Problem Set #5

Assigned September 20, 2013 – Due Friday, September 27, 2013

Please show all work for credit

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

Thermal expansion and isothermal compressibility

1. Engel - P3.20 (Thermal expansion derivation for an ideal and real gas)
2. Atkins – 2.32(b) (expansion coefficient)
3. Atkins – 2.33(b) (compressiblity)

Joule-Thomson Coefficient

4. Atkins - 2.20 (Enthalpy change of compressed gas)
5. Atkins - 2.46 (Joule-Thompson coefficient of tetrafluoroethane from table data)

Enthalpy and Phase Changes

6. Atkins - 2.6(b) (Methanol condensation)

Thermochemistry

7. Atkins - 2.25 (b) (Enthalpy of formation of NOCl(g)) * Need Table 2.8
8. Atkins – 2.19(b) (diborame formation)
9. Atkins - 2.18 (Silane oxidation)
10. Atkins – 2.42 (anerobic oxidation)
11. Engel - P4.21 (calorimeter calibration)
12. Engel - P4.24 (Photosynthetic glucose production, ΔH)
13. Engel – P4.37 (N2 fixation, glycine production)

Extra, do not hand in

Good model problems for exam

1. Engel - P3.14 (Internal Energy derivatives derivation)
2. Engel - P3.21 (Joule coefficient for ideal and van der Waals gas)
3. Engel – P3.26 $(dCv/dV)_T$ calc
4. Engel - P3.11 (isothermal compressibilty coefficient for van der Waals gas)
5. Atkins 2.16(b) (Liquid vaporization)

Tests of your understanding

6. Atkins – 2.30(b) (J-T coefficient calculation)
7. Atkins - 2.34(b) (Joule-Thompson experiment with CO_2) – de-emphasize
8. Atkins – 2.12 (glucose combustion)
9. Atkins - 2.43 (Alkyl radicals)
10. Engel - P3.19 (use Joule coefficient for ΔH calc, ideal and Van der Waals gas)
11. Engel – P3.22 (derivation suing calculus methods) Engel P4.8 (reaction enthalpy at high T, needs tabulated Cp(T) values)
12. Engel - P4.8 (reaction enthalpy at high T, needs tabulated Cp(T) values)
13. Engel - P4.5 (CaC_2(s) enthalpy of formation)
14. Engel - P4.19 (Bond enthalpy calculations) * Need Table 4.3 in Chapter 4 and Table 4.1 and Table 4.2 in back of book – may de-emphasize
15. Engel – P.4.25 (ecology)

Thermal expansion and isothermal compressibility

1. **Engel - P3.20**

P3.20) Using the result of Equation (3.8), $(\partial P/\partial T)_V = \beta/\kappa$, express β as a function of κ, and V_m for an ideal gas, and β as a function of b, κ, and V_m for a van der Waals gas.

For an ideal gas:

$$\left(\frac{\partial p}{\partial T}\right)_p = \frac{R}{V_m} = \frac{\beta}{\kappa} \text{ and } \beta = \frac{\kappa R}{V_m}$$

For the van der Waals gas:

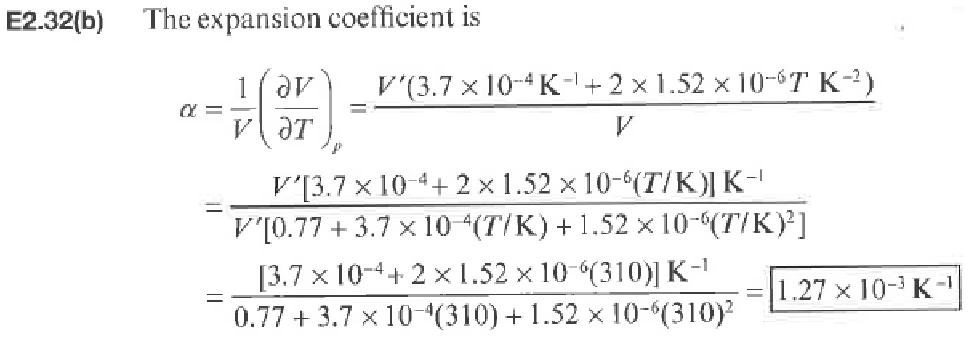
$$\left(\frac{\partial}{\partial T}\left[\frac{RT}{(V_m - b)} - \frac{a}{V_m{}^2}\right]\right)_V = \frac{R}{(V_m - b)} \text{ and } \beta = \frac{\kappa R}{(V_m - b)}$$

2. **Atkins – 2.32(b)**

The volume of a certain liquid varies with temperature

$$V=V'[0.77+3.7 * 10^{-4}(T/K) +1.52 * 10^{-6}(T/K)^2]$$

Where V' is its volume at 300K. Calculate its expansion coefficient, α, at 310K.



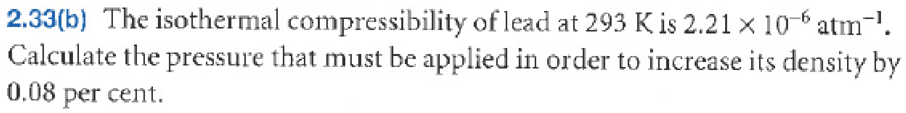
E2.32(b) The expansion coefficient is

$$\alpha = \frac{1}{V}\left(\frac{\partial V}{\partial T}\right)_p = \frac{V'(3.7\times10^{-4}\,\text{K}^{-1} + 2\times1.52\times10^{-6}T\,\text{K}^{-2})}{V}$$

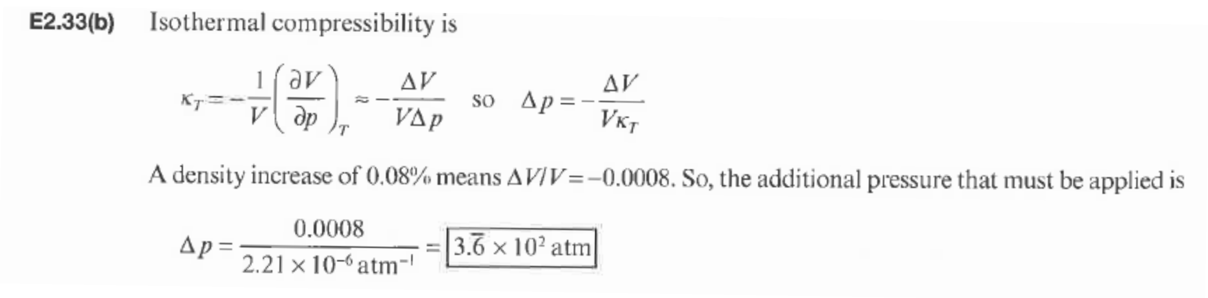
$$= \frac{V'[3.7\times10^{-4} + 2\times1.52\times10^{-6}(T/\text{K})]\,\text{K}^{-1}}{V'[0.77 + 3.7\times10^{-4}(T/\text{K}) + 1.52\times10^{-6}(T/\text{K})^2]}$$

$$= \frac{[3.7\times10^{-4} + 2\times1.52\times10^{-6}(310)]\,\text{K}^{-1}}{0.77 + 3.7\times10^{-4}(310) + 1.52\times10^{-6}(310)^2} = \boxed{1.27\times10^{-3}\,\text{K}^{-1}}$$

3. **Atkins – 2.33(b)**



2.33(b) The isothermal compressibility of lead at 293 K is 2.21×10^{-6} atm^{-1}. Calculate the pressure that must be applied in order to increase its density by 0.08 per cent.



E2.33(b) Isothermal compressibility is

$$\kappa_T = -\frac{1}{V}\left(\frac{\partial V}{\partial p}\right)_T \approx -\frac{\Delta V}{V\Delta p} \quad \text{so} \quad \Delta p = -\frac{\Delta V}{V\kappa_T}$$

