Problem Set #3

Assigned September 6, 2013 – Due Friday, September 13, 2013

Please show all work for credit

To "warm up" or practice try the Atkins Exercises, which are generally simple one step problems

Partial Derivatives

   1. **Engle – P. 3.2 (First and second partial derivatives)**

   P3.2 The function $f(x,y)$ is given by $f(x,y) = xy \sin 5x + x^2 \sqrt{y} \ln y + 3e^{-2x^2} \cos y$. Determine

   $$\left(\frac{\partial f}{\partial x}\right)_y, \left(\frac{\partial f}{\partial y}\right)_x, \left(\frac{\partial^2 f}{\partial x^2}\right)_y, \left(\frac{\partial^2 f}{\partial y^2}\right)_x, \left(\frac{\partial}{\partial y}\left(\frac{\partial f}{\partial x}\right)_y\right)_x$$

   and $\left(\frac{\partial}{\partial x}\left(\frac{\partial f}{\partial y}\right)_x\right)_y$

   a. Is $\left(\frac{\partial}{\partial y}\left(\frac{\partial f}{\partial x}\right)_y\right)_x = \left(\frac{\partial}{\partial x}\left(\frac{\partial f}{\partial y}\right)_x\right)_y$?

   b. Obtain an expression for the total differential df.

$$\left(\frac{\partial f}{\partial x}\right)_y = 5\,x\,y\,\text{Cos}[5x] + y\,\text{Sin}[5x] - 12\,x\,e^{-2x^2}\text{Cos}[y] + 2\,x\,\sqrt{y}\,\ln y \;.$$

$$\left(\frac{\partial f}{\partial y}\right)_x = x\,\text{Sin}[5x] + \frac{x^2}{\sqrt{y}} + \frac{x^2\,\ln y}{2\sqrt{y}} - 3\,e^{-2x^2}\text{Sin}[y]$$

$$\left(\frac{\partial^2 f}{\partial x^2}\right)_y = 10\,y\,\text{Cos}[5x] - 25\,x\,y\,\text{Sin}[5x] - 12\,e^{-2x^2}\text{Cos}[y] + 48\,e^{-2x^2}x^2\,\text{Cos}[y] + 2\sqrt{y}\,\ln y$$

$$\left(\frac{\partial^2 f}{\partial y^2}\right)_x = -3\,e^{-2x^2}\text{Cos}[y] - \frac{x^2\,\ln y}{4y^{3/2}}$$

$$\left(\frac{\partial f}{\partial x}\left(\frac{\partial f}{\partial y}\right)_x\right)_y = \frac{2\,x}{\sqrt{y}} + \frac{x\,\ln y}{\sqrt{y}} + \text{Sin}[5x] + 5\,x\,\text{Cos}[5\,x] + 12\,e^{-2x^2}x\,\text{Sin}[y]$$

a) $\left(\frac{\partial f}{\partial y}\left(\frac{\partial f}{\partial x}\right)_y\right)_x = 5\,x\,\text{Cos}[5\,x] + 12\,e^{-2x^2}x\,\text{Sin}[y] + \frac{2\,x}{\sqrt{y}} + \frac{x\,\ln y}{\sqrt{y}} + \text{Sin}[5x] = \left(\frac{\partial f}{\partial x}\left(\frac{\partial f}{\partial y}\right)_x\right)_y$

b) $df = \left(\frac{\partial f}{\partial x}\right)_y dx + \left(\frac{\partial f}{\partial y}\right)_x dy = \left(5\,x\,y\,\text{Cos}[5x] + y\,\text{Sin}[5x] - 12\,x\,e^{-2x^2}\text{Cos}[y] + 2\,x\,\sqrt{y}\,\ln y\right)dx$

$+ \left(x\,\text{Sin}[5x] + \frac{x^2}{\sqrt{y}} + \frac{x^2\,\ln y}{2\sqrt{y}} - 3\,e^{-2x^2}\text{Sin}[y]\right)dy$

2. **Atkins – P. 2.22 (Exact differentials)**

Show that the following functions have exact diffreentials: (a) x^2y+3y^2, (b) $x\cos(xy)$, (c) x^3y^2, (d) $t(t+e^s)+s$

A function has an exact differential if its mixed partial derivatives are equal. That is, $f(x,y)$ has an exact differential if

$$\frac{\partial}{\partial x}\left(\frac{\partial f}{\partial y}\right) = \frac{\partial}{\partial y}\left(\frac{\partial f}{\partial x}\right)$$

(a) $\frac{\partial}{\partial y}\left(\frac{\partial f}{\partial x}\right) = \frac{\partial}{\partial y}(2xy) = 2x$ and $\frac{\partial}{\partial x}\left(\frac{\partial f}{\partial y}\right) = \frac{\partial}{\partial x}(x^2 + 6y) = 2x$

(b) $\frac{\partial}{\partial y}\left(\frac{\partial f}{\partial x}\right) = \frac{\partial}{\partial y}(\cos xy - xy\sin xy)$

$\qquad\qquad = -x\sin xy - x\sin xy - x^2y\cos xy = -2x\sin xy - x^2y\cos xy$

and $\frac{\partial}{\partial x}\left(\frac{\partial f}{\partial y}\right) = \frac{\partial}{\partial x}(-x^2\sin xy) = -2x\sin xy - x^2y\cos xy$

