integrating,

$$\Delta u = \int_{u_1}^{u_v} du = \int_{h_1}^{h_v} dh - P \int_{v_1}^{v_v} dv$$

$$= 2760.4 - 812.6 - 0.753(2592 - 1.493) \times 1/10$$

$$= \underline{1753 \text{ kJkg}}.$$

[2.18] A 20 kg mass falls 10 meters at constant velocity, thereby causing a paddle wheel to stir 500 gm of adiabatically contained water initially at 25°C. Assume for the water a negligible change in volume and that $C_v \approx C_p$.

(a) Find the internal energy change and temperature of the water after the weight has fallen 2, 4, 6, 8, and 10 meters.

(b) Plot both internal energy change and gravitational potential energy versus temperature. What does the plot suggest?

Frictionless Pulley

10 m

0 m

20 kg

Adiabatic Container

500 gm H_2O
$T_I = 25°C$

$500 \text{ gm } H_2O = 500 \text{ gm} \left(\dfrac{1 \text{ mol}}{18 \text{ gm}}\right) = 27.78 \text{ moles } H_2O$

Solution

(a) *Work-Energy Principal*: As the 20 kg mass falls, its gravitational potential energy, E_P, decreases and is converted into rotational kinetic energy of the paddle wheel. The paddle rotates and does work on the water, thereby changing the internal energy of the water as follows:

$$\Delta E'_{P,20 \text{ kg mass}} = -\Delta U'_{H_2O} = +W'_{Ad,H_2O}$$

$$E'_P = mgh = (20 \text{ kg})(9.81 \text{ m/s}^2)h = (196.2 \text{ N})h$$

$$E'_{P,10 \text{ m}} = (196.2 \text{ N})(10 \text{ m}) = \underline{1962.0 \text{ J}}$$

Distance Fallen = 0 m: $h = 10$ m

$$\Delta E'_P = E'_{P,10 \text{ m}} - E'_{p,10m} = \Delta U = -W_{Ad} = 0$$

$$\Delta U' = -W_{Ad} = \underline{\underline{0 \text{ J}}}$$

$$T = \underline{\underline{25°C}}$$

Distance Fallen = 2 m: $h = 8$ m

$$\Delta E'_P = (196.2 \text{ N})(8 \text{ m}) - 1962.0 \text{ J} = \underline{-392.4 \text{ J}}$$

$$\Delta U' = -W_{Ad} = \underline{392.4 \text{ J}}$$

$$\Delta U'_V \text{ (J)} = 392.4 = \int_{298}^{T} n_{H_2O(l)} C_v^{H_2O(l)} dT = \int_{298}^{T} (27.78)(75.44) dT$$

$$(27.78)(75.44)[T]_{298}^{T} = \underline{392.4 \text{ J}}$$

$$T(K) = \dfrac{392.4}{(27.78)(75.44)} + 298 = 298.19$$

or $T = \underline{25.19°C}$

Distance Fallen = 4 m: $h = 6$ m

$$\Delta E'_P = (196.2 \text{ N})(6 \text{ m}) - 1962.0 \text{ J} = -784.8 \text{ J}$$

$$\Delta U' = -W_{Ad} = \underline{784.8 \text{ J}}$$

$$\Delta U'_V \text{ (J)} = 784.8 = \int_{298}^{T} (27.78)(75.44) dT$$

$$T(K) = \dfrac{784.8}{2095.7} + 298 = 298.37$$

or $T = \underline{25.37°C}$

Distance Fallen = 6 m: $h = 4$ m

$$\Delta E'_P = (196.2 \text{ N})(4 \text{ m}) - 1962.0 \text{ J} = -1177.2 \text{ J}$$

$$\Delta U' = -W_{Ad} = \underline{1177.2 \text{ J}}$$

$$\Delta U'_V \text{ (J)} = 1177.2 = \int_{298}^{T} (27.78)(75.44) dT$$

$$T(K) = \dfrac{1177.2}{2095.7} + 298 = 298.56$$

or $T = \underline{25.56°C}$

Distance Fallen = 8 m: $h = 2$ m

$$\Delta E'_P = (196.2 \text{ N})(2 \text{ m}) - 1962.0 \text{ J} = -1569.6 \text{ J}$$

$$\Delta U' = -W_{Ad} = \underline{1569.6 \text{ J}}$$

$$\Delta U'_V \text{ (J)} = 1569.6 = \int_{298}^{T} (27.78)(75.44) dT$$

$$T(K) = \dfrac{1569.6}{2095.7} + 298 = 298.75$$

or $T = \underline{25.75°C}$

Distance Fallen = 10 m : $h = 0$ m

$$\Delta E'_P = (196.2 \text{ N})(0 \text{ m}) - 1962.0 \text{ J} = -1962.0 \text{ J}$$

$$\Delta U' = -W_{Ad} = \underline{1962.0 \text{ J}}$$

$$\Delta U'_V \text{ (J)} = 1962.0 = \int_{298}^{T} (27.78)(75.44) dT$$

$$T(K) = \frac{1962.0}{2095.7} + 298 = 298.94$$

or $T = \underline{\underline{25.94°C}}$.

(b) Linear plat is consistent with C_v = constant.

Distance Fallen (m)	E_p (J)	$\Delta U' = - W'_{Ad.}$ (J)	$T(^0C)$
0.0	1962.0	0.0	25.0
2.0	1570.0	392.4	25.2
4.0	1177.0	784.8	25.4
6.0	784.8	1177.0	25.6
8.0	392.4	1570.0	25.8
10.0	0.0	1962.0	25.9

linear plot - consistent with C_v = constant.