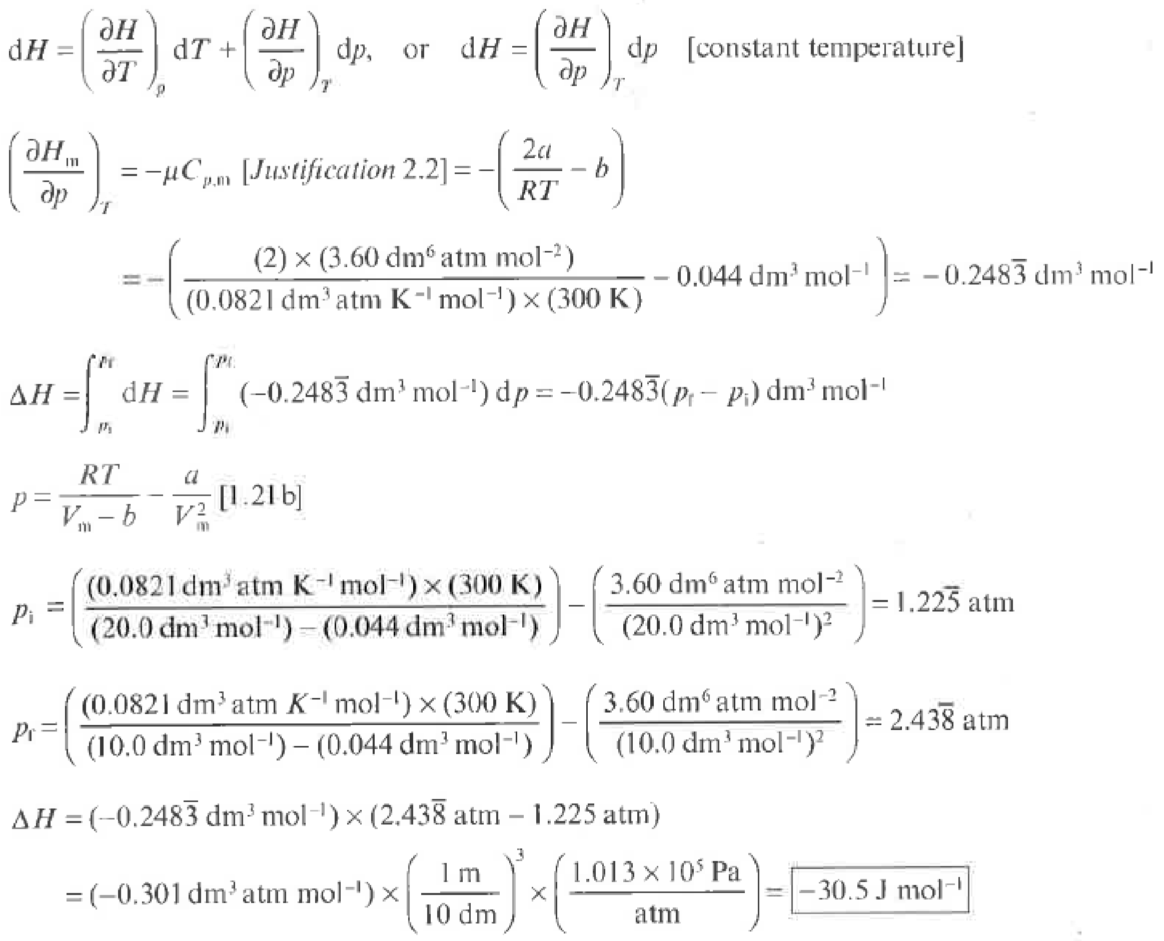
A density increase of 0.08% means $\Delta V/V = -0.0008$. So, the additional pressure that must be applied is

$$\Delta p = \frac{0.0008}{2.21\times10^{-6}\,\text{atm}^{-1}} = \boxed{3.\overline{6}\times10^2\,\text{atm}}$$

Joule-Thomson Coefficient

4. **Atkins – 2.20**

   A sample consisting of 1.00 mol of a van der Waals gas is compressed from 20.0 dm^3 to 10 dm^3 at 300K. In the process, 20.2 kJ of work is done on the gas. Given that $\mu= [(2a/RT)-b]/C_{p,m}$, with $C_{p,m} = 38.4\ J\ K^{-1}\ mol^{-1}$, $a = 3.60\ dm^6\ atm\ mol^{-2}$, and $b=0.044\ dm^3\ mol^{-1}$, calculate ΔH for the process.



$$\mathrm{d}H=\left(\frac{\partial H}{\partial T}\right)_p \mathrm{d}T+\left(\frac{\partial H}{\partial p}\right)_T \mathrm{d}p, \quad \text{or} \quad \mathrm{d}H=\left(\frac{\partial H}{\partial p}\right)_T \mathrm{d}p \quad [\text{constant temperature}]$$

$$\left(\frac{\partial H_\mathrm{m}}{\partial p}\right)_T=-\mu C_{p,\mathrm{m}}\ [\textit{Justification } 2.2]=-\left(\frac{2a}{RT}-b\right)$$

$$=-\left(\frac{(2)\times(3.60\ \mathrm{dm^6\ atm\ mol^{-2}})}{(0.0821\ \mathrm{dm^3\ atm\ K^{-1}\ mol^{-1}})\times(300\ \mathrm{K})}-0.044\ \mathrm{dm^3\ mol^{-1}}\right)=-0.248\overline{3}\ \mathrm{dm^3\ mol^{-1}}$$

$$\Delta H=\int_{p_\mathrm{i}}^{p_\mathrm{f}}\mathrm{d}H=\int_{p_\mathrm{i}}^{p_\mathrm{f}}(-0.248\overline{3}\ \mathrm{dm^3\ mol^{-1}})\,\mathrm{d}p=-0.248\overline{3}(p_\mathrm{f}-p_\mathrm{i})\ \mathrm{dm^3\ mol^{-1}}$$

$$p=\frac{RT}{V_\mathrm{m}-b}-\frac{a}{V_\mathrm{m}^2}\ [1.21\mathrm{b}]$$

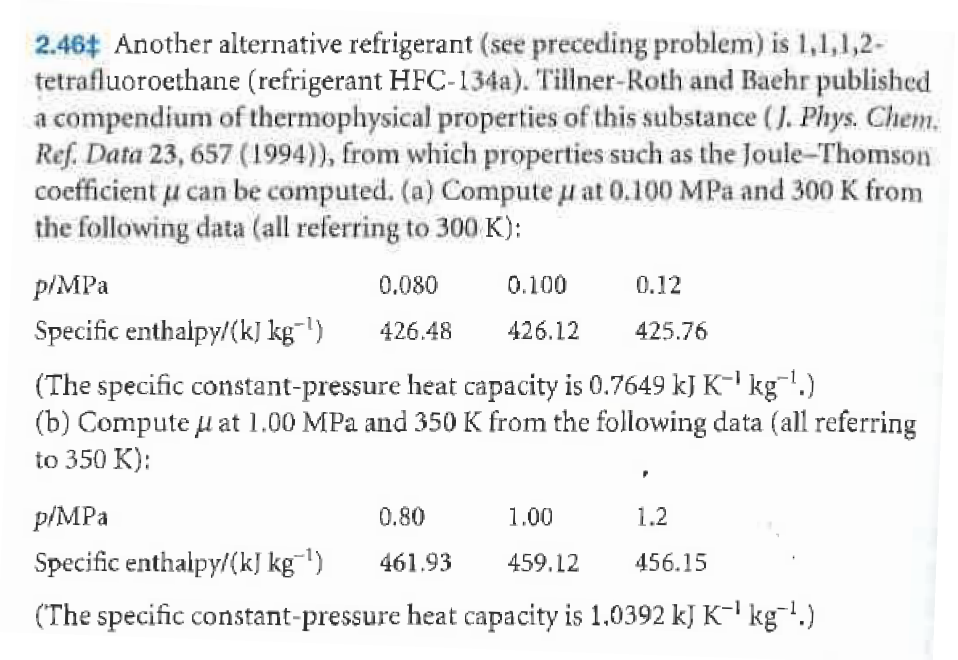
$$p_\mathrm{i}=\left(\frac{(0.0821\ \mathrm{dm^3\ atm\ K^{-1}\ mol^{-1}})\times(300\ \mathrm{K})}{(20.0\ \mathrm{dm^3\ mol^{-1}})-(0.044\ \mathrm{dm^3\ mol^{-1}})}\right)-\left(\frac{3.60\ \mathrm{dm^6\ atm\ mol^{-2}}}{(20.0\ \mathrm{dm^3\ mol^{-1}})^2}\right)=1.22\overline{5}\ \mathrm{atm}$$

$$p_\mathrm{f}=\left(\frac{(0.0821\ \mathrm{dm^3\ atm}\ K^{-1}\ \mathrm{mol^{-1}})\times(300\ \mathrm{K})}{(10.0\ \mathrm{dm^3\ mol^{-1}})-(0.044\ \mathrm{dm^3\ mol^{-1}})}\right)-\left(\frac{3.60\ \mathrm{dm^6\ atm\ mol^{-2}}}{(10.0\ \mathrm{dm^3\ mol^{-1}})^2}\right)=2.43\overline{8}\ \mathrm{atm}$$

$$\Delta H=(-0.248\overline{3}\ \mathrm{dm^3\ mol^{-1}})\times(2.43\overline{8}\ \mathrm{atm}-1.225\ \mathrm{atm})$$

$$=(-0.301\ \mathrm{dm^3\ atm\ mol^{-1}})\times\left(\frac{1\ \mathrm{m}}{10\ \mathrm{dm}}\right)^3\times\left(\frac{1.013\times10^5\ \mathrm{Pa}}{\mathrm{atm}}\right)=\boxed{-30.5\ \mathrm{J\ mol^{-1}}}$$

5. **Atkins – 2.46**



2.46‡ Another alternative refrigerant (see preceding problem) is 1,1,1,2-tetrafluoroethane (refrigerant HFC-134a). Tillner-Roth and Baehr published a compendium of thermophysical properties of this substance (*J. Phys. Chem. Ref. Data* 23, 657 (1994)), from which properties such as the Joule–Thomson coefficient μ can be computed. (a) Compute μ at 0.100 MPa and 300 K from the following data (all referring to 300 K):

p/MPa	0.080	0.100	0.12
Specific enthalpy/(kJ kg^{-1})	426.48	426.12	425.76

(The specific constant-pressure heat capacity is 0.7649 kJ K^{-1} kg^{-1}.)
(b) Compute μ at 1.00 MPa and 350 K from the following data (all referring to 350 K):

p/MPa	0.80	1.00	1.2
Specific enthalpy/(kJ kg^{-1})	461.93	459.12	456.15

(The specific constant-pressure heat capacity is 1.0392 kJ K^{-1} kg^{-1}.)