(c) $\frac{\partial}{\partial y}\left(\frac{\partial f}{\partial x}\right) = \frac{\partial}{\partial y}(3x^2y^2) = 6x^2y$ and $\frac{\partial}{\partial x}\left(\frac{\partial f}{\partial y}\right) = \frac{\partial}{\partial x}(2x^3y) = 6x^2y$

(d) $\frac{\partial}{\partial t}\left(\frac{\partial f}{\partial s}\right) = \frac{\partial}{\partial t}(te^s + 1) = e^s$ and $\frac{\partial}{\partial s}\left(\frac{\partial f}{\partial t}\right) = \frac{\partial}{\partial s}(2t + e^s) = e^s$

Real Gases

3. **Atkins P. 1.8 (From last week, virial gas coefficients and compressibility)**

At 273 K measurements on argon gave B= −21.7 cm^{3}mol^{-1} and C=1200cm^{6}mol^{-2}, where B and C are the second and third virial coefficients in the expansion of Z in powers of $1/V_m$. Assuming that the perfect gas law holds sufficiently well for the estimation of the second and third terms of the expansion, calculate the compression factor of argon at 100 atm and 273 K. From your result, estimate the molar volume of argon under these conditions.

From the definition of Z [1.17] and the virial equation [1.19b], Z may be expressed in virial form as

$$Z = 1 + B\left(\frac{1}{V_m}\right) + C\left(\frac{1}{V_m}\right)^2 + \cdots$$

Since $V_m = \frac{RT}{p}$ [assumption of perfect gas], $\frac{1}{V_m} = \frac{p}{RT}$, hence on substitution and dropping terms beyond the second power of $\left(\frac{1}{V_m}\right)$

$$Z = 1 + B\left(\frac{p}{RT}\right) + C\left(\frac{p}{RT}\right)^2$$

$$Z = 1 + (-21.7 \times 10^{-3}\,\text{dm}^3\,\text{mol}^{-1}) \times \left(\frac{100\,\text{atm}}{(0.08206\,\text{dm}^3\,\text{atm mol}^{-1}\,\text{K}^{-1}) \times (273\,\text{K})}\right)$$

$$+ (1.200 \times 10^{-3}\,\text{dm}^6\,\text{mol}^{-2}) \times \left(\frac{100\,\text{atm}}{(0.08206\,\text{dm}^3\,\text{atm mol}^{-1}\,\text{K}^{-1}) \times (273\,\text{K})}\right)^2$$

$$Z = 1 - (0.0968) + (0.0239) = \boxed{0.927}$$

$$V_m = (0.927) \times \left(\frac{RT}{p}\right) = (0.927) \times \left(\frac{(0.0821\,\text{dm}^3\,\text{atm K}^{-1}\,\text{mol}^{-1}) \times (273\,\text{K})}{100\,\text{atm}}\right) = \boxed{0.208\,\text{dm}^3}$$

4. **Atkins – Ex. 2.4(b) (heat expansion)**

   A sample consisting of 2.00 mol of perfect gas molecules, for which
   $C_{V,m} = 5/2R$, initially at $P_1 = 111$ kPa and $T_1 = 277$ K, is heated reversibly to
   356 K at constant volume. Calculate the final pressure, ΔU, q, and w.

   The perfect gas law leads to

   $$\frac{p_1 V}{p_2 V} = \frac{nRT_1}{nRT_2}, \quad \text{or} \quad p_2 = \frac{p_1 T_2}{T_1} = \frac{(111\text{ k Pa}) \times (356\text{ K})}{277\text{ K}} = \boxed{143\text{ k Pa}}$$

   There is no change in volume, so $\boxed{w = 0}$. The heat flow is

   $$q = \int C_V \, dT \approx C_V \Delta T = (2.5) \times (8.3145\text{ J K}^{-1}\text{ mol}^{-1}) \times (2.00\text{ mol}) \times (356 - 277)\text{ K}$$
   $$= \boxed{3.28 \times 10^3\text{ J}}$$

   $$\Delta U = q + w = \boxed{3.28 \times 10^3\text{ J}}$$

5. **Atkins – Ex. 2.8(b) (heat capacity)**

   The constant-pressure heat capacity of a sample of a perfect gas was found to vary with
   temperature according to the expression $C_p/(\text{J K}^{-1}) = 20.17 + 0.4001(T/\text{K})$. Calculate q,
   w, ΔU, and ΔH when the temperature is raised from 0°C to 100°C (a) at constant
   pressure, (b) at constant volume.

   (a) At constant pressure, $q = \Delta H$.

   $$q = \int C_p \, dT = \int_{0+273\text{K}}^{100+273\text{K}} [20.17 + (0.4001)T/\text{K}] \, dT \text{ J K}^{-1}$$

   $$= \left[(20.17)T + \frac{1}{2}(0.4001) \times \left(\frac{T^2}{\text{K}} \right) \right]_{273\text{K}}^{373\text{K}} \text{ J K}^{-1}$$

   $$= [(20.17) \times (373 - 273) + \tfrac{1}{2}(0.4001) \times (373^2 - 273^2)]\text{J} = \boxed{14.9 \times 10^3\text{ J}} = \Delta H$$

   $$w = -p\Delta V = -nR\Delta T = -(1.00\text{ mol}) \times (8.3145\text{ J K}^{-1}\text{ mol}^{-1}) \times (100\text{ K}) = \boxed{-831\text{ J}}$$

   $$\Delta U = q + w = (14.9 - 0.831)\text{ kJ} = \boxed{14.1\text{ kJ}}$$

   (b) The energy and enthalpy of a perfect gas depend on temperature alone. Thus, $\Delta H = \boxed{14.9\text{ kJ}}$
   and $\Delta U = \boxed{14.1\text{ kJ}}$, as above. At constant volume, $w = \boxed{0}$ and $\Delta U = q$, so $q = \boxed{+14.1\text{ kJ}}$.