We compute μ from

$$\mu = -\frac{1}{C_p}\left(\frac{\partial H}{\partial p}\right)_T$$

and we estimate $\left(\frac{\partial H}{\partial p}\right)_T$ from the enthalpy and pressure data. We are given both enthalpy and heat capacity data on a mass basis rather than a molar basis; however, the masses will cancel, so we need not convert to a molar basis.

(a) At 300 K

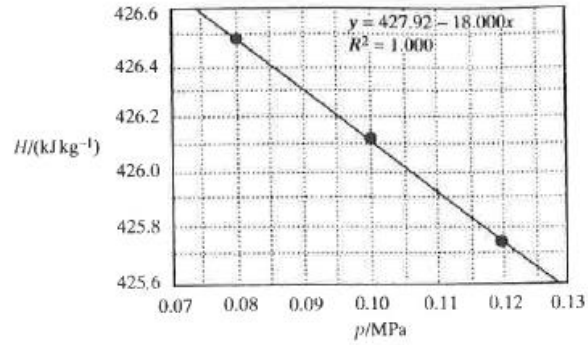


Figure 2.4(a)

The regression analysis gives the slope as $-18.0\ \text{J g}^{-1}\ \text{MPa}^{-1} \approx \left(\frac{\partial H}{\partial p}\right)_T$ (see Figure 2.4(a))

so $\mu = -\frac{-18.0\ \text{kJ kg}^{-1}\ \text{MPa}^{-1}}{0.7649\ \text{kJ kg}^{-1}\ \text{K}^{-1}} = \boxed{23.5\ \text{K MPa}^{-1}}$

(b) At 350 K

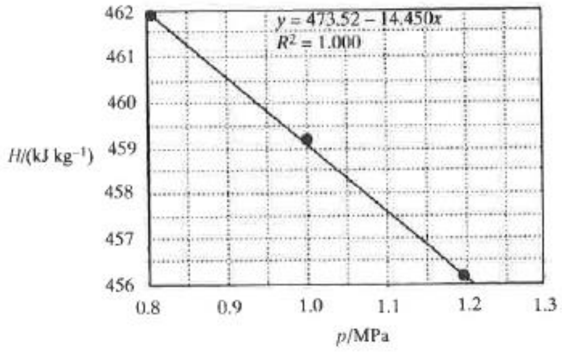


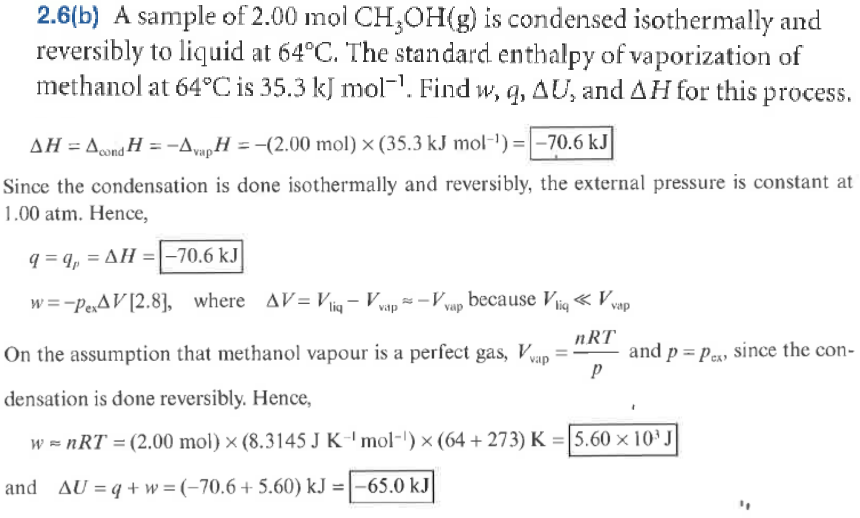
Figure 2.4(b)

The regression analysis gives the slope as $-14.5\ \text{J g}^{-1}\ \text{MPa}^{-1} \approx \left(\frac{\partial H}{\partial p}\right)_T$ (see Figure 2.4(b))

so $\mu = -\frac{-14.5\ \text{kJ kg}^{-1}\ \text{MPa}^{-1}}{1.0392\ \text{kJ kg}^{-1}\ \text{K}^{-1}} = \boxed{14.0\ \text{K MPa}^{-1}}$

Enthalpy and Phase Changes

6. Atkins – 2.6(b)



2.6(b) A sample of 2.00 mol $CH_3OH(g)$ is condensed isothermally and reversibly to liquid at 64°C. The standard enthalpy of vaporization of methanol at 64°C is 35.3 kJ mol^{-1}. Find w, q, ΔU, and ΔH for this process.

$$\Delta H = \Delta_{\text{cond}} H = -\Delta_{\text{vap}} H = -(2.00 \text{ mol}) \times (35.3 \text{ kJ mol}^{-1}) = \boxed{-70.6 \text{ kJ}}$$

Since the condensation is done isothermally and reversibly, the external pressure is constant at 1.00 atm. Hence,

$$q = q_p = \Delta H = \boxed{-70.6 \text{ kJ}}$$

$$w = -p_{\text{ex}} \Delta V \,[2.8], \quad \text{where} \quad \Delta V = V_{\text{liq}} - V_{\text{vap}} \approx -V_{\text{vap}} \text{ because } V_{\text{liq}} \ll V_{\text{vap}}$$

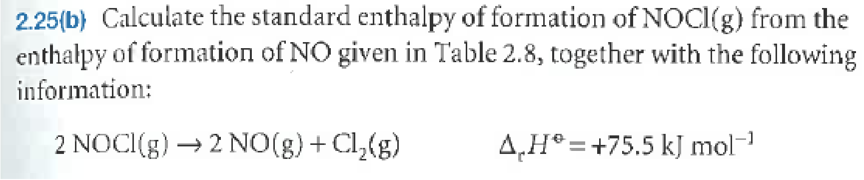
On the assumption that methanol vapour is a perfect gas, $V_{\text{vap}} = \dfrac{nRT}{p}$ and $p = p_{\text{ex}}$, since the condensation is done reversibly. Hence,

$$w \approx nRT = (2.00 \text{ mol}) \times (8.3145 \text{ J K}^{-1} \text{mol}^{-1}) \times (64 + 273) \text{ K} = \boxed{5.60 \times 10^3 \text{ J}}$$

and $\Delta U = q + w = (-70.6 + 5.60) \text{ kJ} = \boxed{-65.0 \text{ kJ}}$

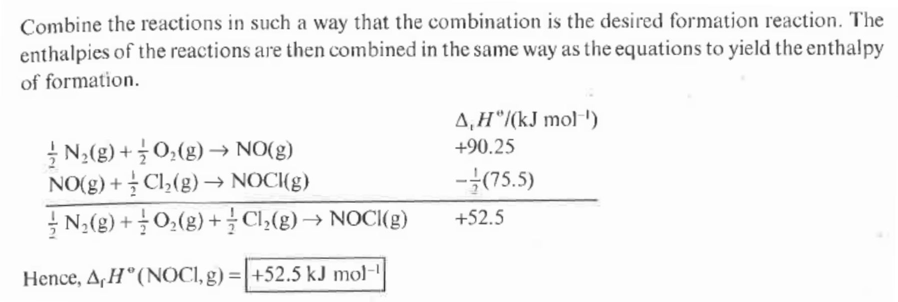
Thermochemistry

7. Atkins – 2.25(b)



2.25(b) Calculate the standard enthalpy of formation of NOCl(g) from the enthalpy of formation of NO given in Table 2.8, together with the following information:

$$2\,NOCl(g) \rightarrow 2\,NO(g) + Cl_2(g) \qquad \Delta_r H^\ominus = +75.5 \text{ kJ mol}^{-1}$$

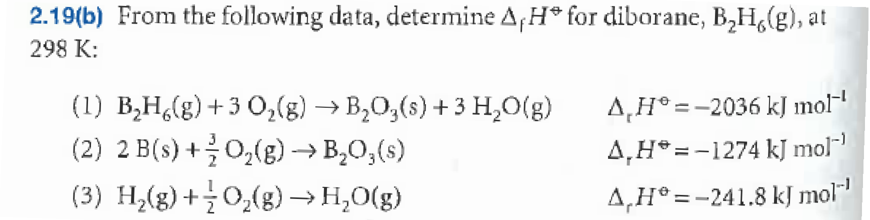


Combine the reactions in such a way that the combination is the desired formation reaction. The enthalpies of the reactions are then combined in the same way as the equations to yield the enthalpy of formation.