6. **Atkins Life Science – P. 1.19 (Heat capacity derivation and calculation)**

   (a) Show that for a perfect gas, $C_{p,m}$- $C_{v,m}$=R. (b) When 229 J of energy is supplied as heat at constant pressure to 3.00 mol CO2 (g), the temperature of the sample increases by 2.06K. Calculate the molar heat capacities at constant volume and constant pressure of the gas.

   (a)   The molar internal energy and enthalpy of a perfect gas are related by eqn 1.12b ($H_m = U_m + RT$), which we can write as $H_m - U_m = RT$. When the temperature increases by ΔT, the molar enthalpy increases by ΔH_m and the internal energy increases by ΔU_m, so $\Delta H_m - \Delta U_m = R\Delta T$. Now, divide both sides by ΔT, which gives

   $$\frac{\Delta H_m}{\Delta T} - \frac{\Delta U_m}{\Delta T} = R$$

   We recognize the first term on the left as the molar constant-pressure heat capacity, $C_{p,m}$, and the second term as the molar constant-volume heat capacity, $C_{V,m}$. Therefore,

   $$C_{p,m} - C_{V,m} = R \quad [1.15, \text{ perfect gas}]$$

   (b) $C_p = \frac{q_p}{\Delta T}$ [1.13 and 1.14a] and division by n gives $C_{p,m} = \frac{q_p}{n\Delta T}$. Thus,

   $$C_{p,m} = \frac{q_p}{n\Delta T} = \frac{229 \text{ J}}{(3.00 \text{ mol}) \times (2.06 \text{ K})} = \boxed{37.1 \text{ J K}^{-1} \text{ mol}^{-1}}$$

   $$C_{V,m} = C_{p,m} - R [1.15] = (37.1 - 8.3145) \text{ J K}^{-1} \text{ mol}^{-1} = \boxed{28.8 \text{ J K}^{-1} \text{ mol}^{-1}}$$

7. **Atkins – P. 2.11 (Heat capacity – simple use)**

   An average human produces about 10 MJ of heat each day through metabolic activity. If a human body were an isolated system of mass 65 kg with the heat capacity of water, what temperature rise would the body experience? Human bodies are actually open systems, and the main mechanism of heat loss is through the evaporation of water. What mass of water should be evaporated each day to maintain constant temperature?

Part1:

$$\Delta T = \frac{q}{Mass \times C_{water}} = \frac{1 \times 10^7 J}{65kg \times 4180 J kg^{-1} K^{-1}} = 36.81K = 37K$$

Part2: First of all, everything happens in an isobaric process ($P = 1atm$), we can also treat the water vapor as a perfect gas, so $q = \Delta H_m * n$. From the example 2.3 on the book, the enthalpy change of vaporization per mole of H_2O is $\Delta H_m = +41 kJmol^{-1}$

$$\Delta n_{water} = \frac{q}{\Delta H_m} = \frac{1 \times 10^7 J}{41 kJmol^{-1}} = 243.9 mol$$

$$\Delta Mass_{water} = M_{water} \times \Delta n_{water} = 18.02 gmol^{-1} \times 243.9 mol = 4.4kg$$

8. **Atkins – Ex. 2.3(b) (expansion work)**

   A sample consisting of 2.00 mol He is expanded isothermally at 22°C from 22.8 dm³ to 31.7 dm³ (a) reversibly, (b) against a constant external pressure equal to the final pressure of the gas, and (c) freely (against zero external pressure). For the three processes calculate q, w, ΔU, and ΔH.

   For all cases $\Delta U = 0$, since the internal energy of a perfect gas depends only on temperature. (See Section 2.2a and Section 2.11(b) for a more complete discussion.) From the definition of enthalpy, $H = U + pV$, so $\Delta H = \Delta U + \Delta(pV) = \Delta U + \Delta(nRT)$ (perfect gas). Hence, $\Delta H = 0$ as well, at constant temperature for all processes in a perfect gas.

   (a) $\boxed{\Delta U = \Delta H = 0}$

   $$w = -nRT \ln\left(\frac{V_f}{V_i}\right) \text{ [2.10]}$$

   $$= -(2.00 \text{ mol}) \times (8.3145 \text{ J K}^{-1} \text{ mol}^{-1}) \times (22 + 273) \text{ K} \times \ln\frac{31.7 \text{ dm}^3}{22.8 \text{ dm}^3} = \boxed{-1.62 \times 10^3 \text{ J}}$$

   $$q = -w = \boxed{1.62 \times 10^3 \text{ J}}$$

   (b) $\boxed{\Delta U = \Delta H = 0}$

   $$w = -p_{ex}\Delta V \text{ [2.8]}$$

   where p_{ex} in this case can be computed from the perfect gas law

   $$pV = nRT$$

   so $$p = \frac{(2.00 \text{ mol}) \times (8.3145 \text{ JK}^{-1} \text{ mol}^{-1}) \times (22 + 273) \text{ K}}{31.7 \text{ dm}^3} \times (10 \text{ dm m}^{-1})^3 = 1.55 \times 10^5 \text{ Pa}$$

   and $$w = \frac{-(1.55 \times 10^5 \text{ Pa}) \times (31.7 - 22.8) \text{ dm}^3}{(10 \text{ dm m}^{-1})^3} = \boxed{-1.38 \times 10^3 \text{ J}}$$

   $$q = -w = \boxed{1.38 \times 10^3 \text{ J}}$$

   (c) $\boxed{\Delta U = \Delta H = 0}$

   $\boxed{w = 0}$ [free expansion] $q = \Delta U - w = 0 - 0 = \boxed{0}$

   COMMENT. An isothermal free expansion of a perfect gas is also adiabatic.

9. Atkins – P. 2.2 (Work of Gas Expansion)

A sample consisting of 1.0 mol CaCO₃(s) was heated to 800°C, when it decomposed. The heating was carried out in a container fitted with a piston that was initially resting on the solid. Calculate the work done during complete decomposition at 1.0 atm. What work would be done if instead of having a piston the container was open to the atmosphere?

$$w = -p_{ex}\Delta V \text{ [2.8]} \quad V_f = \frac{nRT}{p_{ex}} \gg V_i; \quad \text{so} \quad \Delta V \approx V_f$$

Hence, $\quad w \approx (-p_{ex}) \times \left(\frac{nRT}{p_{ex}}\right) = -nRT = (-1.0 \text{ mol}) \times (8.314 \text{ J K}^{-1} \text{mol}^{-1}) \times (1073 \text{ K})$

$$w \approx \boxed{-8.9 \text{ kJ}}$$

Even if there is no physical piston, the gas drives back the atmosphere, so the work is also

$$w \approx \boxed{-8.9 \text{ kJ}}$$

10. Engel - P2.9 (heat. metabolism)

A hiker caught in a thunderstorm loses heat when her clothing becomes wet. She is packing emergency rations that, if completely metabolized, will release 30. kJ of heat per gram of rations consumed. How much rations must the hiker consume to avoid a reduction in body temperature of 4.0 K as a result of heat loss? Assume the heat capacity of the body equals that of water. Assume the hiker weighs 55 kg. State any additional assumptions.

We start by calculating the heat that corresponds to a temperature decrease of 4 K. Using $q = C_p \Delta T$, we obtain:

$$q_{4K} = C_p \Delta T = (75.3 \text{ J K}^{-1} \text{mol}^{-1}) \times (4.0 \text{ K}) \times \frac{1}{(18.02 \times 10^{-3} \text{ kg mol}^{-1})} = 17000 \text{ J kg}^{-1}$$

We then determine the heat lost for a 55 kg person as:

$$q_{person} = q_{4K} \text{ m} = (17000 \text{ J kg}^{-1}) \times (55 \text{ kg}) = 9.2 \times 10^5 \text{ J}$$

And finally the mass of rations that needs to be consumed is given by:

$$m_{rations} = \frac{q_{person}}{q_{rations}} = \frac{(9.2 \times 10^5 \text{ J})}{(3.0 \times 10^4 \text{ J g}^{-1})} = \underline{31.0 \text{ g}}$$

11. Engel - P2.14 (heat. work)

According to a story told by Lord Kelvin, one day when walking down from Chamonix to commence a tour of Mt. Blanc, "whom should I meet walking up (the trail) but (James) Joule, with a long thermometer in his hand, and a carriage with a lady in it not far off. He told me he had been married since we parted from Oxford, and he was going to try for (the measurement of the) elevation of temperature in waterfalls." Suppose Joule encountered a waterfall 30. meters height. Calculate the temperature difference between the top and bottom of this waterfall.

The decrease in potential energy (m×g×h) must equal the heat evolved as the water falls. (m×C_p×ΔT). Note that the mass cancels, so we need to use the heat capacity for mass, 4.18 kJ kg^{-1}K^{-1}, and also note that J=$kg \cdot m^2 \cdot s^{-2}$. Heat is evolved so T increases, so the bottom temp is higher than the top, and the difference is ΔT:

$$m\,g\,h = m\,C_{p,m}\,\Delta T$$

$$\Delta T = \frac{g\,h}{C_{p,m}} = \frac{\left(9.81\,\text{m s}^{-2}\right)\times\left(30.0\,\text{m}\right)}{\left(4180\,\text{J m}^{-1}\,\text{K}^{-1}\right)} = \underline{0.0704\,\text{K}}$$

12. Atkins – P. 2.8 (D-ribose energy of combustion)

A sample of the sugar D-ribose ($C_5H_{10}O_5$) of mass 0.727 g was placed in a constant-volume calorimeter and then ignited in the presence of excess oxygen. The temperature rose by 0.910 K. In a separate experiment in the same calorimeter, the combustion of 0.825 g of benzoic acid, for which the internal energy of combustion is -3251 kJ mol^{-1}, gave a temperature rise of 1.940 K. Calculate the internal energy of combustion of D-ribose and its enthalpy of formation.