	$\Delta_r H^\ominus/(\text{kJ mol}^{-1})$
$\frac{1}{2} N_2(g) + \frac{1}{2} O_2(g) \rightarrow NO(g)$	+90.25
$NO(g) + \frac{1}{2} Cl_2(g) \rightarrow NOCl(g)$	$-\frac{1}{2}(75.5)$
$\frac{1}{2} N_2(g) + \frac{1}{2} O_2(g) + \frac{1}{2} Cl_2(g) \rightarrow NOCl(g)$	+52.5

Hence, $\Delta_f H^\ominus(\text{NOCl, g}) = \boxed{+52.5 \text{ kJ mol}^{-1}}$

8. Atkins – 2.19(b)

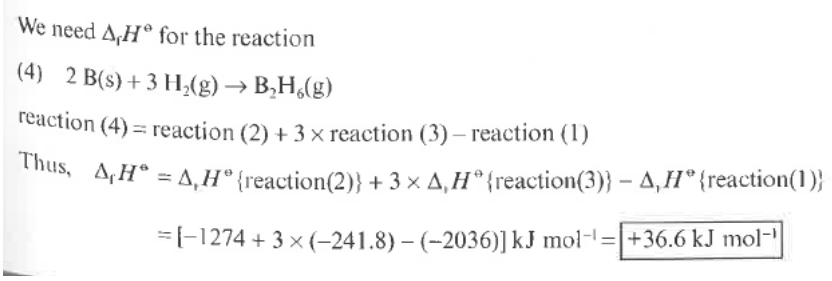


2.19(b) From the following data, determine $\Delta_f H^\ominus$ for diborane, $B_2H_6(g)$, at 298 K:

(1) $B_2H_6(g) + 3\,O_2(g) \rightarrow B_2O_3(s) + 3\,H_2O(g)$ $\quad \Delta_r H^\ominus = -2036 \text{ kJ mol}^{-1}$

(2) $2\,B(s) + \frac{3}{2} O_2(g) \rightarrow B_2O_3(s)$ $\quad \Delta_r H^\ominus = -1274 \text{ kJ mol}^{-1}$

(3) $H_2(g) + \frac{1}{2} O_2(g) \rightarrow H_2O(g)$ $\quad \Delta_r H^\ominus = -241.8 \text{ kJ mol}^{-1}$



We need $\Delta_r H^\ominus$ for the reaction

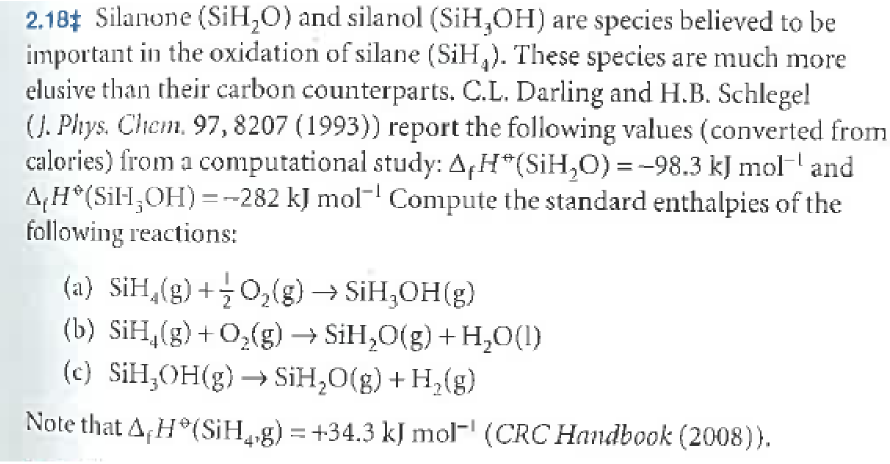
(4) $2\,B(s) + 3\,H_2(g) \rightarrow B_2H_6(g)$

reaction (4) = reaction (2) + 3 × reaction (3) – reaction (1)

Thus, $\Delta_f H^\ominus = \Delta_r H^\ominus\{\text{reaction(2)}\} + 3 \times \Delta_r H^\ominus\{\text{reaction(3)}\} - \Delta_r H^\ominus\{\text{reaction(1)}\}$

$$= [-1274 + 3 \times (-241.8) - (-2036)] \text{ kJ mol}^{-1} = \boxed{+36.6 \text{ kJ mol}^{-1}}$$

9. Atkins – 2.18



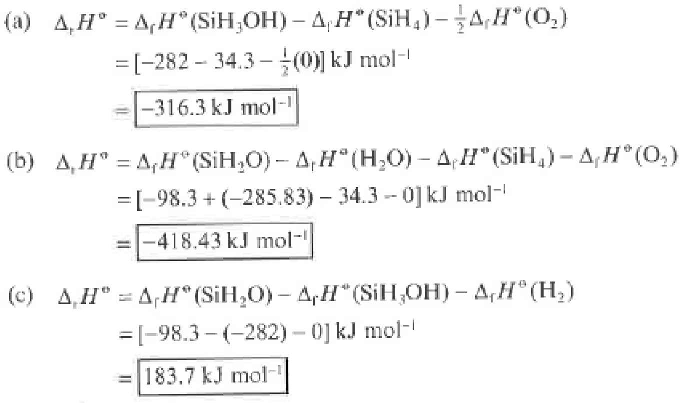
2.18‡ Silanone (SiH_2O) and silanol (SiH_3OH) are species believed to be important in the oxidation of silane (SiH_4). These species are much more elusive than their carbon counterparts. C.L. Darling and H.B. Schlegel (*J. Phys. Chem.* 97, 8207 (1993)) report the following values (converted from calories) from a computational study: $\Delta_f H^\ominus(SiH_2O) = -98.3\ \mathrm{kJ\ mol^{-1}}$ and $\Delta_f H^\ominus(SiH_3OH) = -282\ \mathrm{kJ\ mol^{-1}}$ Compute the standard enthalpies of the following reactions:

(a) $SiH_4(g) + \frac{1}{2}O_2(g) \rightarrow SiH_3OH(g)$

(b) $SiH_4(g) + O_2(g) \rightarrow SiH_2O(g) + H_2O(l)$

(c) $SiH_3OH(g) \rightarrow SiH_2O(g) + H_2(g)$

Note that $\Delta_f H^\ominus(SiH_4, g) = +34.3\ \mathrm{kJ\ mol^{-1}}$ (*CRC Handbook* (2008)).

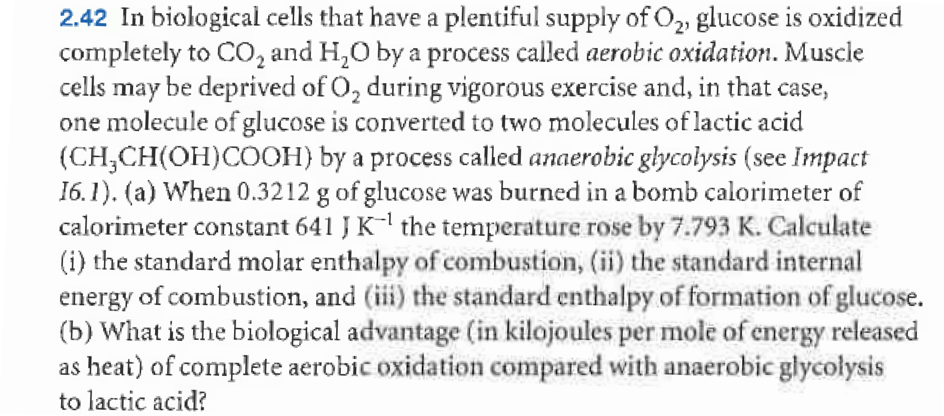


(a)
$$\begin{aligned}\Delta_r H^\circ &= \Delta_f H^\circ(SiH_3OH) - \Delta_f H^\circ(SiH_4) - \tfrac{1}{2}\Delta_f H^\circ(O_2)\\ &= [-282 - 34.3 - \tfrac{1}{2}(0)]\ \mathrm{kJ\ mol^{-1}}\\ &= \boxed{-316.3\ \mathrm{kJ\ mol^{-1}}}\end{aligned}$$