The calorimeter is a constant-volume instrument as described in the text (Section 2.4), therefore

$$\Delta U = q_V$$

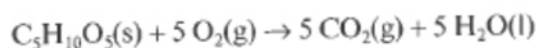The calorimeter constant is determined from the data for the combustion of benzoic acid

$$\Delta U = \left(\frac{0.825\ g}{122.12\ g\ mol^{-1}} \right) \times (-3251\ kJ\ mol^{-1}) = -21.9\overline{6}\ kJ$$

Since $\Delta T = 1.940$ K, $C = \dfrac{|q|}{\Delta T} = \dfrac{21.9\overline{6}\ kJ}{1.940\ K} = 11.3\overline{2}\ kJ\ K^{-1}$

For D-ribose, $\Delta U = -C\Delta T = -(11.3\overline{2}\ kJ\ K^{-1}) \times (0.910\ K)$

Therefore, $\Delta_c U = \dfrac{\Delta U}{n} = -(11.3\overline{2}\ kJ\ K^{-1}) \times (0.910\ K) \times \left(\dfrac{150.13\ g\ mol^{-1}}{0.727\ g} \right) = -212\overline{7}\ kJ\ mol^{-1}$

The combustion reaction for D-ribose is

$$C_5H_{10}O_5(s) + 5\ O_2(g) \rightarrow 5\ CO_2(g) + 5\ H_2O(l)$$

Since there is no change in the number of moles of gas, $\Delta_c H = \Delta U$ [2.21]

The enthalpy of formation is obtained from the sum

	$\Delta H/(kJ\ mol^{-1})$
$5\ CO_2(g) + 5\ H_2O(l) \rightarrow C_5H_{10}O_5(s) + 5\ O_2(g)$	2127
$5\ C(s) + 5\ O_2(g) \rightarrow 5\ CO_2(g)$	$5 \times (-393.51)$
$5\ H_2(g) + \frac{2}{5}O_2(g) \rightarrow 5\ H_2O(l)$	$5 \times (-285.83)$
$5\ C(s) + 5\ H_2(g) + \frac{2}{5}O_2(g) \rightarrow C_5H_{10}O_5(s)$	-1270

Hence, $\Delta_f H = \boxed{-1270\ kJ\ mol^{-1}}$

13. Atkins Life Science – P. 1.32 and Fig. 1.27 (Enthalpy of protein folding)

Figure 1.27 shows the experimental DSC scan of hen white lysozyme (G. Privalovet al.,
Anal. Biochem. 79, 232 (1995)) converted to kilojoules (from calories). Determine the enthalpy of unfolding of this protein by integration of the curve and the change in heat capacity accompanying the transition.
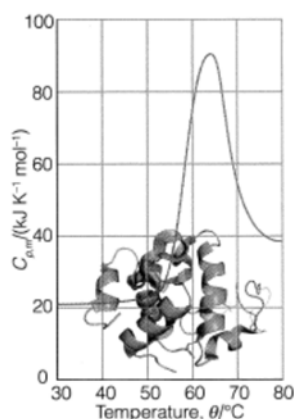
Fig. 1.27 Experimental DSC scan of hen white lysozyme.

Figure 1.4 is a modification of text Figure 1.27, the DSC thermogram of hen white lysozyme. It is apparent that the unfolding of the protein is endothermic with a so-called "melting temperature" of $T_m = 64.5°C$. The figure indicates the heat-capacity variation with temperature of both the native protein state and the denatured state. The baseline of the figure accounts for the heat-capacity variation of the native and denatured states during the period of denaturation. The additional contribution to the heat capacity, $C_{p,ex}$, due to the unfolding transition is given by the difference between the DSC curve and the baseline:

$$C_{p,ex} = C_{p,m} - C_{p,\text{baseline}}$$

The enthalpy of the transition is given by the thermogram area between the DSC curve and the baseline over the temperature range of 53°C to 79°C:

$$\Delta_{trs}H = \int_{326\,K}^{352\,K} C_{p,ex}\,dT \quad [1.18]$$

We can get a good estimate of the area represented by the above integral by dividing the temperature range into 2°C (i.e., 2 K) intervals with the middle of each interval aligned on the baseline and serving as the narrow base of a rectangle that extends vertically to a height at which the top of the rectangle intersects the DSC curve. We read both $C_{p,m}$ and $C_{p,\text{baseline}}$ for each rectangle and calculate $C_{p,ex}$. The thermogram area estimate for the integral of eqn 1.18 is the sum of all the rectangle areas:

$$\Delta_{trs}H = \sum_{\text{all rectangles}} (\text{rectangle area}) = (\text{rectangle width}) \sum_{\text{all rectangles}} (\text{rectangle height})$$

$$= (2\,K) \sum_{\text{all rectangles}} (C_{p,ex})_{\text{rectangle}}$$

This procedure yields the following table of thermogram readings with the indicated temperature being the middle of each rectangle temperature interval. (The $C_{p,ex}$ values have been estimated to 0.1 kJ K^{-1} mol^{-1}. Since this estimate is very uncertain, at the end of the calculation we round-off to the next larger digit.)

θ/°C	$C_{p,ex}$/kJ K^{-1} mol^{-1}	θ/°C	$C_{p,ex}$/kJ K^{-1} mol^{-1}	θ/°C	$C_{p,ex}$/kJ K^{-1} mol^{-1}
54	0.6	64	59.4	74	3.8
56	5.6	66	51.9	76	1.3
58	15.0	68	30.0	78	0.3
60	30.0	70	15.0		
62	49.4	72	8.1		

Performing the requisite sum and calculating the transition enthalpy gives:

$$\sum_{\text{all rectangles}} (C_{p,ex})_{\text{rectangle}} = 270.\overline{4}\ \text{kJ K}^{-1}\ \text{mol}^{-1}$$

$$\Delta_{\text{trs}}H = (2\ \text{K}) \sum_{\text{all rectangles}} (C_{p,ex})_{\text{rectangle}} = (2\ \text{K}) \times (270.\overline{4}\ \text{kJ K}^{-1}\ \text{mol}^{-1}) = \boxed{541\ \text{kJ mol}^{-1}}$$
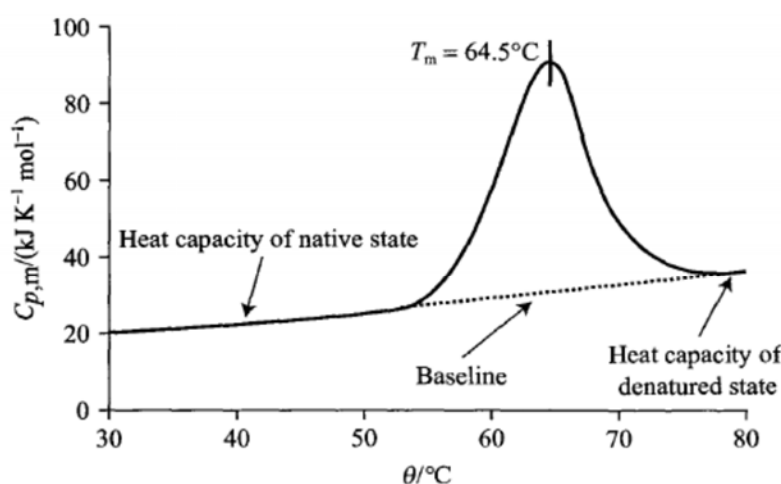

Figure 1.4

14. Atkins Life Science – P. 1.42 (Enthalpy of water vaporization)

Estimate the enthalpy of vaporization of water at 100°C from its value at 25°C (+44.01 kJ mol^{-1}) given the constant-pressure heat capacities of 75.29 J K^{-1} mol^{-1} and 33.58 J K^{-1} mol^{-1} for liquid and gas, respectively.

$$\Delta_{\text{vap}}H^{\circ}(T') = \Delta_{\text{vap}}H^{\circ}(T) + \Delta_r C_p^{\circ} \times (T' - T) \quad [1.24]$$

$$\Delta_{\text{vap}}H^{\circ}(373\ \text{K}) = 44.01\ \text{kJ mol}^{-1} + (33.58\ \text{J K}^{-1}\ \text{mol}^{-1} - 75.29\ \text{J K}^{-1}\ \text{mol}^{-1}) \times (373\ \text{K} - 298\ \text{K})$$

$$= \boxed{40.88\ \text{kJ mol}^{-1}}$$

Extra problems - Practice for exams, do not hand in:

1. **Atkins – P. 2.26 (Heat capacity derivation)**

   Starting from the expression $C_p-C_v=T\cdot(\frac{\partial p}{\partial T})_T\cdot(\frac{\partial V}{\partial T})_p$, use the appropriate relations between partial derivatives to show that:

   $$C_p-C_v=-\frac{T(\frac{\partial V}{\partial T})_p^2}{(\frac{\partial V}{\partial p})_T}$$

   Evaluate C_p-C_v for a perfect gas.

   Using Euler's chain relationship and the reciprocal identity [MB2.3c]

   $$\left(\frac{\partial p}{\partial T}\right)_V = -\left(\frac{\partial p}{\partial V}\right)_T\left(\frac{\partial V}{\partial T}\right)_p$$

   Substituting into the given expression for $C_p - C_V$

   $$C_p - C_V = -T\left(\frac{\partial p}{\partial V}\right)_T\left(\frac{\partial V}{\partial T}\right)_p^2$$

   Using the reciprocal identity again

   $$C_p - C_V = -\frac{T\left(\frac{\partial V}{\partial T}\right)_p^2}{\left(\frac{\partial V}{\partial p}\right)_T}$$

   For a perfect gas, $pV = nRT$, so

   $$\left(\frac{\partial V}{\partial T}\right)_p^2 = \left(\frac{nR}{p}\right)^2 \quad \text{and} \quad \left(\frac{\partial V}{\partial p}\right)_T = -\frac{nRT}{p^2}$$

   so $C_p - C_V = -\dfrac{-T\left(\dfrac{nR}{p}\right)^2}{-\dfrac{nRT}{p^2}} = \boxed{nR}$

2. Atkins – P. 2.6 (isothermal expansion)

Calculate the work done during the isothermal reversible expansion of a van der Waals gas. Account physically for the way in which the coefficients a and b appear in the final expression. Plot on the same graph the indicator diagrams for the isothermal reversible expansion of (a) a perfect gas, (b) a van der Waals gas in which a=0 and b=5.11x10^{-2} dm^3 mol^{-1}, and (c) a=4.2dm^6 atm mol^{-2} and b=0. The values selected exaggerate the imperfections but give rise to significant effects on the indicator diagrams. Take V$_i$=1.0 dm^3, n=1.0 mol, and T=298 K.

$$w = -\int_{V_1}^{V_2} p\, dV \quad \text{with} \quad p = \frac{nRT}{V-nb} - \frac{n^2a}{V^2} \quad [1.21a]$$

$$\text{Therefore,} \quad w = -nRT\int_{V_1}^{V_2} \frac{dV}{V-nb} + n^2a\int_{V_1}^{V_2}\frac{dV}{V^2} = \boxed{-nRT\ln\left(\frac{V_2-nb}{V_1-nb}\right) - n^2a\left(\frac{1}{V_2}-\frac{1}{V_1}\right)}$$