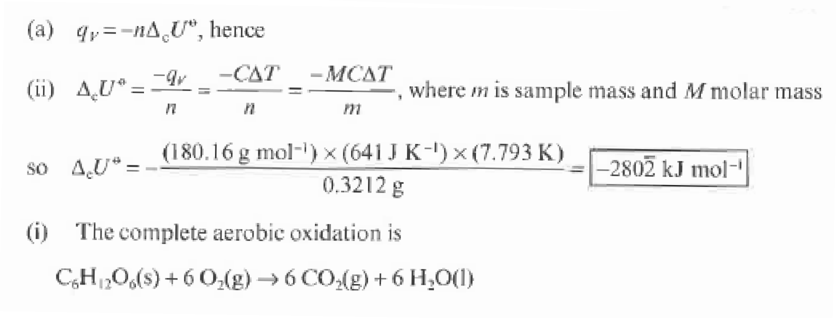
(b)
$$\begin{aligned}\Delta_r H^\circ &= \Delta_f H^\circ(SiH_2O) - \Delta_f H^\circ(H_2O) - \Delta_f H^\circ(SiH_4) - \Delta_f H^\circ(O_2)\\ &= [-98.3 + (-285.83) - 34.3 - 0]\ \mathrm{kJ\ mol^{-1}}\\ &= \boxed{-418.43\ \mathrm{kJ\ mol^{-1}}}\end{aligned}$$

(c)
$$\begin{aligned}\Delta_r H^\circ &= \Delta_f H^\circ(SiH_2O) - \Delta_f H^\circ(SiH_3OH) - \Delta_f H^\circ(H_2)\\ &= [-98.3 - (-282) - 0]\ \mathrm{kJ\ mol^{-1}}\\ &= \boxed{183.7\ \mathrm{kJ\ mol^{-1}}}\end{aligned}$$

10. Atkins – 2.18



2.42 In biological cells that have a plentiful supply of O_2, glucose is oxidized completely to CO_2 and H_2O by a process called *aerobic oxidation*. Muscle cells may be deprived of O_2 during vigorous exercise and, in that case, one molecule of glucose is converted to two molecules of lactic acid ($CH_3CH(OH)COOH$) by a process called *anaerobic glycolysis* (see *Impact I6.1*). (a) When 0.3212 g of glucose was burned in a bomb calorimeter of calorimeter constant 641 J K^{-1} the temperature rose by 7.793 K. Calculate (i) the standard molar enthalpy of combustion, (ii) the standard internal energy of combustion, and (iii) the standard enthalpy of formation of glucose. (b) What is the biological advantage (in kilojoules per mole of energy released as heat) of complete aerobic oxidation compared with anaerobic glycolysis to lactic acid?



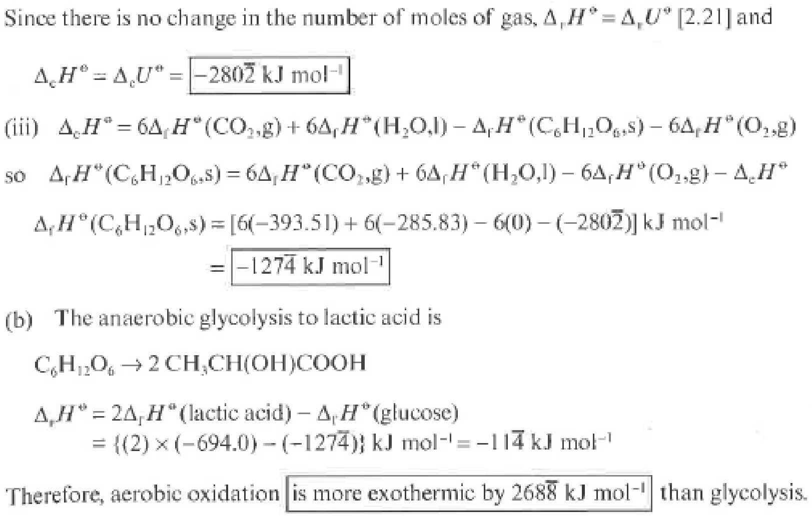
(a) $q_V = -n\Delta_c U^\ominus$, hence

(ii) $\Delta_c U^\ominus = \dfrac{-q_V}{n} = \dfrac{-C\Delta T}{n} = \dfrac{-MC\Delta T}{m}$, where m is sample mass and M molar mass

so $$\Delta_c U^\ominus = -\frac{(180.16\ \mathrm{g\ mol^{-1}}) \times (641\ \mathrm{J\ K^{-1}}) \times (7.793\ \mathrm{K})}{0.3212\ \mathrm{g}} = \boxed{-280\bar{2}\ \mathrm{kJ\ mol^{-1}}}$$

(i) The complete aerobic oxidation is

$$C_6H_{12}O_6(s) + 6\,O_2(g) \rightarrow 6\,CO_2(g) + 6\,H_2O(l)$$



Since there is no change in the number of moles of gas, $\Delta_r H^\circ = \Delta_r U^\circ$ [2.21] and

$$\Delta_c H^\circ = \Delta_c U^\circ = \boxed{-280\overline{2}\ \mathrm{kJ\ mol^{-1}}}$$

(iii) $\Delta_c H^\circ = 6\Delta_f H^\circ(\mathrm{CO_2,g}) + 6\Delta_f H^\circ(\mathrm{H_2O,l}) - \Delta_f H^\circ(\mathrm{C_6H_{12}O_6,s}) - 6\Delta_f H^\circ(\mathrm{O_2,g})$

so $\Delta_f H^\circ(\mathrm{C_6H_{12}O_6,s}) = 6\Delta_f H^\circ(\mathrm{CO_2,g}) + 6\Delta_f H^\circ(\mathrm{H_2O,l}) - 6\Delta_f H^\circ(\mathrm{O_2,g}) - \Delta_c H^\circ$

$$\Delta_f H^\circ(\mathrm{C_6H_{12}O_6,s}) = [6(-393.51) + 6(-285.83) - 6(0) - (-280\overline{2})]\ \mathrm{kJ\ mol^{-1}}$$
$$= \boxed{-127\overline{4}\ \mathrm{kJ\ mol^{-1}}}$$

(b) The anaerobic glycolysis to lactic acid is

$$\mathrm{C_6H_{12}O_6 \rightarrow 2\ CH_3CH(OH)COOH}$$

$$\Delta_r H^\circ = 2\Delta_f H^\circ(\text{lactic acid}) - \Delta_f H^\circ(\text{glucose})$$
$$= \{(2)\times(-694.0) - (-127\overline{4})\}\ \mathrm{kJ\ mol^{-1}} = -11\overline{4}\ \mathrm{kJ\ mol^{-1}}$$

Therefore, aerobic oxidation $\boxed{\text{is more exothermic by } 268\overline{8}\ \mathrm{kJ\ mol^{-1}}}$ than glycolysis.

11. Engel – P4.21

P4.21) Benzoic acid, 1.35 g, is reacted with oxygen in a constant volume calorimeter to form $H_2O(l)$ and $CO_2(g)$. The mass of the water in the inner bath is 1.240×10^3 g. The temperature of the calorimeter and its contents rise 3.45 K as a result of this reaction. Calculate the calorimeter constant.

The reaction is, with $\Delta n = ½$:

$$\mathrm{C_6H_5COOH(s)} + \frac{15}{2}\mathrm{O_2\ (g)} \longrightarrow 7\,\mathrm{CO_2\ (g)} + 3\,\mathrm{H_2O}(\ell)$$

$$\Delta U^\circ_{\text{combustion}} = \Delta H^\circ_{\text{combustion}} - \Delta n\,R\,T$$
$$= \left(-3226.87\ \mathrm{kJ\ mol^{-1}}\right) - \left(\tfrac{1}{2}\right)\times\left(8.314472\ \mathrm{J\ K^{-1}\ mol^{-1}}\right)\times\left(298.15\ \mathrm{K}\right) = 3228.11\ \mathrm{kJ\ mol^{-1}}$$

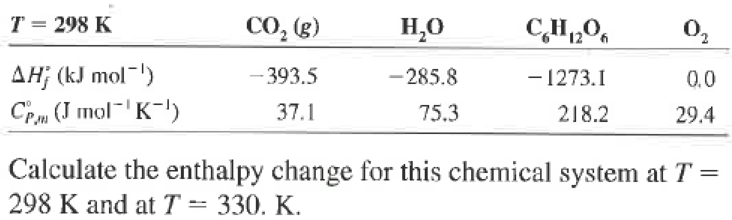
$$C_{\text{calorimeter}} = \frac{\left(-\dfrac{m_s}{M_s}\Delta U_R - \dfrac{m_{H_2O}}{M_{H_2O}} C_{H_2O}\Delta T\right)}{\Delta T}$$

$$= \frac{\left(-\dfrac{(1.350\ \mathrm{g})}{\left(122.13\ \mathrm{g\ mol^{-1}}\right)}\times\left(-3226.87\ \mathrm{kJ\ mol^{-1}}\right) - \dfrac{\left(1.240\times10^3\ \mathrm{g}\right)}{\left(18.02\ \mathrm{g\ mol^{-1}}\right)}\times\left(75.291\ \mathrm{J\ K^{-1}\ mol^{-1}}\right)\times\left(3.45^\circ\mathrm{C}\right)\right)}{\left(3.45^\circ\mathrm{C}\right)}$$

$$\underline{= 5.16\times10^3\ \mathrm{J\ ^\circ C^{-1}}}$$

12. Engel – P4.24

$6CO_2\,(g) + 6H_2O\,(l) \rightarrow C_6H_{12}O_6\,(s) + 6O_2\,(g)$.