This expression can be interpreted more readily if we assume $V \gg nb$, which is certainly valid at all but the highest pressures. Then, using the first term of the Taylor series expansion,

$$\ln(1-x) = -x - \frac{x^2}{2}\cdots \quad \text{for } |x| \ll 1$$

$$\ln(V-nb) = \ln V + \ln\left(1-\frac{nb}{V}\right) \approx \ln V - \frac{nb}{V}$$

and, after substitution

$$w \approx -nRT\ln\left(\frac{V_2}{V_1}\right) + n^2bRT\left(\frac{1}{V_2}-\frac{1}{V_1}\right) - n^2a\left(\frac{1}{V_2}-\frac{1}{V_1}\right)$$

$$\approx -nRT\ln\left(\frac{V_2}{V_1}\right) - n^2(a-bRT)\left(\frac{1}{V_2}-\frac{1}{V_1}\right)$$

$$\approx +w_0 - n^2(a-bRT)\left(\frac{1}{V_2}-\frac{1}{V_1}\right) = \text{perfect gas value} + \text{van der Waals correction.}$$

w_0, the perfect gas value, is negative in expansion and positive in compression. Considering the correction term, in expansion $V_2 > V_1$, so $\left(\frac{1}{V_2}-\frac{1}{V_1}\right) < 0$. If attractive forces predominate, $a > bRT$ and the work done *by* the van der Waals gas is less in magnitude (less negative) than the perfect gas—the gas cannot easily expand. If repulsive forces predominate, $bRT > a$ and the work done *by* the van der Waals gas is greater in magnitude than the perfect gas—the gas easily expands. In the numerical calculations, consider a doubling of the initial volume.

(a) $w_0 = -nRT \ln\left(\dfrac{V_f}{V_i}\right) = (-1.0\ \text{mol}^{-1}) \times (8.314\ \text{J K}^{-1}\,\text{mol}^{-1}) \times (298\ \text{K}) \times \ln\left(\dfrac{2.0\ \text{dm}^3}{1.0\ \text{dm}^3}\right)$

$w_0 = -1.7\overline{2} \times 10^3\ \text{J} = \boxed{-1.7\ \text{kJ}}$

(b) $w = w_0 - (1.0\ \text{mol})^2 \times [0 - (5.11 \times 10^{-2}\ \text{dm}^3\,\text{mol}^{-1}) \times (8.314\ \text{J K}^{-1}\,\text{mol}^{-1}) \times (298\ \text{K})]$

$\times \left(\dfrac{1}{2.0\ \text{dm}^3} - \dfrac{1}{1.0\ \text{dm}^3}\right) = (-1.7\overline{2} \times 10^3\ \text{J}) - (63\ \text{J}) = -1.7\overline{8} \times 10^3\ \text{J} = \boxed{-1.8\ \text{kJ}}$

(c) $w = w_0 - (1.0\ \text{mol})^2 \times (4.2\ \text{dm}^6\,\text{atm}\,\text{mol}^{-2}) \times \left(\dfrac{1}{2.0\ \text{dm}^3} - \dfrac{1}{1.0\ \text{dm}^3}\right)$

$w = w_0 + 2.1\ \text{dm}^3\,\text{atm}$

$= (-1.7\overline{2} \times 10^3\ \text{J}) + (2.1\ \text{dm}^3\,\text{atm}) \times \left(\dfrac{1\ \text{m}}{10\ \text{dm}}\right)^3 \times \left(\dfrac{1.01 \times 10^5\ \text{Pa}}{1\ \text{atm}}\right)$

$= (-1.7\overline{2} \times 10^3\ \text{J}) + (0.21 \times 10^3\ \text{J}) = \boxed{-1.5\ \text{kJ}}$

Schematically, the indicator diagrams for the cases (a), (b), and (c) would appear as in Figure 2.2. For case (b) the pressure is always greater than the perfect gas pressure and for case (c) always less. Therefore,

$$\int_{V_1}^{V_2} p\,dV(\text{c}) < \int_{V_1}^{V_2} p\,dV(\text{a}) < \int_{V_1}^{V_2} p\,dV(\text{b})$$

and we see that $w(\text{b}) > w(\text{a}) > w(\text{c})$.
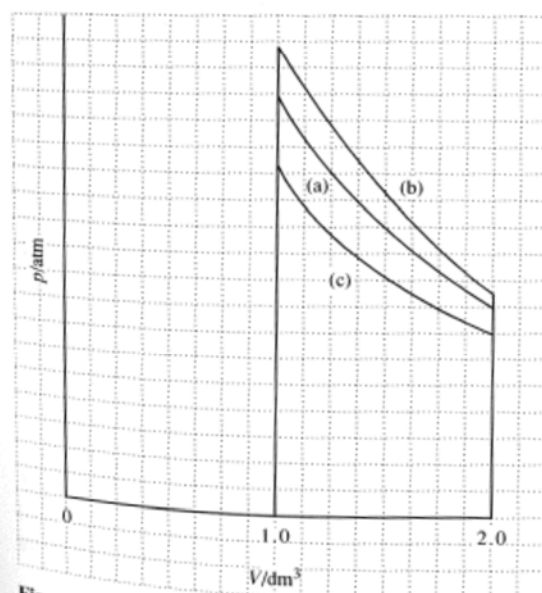

Figure 2.2

3. Atkins – P. 2.12 (Glucose energy)

Glucose and fructose are simple sugars with the molecular formula $C_6H_{12}O_6$. Sucrose, or table sugar, is a complex sugar with molecular formula $C_{12}H_{22}O_{11}$ that consists of a glucose unit covalently bound to a fructose unit (a water molecule is given off as a result of the reaction between glucose and fructose to form sucrose). (a) Calculate the energy released as heat when a typical table sugar cube of mass 1.5 g is burned in air. (b) To what height could you climb on the energy a table sugar cube provides assuming 25 per cent of the energy is available for work? (c) The mass of a typical glucose tablet is 2.5 g. Calculate the energy released as heat when a glucose tablet is burned in air. (d) To what height could YOU climb on the energy a cube provides assuming 25 per cent of the energy is available for work?

(a) The magnitude of the energy released as heat is

$$q = -n\Delta_c H^\circ = -\frac{1.5g}{342.3g\,mol^{-1}} \times (-5645\ kJ\ mol^{-1}) = \boxed{+25\ kJ}$$

(b) Effective work available is $\approx 25\ kJ \times 0.25 = 6.2\ kJ$

Because $w = mgh$, and $m \approx 65$ kg

$$h \approx \frac{6.2 \times 10^3\ J}{65\ kg \times 9.81\ m\ s^{-2}} = \boxed{9.7\ m}$$

(c) The energy released as heat is

$$q = -\Delta_c H = -n\Delta_c H^\circ = -\left(\frac{2.5\ g}{180\ g\ mol^{-1}}\right) \times (-2808\ kJ\ mol^{-1}) = \boxed{39\ kJ}$$

(d) If one-quarter of this energy were available as work a 65 kg person could climb to a height h given by

4. **Atkins – P. 2.47 (Differential scanning calorimetry)**

   Differential scanning calorimetry is used to examine the role of solvent-protein interactions in the denaturation process. Figure 2.34 shows the thermogram for ubiquitin in water with the signal observed for ubiquitin in methanol/water mixtures. Suggest an interpretation of the thermograms.
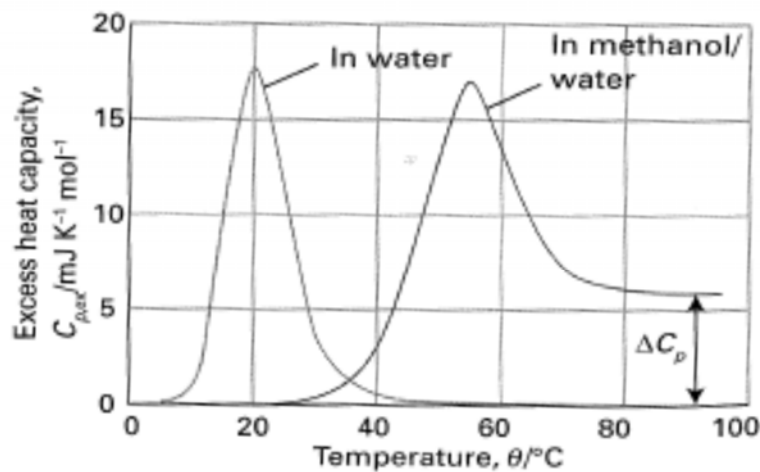

Fig. 2.34

   The simplest interpretation is that the structure of the protein in MeOH is more stable, i.e. it undergoes a denaturation (sometimes termed melting) transition at a higher temperature. Beyond that the ΔCp suggests that parts of the protein that were not in solvent are now exposed to solvent and have different motions/conformations available and that this exposure results in a different distribution of energy states in MeOH than in H_2O. Methanol interacts with the protein to desolvate it, displacing water, with weaker H-bonds to the amides, which will denature the protein to some extent, but at the same time can stabilize a non-native state.

5. **Engel question Q2.4 (heat,work)**

   Why is it incorrect to speak of the heat or work associated with a system?

   Heat and work exist only during the transitions of a given system between states. A system in a particular state does not have heat or work, only energy.

6. **Engel question Q2.6 (microwave)**

   A cup of water at 278 K (the system) is placed in a microwave oven and the oven is turned on for 1 minute during which it begins to boil. Which of q, w, and au are positive, negative, or zero?

   The heat, q, is positive since heat flows across the system-surrounding boundary into the system. The work, w, is negative because the vaporized water does work on the surroundings. ΔU is positive because the temperature increases and some of the liquid is vaporized.

7. **Atkins Life Science – P. 1.24 (Endothermic vs. exothermic)**

   Classify as endothermic or exothermic (a) a combustion reaction for which $\Delta H° = -2020$ kJ mol^{-1}, (b) a dissolution for which $\Delta H° = +4.0$ kJ mol^{-1}, (c) vaporization, (d) fusion, and (e)sublimation.

   A positive reaction enthalpy indicates an **endothermic reaction**, while a negative reaction enthalpy indicates an **exothermic reaction**.

   (a) $\Delta_r H° < 0$, exothermic reaction
   (b) $\Delta_r H° > 0$, endothermic reaction
   (c) $\Delta_{vap} H° > 0$, endothermic reaction
   (d) $\Delta_{fus} H° > 0$, endothermic reaction
   (e) $\Delta_{sub} H° > 0$, endothermic reaction