$T = 298$ K	$CO_2\,(g)$	H_2O	$C_6H_{12}O_6$	O_2
ΔH_f° (kJ mol^{-1})	−393.5	−285.8	−1273.1	0.0
$C_{P,m}^\circ$ (J mol^{-1} K^{-1})	37.1	75.3	218.2	29.4

Calculate the enthalpy change for this chemical system at $T =$ 298 K and at $T =$ 330. K.

We first calculate the change in heat capacity:

$$\Delta C_{p,m} = 6\,C_{p,m}(O_2,g) + C_{p,m}(C_6H_{12}O_6,s) - 6\,C_{p,m}(H_2O,\ell) - 6\,C_{p,m}(CO_2,g)$$

$$= 6\times\left(29.4\ \text{J K}^{-1}\ \text{mol}^{-1}\right) + \left(218.2\ \text{J K}^{-1}\ \text{mol}^{-1}\right) - 6\times\left(75.3\ \text{J K}^{-1}\ \text{mol}^{-1}\right) - 6\times\left(37.1\ \text{J K}^{-1}\ \text{mol}^{-1}\right)$$

$$= -279.8\ \text{J K}^{-1}\ \text{mol}^{-1}$$

The enthalpy of reaction at 298 K is:

$$\Delta H^\circ_{\text{reaction}}(298\ \text{K}) = 6\,\Delta H^\circ_f(O_2,g) + \Delta H^\circ_f(C_6H_{12}O_6,s) - 6\,\Delta H^\circ_f(H_2O,\ell) - 6\,\Delta H^\circ_f(CO_2,g)$$

$$= 6\times\left(0\ \text{kJ mol}^{-1}\right) + \left(-1273.1\ \text{kJ mol}^{-1}\right) - 6\times\left(-285.8\ \text{kJ mol}^{-1}\right) - 6\times\left(-393.5\ \text{kJ mol}^{-1}\right)$$

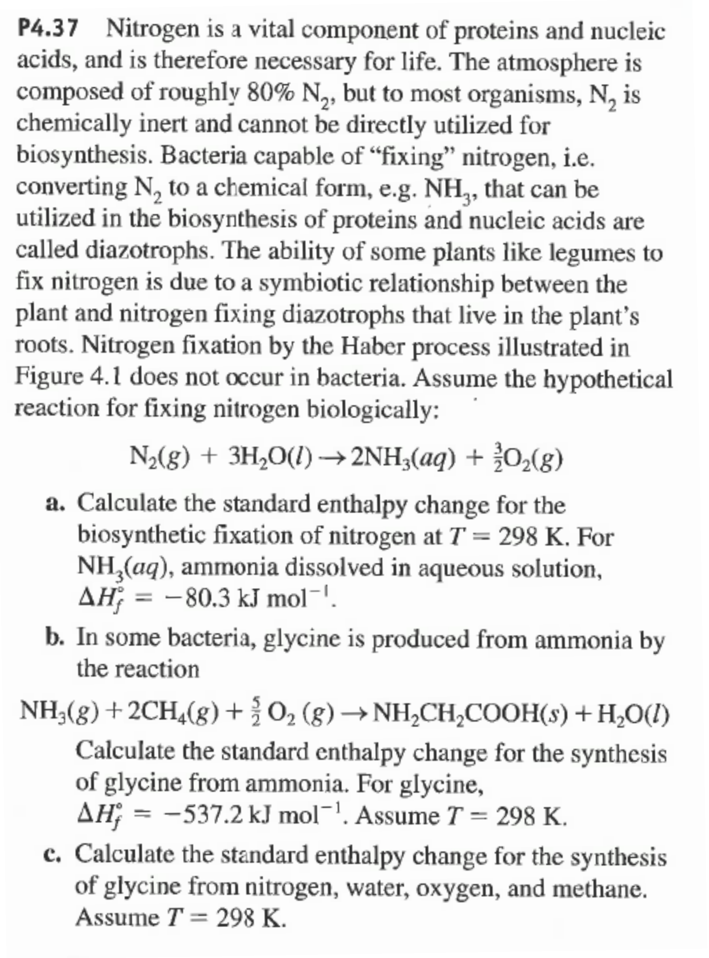
$$= 2802.7\ \text{kJ mol}^{-1}$$

Then the enthalpy at 330 K is:

$$\Delta H^\circ_{\text{reaction}}(330\ \text{K}) = \Delta H^\circ_{\text{reaction}}(298\ \text{K}) + \Delta C_{p,m}\ \Delta T = \left(2802.0\ \text{kJ mol}^{-1}\right) + \left(-279.8\ \text{J K}^{-1}\ \text{mol}^{-1}\right)\times(32\ \text{K})$$

$$\underline{=\ 2793.7\ \text{kJ mol}^{-1}}$$

13. Engel – P4.37



P4.37 Nitrogen is a vital component of proteins and nucleic acids, and is therefore necessary for life. The atmosphere is composed of roughly 80% N_2, but to most organisms, N_2 is chemically inert and cannot be directly utilized for biosynthesis. Bacteria capable of "fixing" nitrogen, i.e. converting N_2 to a chemical form, e.g. NH_3, that can be utilized in the biosynthesis of proteins and nucleic acids are called diazotrophs. The ability of some plants like legumes to fix nitrogen is due to a symbiotic relationship between the plant and nitrogen fixing diazotrophs that live in the plant's roots. Nitrogen fixation by the Haber process illustrated in Figure 4.1 does not occur in bacteria. Assume the hypothetical reaction for fixing nitrogen biologically:

$$N_2(g) + 3H_2O(l) \rightarrow 2NH_3(aq) + \tfrac{3}{2}O_2(g)$$

a. Calculate the standard enthalpy change for the biosynthetic fixation of nitrogen at $T = 298$ K. For $NH_3(aq)$, ammonia dissolved in aqueous solution, $\Delta H_f^\circ = -80.3$ kJ mol^{-1}.

b. In some bacteria, glycine is produced from ammonia by the reaction

$$NH_3(g) + 2CH_4(g) + \tfrac{5}{2}O_2(g) \rightarrow NH_2CH_2COOH(s) + H_2O(l)$$

Calculate the standard enthalpy change for the synthesis of glycine from ammonia. For glycine, $\Delta H_f^\circ = -537.2$ kJ mol^{-1}. Assume $T = 298$ K.

c. Calculate the standard enthalpy change for the synthesis of glycine from nitrogen, water, oxygen, and methane. Assume $T = 298$ K.

a) For elements in standard state, $\Delta H^{o}_{f} = 0$. So the enthalpy of reaction is:

$$\Delta H^{\circ}_{\text{reaction}}(298\,\text{K}) = (2)\,\Delta H^{\circ}_{f}(\text{NH}_3,\text{aq}) + (-3)\,\Delta H^{\circ}_{f}(\text{H}_2\text{O},\ell)$$
$$= 2\times\left(-80.3\,\text{kJ mol}^{-1}\right) + (-3)\times\left(-285.8\,\text{kJ mol}^{-1}\right)\ \underline{=\ 696.8\,\text{kJ mol}^{-1}}$$

b) The enthalpy of reaction is:

$$\Delta H^{\circ}_{\text{reaction}}(298\,\text{K})$$
$$= (3)\,\Delta H^{\circ}_{f}(\text{H}_2\text{O},\ell) + \Delta H^{\circ}_{f}(\text{NH}_2\text{CH}_2\text{COOH,s}) + (-2)\,\Delta H^{\circ}_{f}(\text{CH}_4,\text{g}) + (-1)\,\Delta H^{\circ}_{f}(\text{NH}_3,\text{g})$$
$$= 3\times\left(-285.8\,\text{kJ mol}^{-1}\right) + (1)\left(-537.2\,\text{kJ mol}^{-1}\right) + (\text{-}\,2)\left(-74.6\,\text{kJ mol}^{-1}\right) + (-1)\left(-45.9\,\text{kJ mol}^{-1}\right)$$
$$\underline{=\ -1199.5\,\text{kJ mol}^{-1}}$$

c) To calculate the enthalpy for the formation of glycine we use:

$$\text{N}_2\,(\text{g}) + 3\,\text{H}_2\text{O}\,(\ell) \longrightarrow 2\,\text{NH}_3\,(\text{aq}) + \frac{3}{2}\,\text{O}_2\,(\text{g}) \qquad \Delta H^{\circ}_{\text{reaction}} = 696.8\,\text{kJ}$$

$$2\,\text{NH}_3\,(\text{g}) + 4\,\text{CH}_4\,(\text{g}) + 5\,\text{O}_2\,(\text{g})$$
$$\longrightarrow 2\,\text{NH}_2\text{CH}_2\text{COOH}\,(\text{s}) + 6\,\text{H}_2\text{O}\,(\ell)$$

$$\Delta H^{\circ}_{\text{reaction}} = 2\times(-1199.5\,\text{kJ})$$

$$\text{N}_2\,(\text{g}) + 4\,\text{CH}_4\,(\text{g}) + \frac{7}{2}\,\text{O}_2\,(\text{g})$$
$$\longrightarrow 2\,\text{NH}_2\text{CH}_2\text{COOH}\,(\text{s}) + 3\,\text{H}_2\text{O}\,(\ell) \qquad \Delta H^{\circ}_{\text{reaction}} = -1702.2\ \text{kJ}$$

Therefore, the enthalpy per mole of glycine is:

$$\Delta H^{\circ}_{\text{formation}}(\text{glycine}) = \frac{(-1702.2\ \text{kJ})}{2}\ \ \underline{=\ \ -851.1\ \text{kJ mol}^{-1}}$$

Extra, do not hand in

Good model problems for exam

1. **Engel – P3.14**

Use $(\partial U/\partial V)_T = (\beta T - \kappa P)/\kappa$ to evaluate $(\partial U/\partial V)_T$ for an ideal gas.
For an ideal gas:

$$\kappa = -\frac{1}{V}\left(\frac{\partial V}{\partial p}\right)_T = -\frac{1}{V}\left(-\frac{nRT}{p^2}\right) = \frac{nRT}{Vp^2}$$

$$\beta = \frac{1}{V}\left(\frac{\partial V}{\partial T}\right)_p = \frac{1}{V}\left(\frac{nR}{p}\right) = \frac{nR}{Vp}$$

Therefore:

$$\left(\frac{\partial U}{\partial V}\right)_T = \frac{(\beta T - \kappa p)}{\kappa} = \frac{\beta T}{\kappa} - p = \frac{nRT}{Vp} \times \frac{Vp^2}{nRT} - p \underline{= p - p = 0}$$

2. **Engel – P3.21**
The Joule coefficient is defined by $(\partial T/\partial V)_U = 1/C_V[P - T(\partial P/\partial T)_V]$. Calculate the Joule coefficient for an ideal gas and for a van der Waals gas.
For an ideal gas:

$$p = \frac{nRT}{V}$$

$$\left(\frac{\partial T}{\partial V}\right)_U = \frac{1}{C_V}\left[p - T\left(\frac{\partial p}{\partial T}\right)_V\right] = \frac{1}{C_V}\left[p - \frac{nRT}{V}\right] \underline{= 0}$$

For a van der Waals gas:

$$p = \frac{nRT}{(V - nb)} - \frac{n^2 a}{V^2}$$

$$\left(\frac{\partial T}{\partial V}\right)_U = \frac{1}{C_V}\left[p - T\left(\frac{\partial p}{\partial T}\right)_V\right] = \underline{\frac{1}{C_V}\left[p - \frac{nRT}{(V\text{-}nb)}\right]}$$

3. **Engel – P3.26**

Derive the following expression for calculating the isothermal change in the constant volume heat capacity: $(\partial C_V/\partial V)_T = T(\partial^2 P/\partial T^2)_V$.

$$\left(\frac{\partial C_V}{\partial V}\right)_T = \left(\frac{\partial}{\partial V}\left(\frac{\partial U}{\partial T}\right)_V\right)_T = \left(\frac{\partial}{\partial T}\left(\frac{\partial U}{\partial V}\right)_T\right)_T$$

The order of differentiation can be reversed since U is a state function. Using:

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

We obtain:

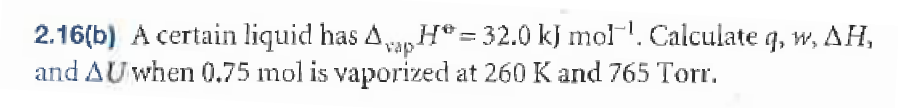
$$\left(\frac{\partial C_V}{\partial V}\right)_T = \left(\frac{\partial}{\partial T}\left(T\left(\frac{\partial p}{\partial T}\right)_V - p\right)\right)_V = \left(\frac{\partial p}{\partial T}\right)_V + T\left(\frac{\partial^2 p}{\partial T^2}\right)_V - \left(\frac{\partial p}{\partial T}\right)_V \underline{= T\left(\frac{\partial^2 p}{\partial T^2}\right)_V}$$

4. **Engel – P3.11**

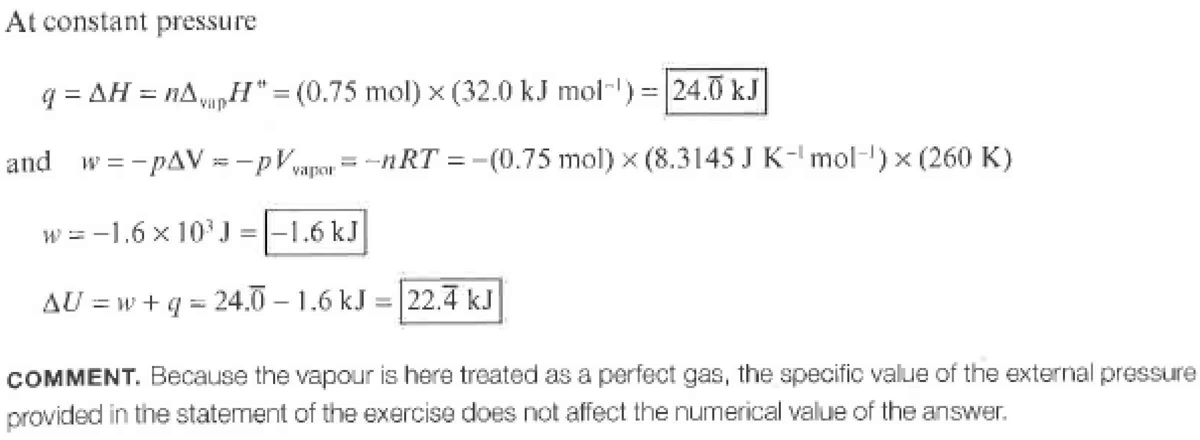
Obtain an expression for the isothermal compressibility $\kappa = -1/V(\partial V/\partial P)_T$ for a van der Waals gas.

$$\kappa = -\frac{1}{V_m}\left(\frac{\partial V_m}{\partial p}\right)_T = -\frac{1}{V_m\left(\frac{\partial p}{\partial V_m}\right)_T} = -\frac{1}{V_m\left(\frac{\partial}{\partial V_m}\left[\frac{RT}{(V_m - b)} - \frac{2}{V_m^{\ 2}}\right]\right)} = -\frac{1}{V_m\left[\frac{2a}{V_m^{\ 3}} - \frac{RT}{(V_m - b)^2}\right]}$$

5. **Atkins – 2.16(b)**



2.16(b) A certain liquid has $\Delta_{vap}H^{\ominus} = 32.0\ \mathrm{kJ\ mol^{-1}}$. Calculate q, w, ΔH, and ΔU when 0.75 mol is vaporized at 260 K and 765 Torr.



At constant pressure

$$q = \Delta H = n\Delta_{vap}H^{\ominus} = (0.75\ \mathrm{mol}) \times (32.0\ \mathrm{kJ\ mol^{-1}}) = \boxed{24.\bar{0}\ \mathrm{kJ}}$$

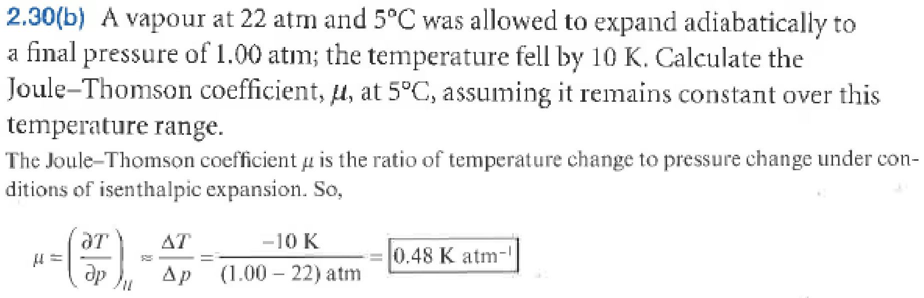
and $w = -p\Delta V = -pV_{vapor} = -nRT = -(0.75\ \mathrm{mol}) \times (8.3145\ \mathrm{J\ K^{-1}\ mol^{-1}}) \times (260\ \mathrm{K})$

$$w = -1.6 \times 10^3\ \mathrm{J} = \boxed{-1.6\ \mathrm{kJ}}$$

$$\Delta U = w + q = 24.\bar{0} - 1.6\ \mathrm{kJ} = \boxed{22.\bar{4}\ \mathrm{kJ}}$$

COMMENT. Because the vapour is here treated as a perfect gas, the specific value of the external pressure provided in the statement of the exercise does not affect the numerical value of the answer.

6. Atkins - 2.30(b)

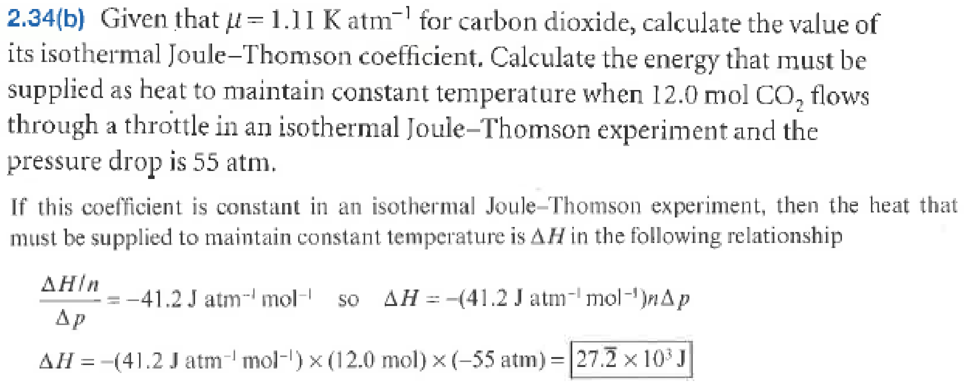


2.30(b) A vapour at 22 atm and 5°C was allowed to expand adiabatically to a final pressure of 1.00 atm; the temperature fell by 10 K. Calculate the Joule–Thomson coefficient, μ, at 5°C, assuming it remains constant over this temperature range.

The Joule–Thomson coefficient μ is the ratio of temperature change to pressure change under conditions of isenthalpic expansion. So,

$$\mu = \left(\frac{\partial T}{\partial p}\right)_H \approx \frac{\Delta T}{\Delta p} = \frac{-10\ \text{K}}{(1.00 - 22)\ \text{atm}} = \boxed{0.48\ \text{K atm}^{-1}}$$

7. Atkins – 2.34(b)



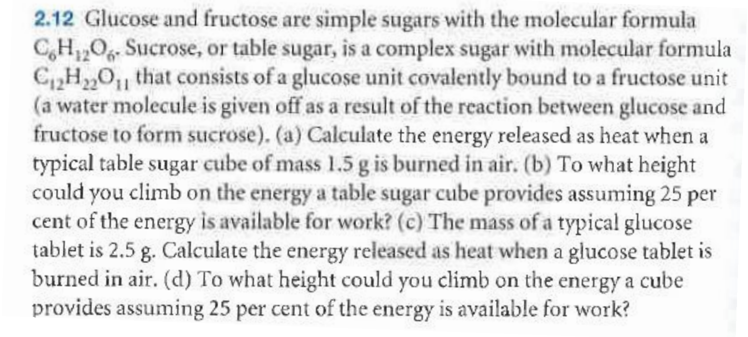
2.34(b) Given that $\mu = 1.11\ \text{K atm}^{-1}$ for carbon dioxide, calculate the value of its isothermal Joule–Thomson coefficient. Calculate the energy that must be supplied as heat to maintain constant temperature when 12.0 mol CO_2 flows through a throttle in an isothermal Joule–Thomson experiment and the pressure drop is 55 atm.

If this coefficient is constant in an isothermal Joule–Thomson experiment, then the heat that must be supplied to maintain constant temperature is ΔH in the following relationship

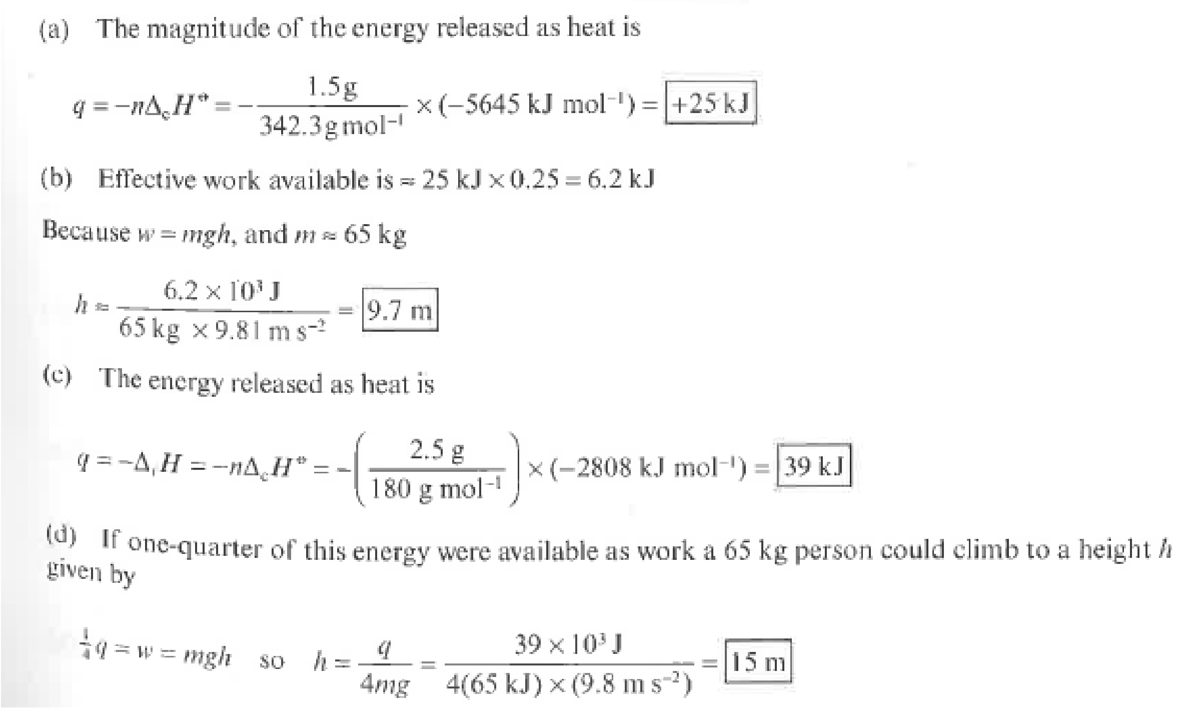
$$\frac{\Delta H/n}{\Delta p} = -41.2\ \text{J atm}^{-1}\ \text{mol}^{-1} \quad \text{so} \quad \Delta H = -(41.2\ \text{J atm}^{-1}\ \text{mol}^{-1})n\Delta p$$

$$\Delta H = -(41.2\ \text{J atm}^{-1}\ \text{mol}^{-1}) \times (12.0\ \text{mol}) \times (-55\ \text{atm}) = \boxed{27.\bar{2} \times 10^3\ \text{J}}$$

8. Atkins – 2.12



2.12 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

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

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

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

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

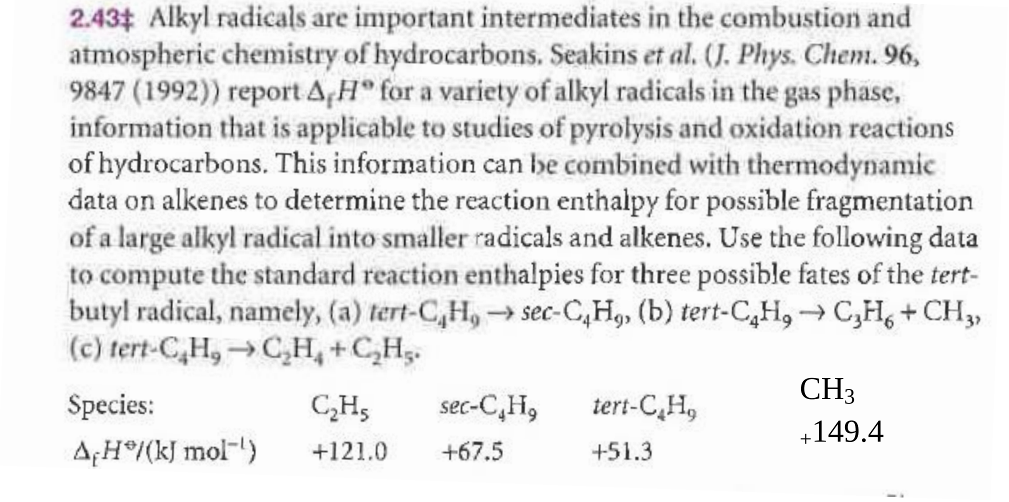
(c) The energy released as heat is

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

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

$$\tfrac{1}{4}q = w = mgh \quad \text{so} \quad h = \frac{q}{4mg} = \frac{39 \times 10^3\ \text{J}}{4(65\ \text{kJ}) \times (9.8\ \text{m s}^{-2})} = \boxed{15\ \text{m}}$$

9. Atkins – 2.43



2.43‡ Alkyl radicals are important intermediates in the combustion and atmospheric chemistry of hydrocarbons. Seakins *et al.* (*J. Phys. Chem.* **96**, 9847 (1992)) report $\Delta_f H^\circ$ for a variety of alkyl radicals in the gas phase, information that is applicable to studies of pyrolysis and oxidation reactions of hydrocarbons. This information can be combined with thermodynamic data on alkenes to determine the reaction enthalpy for possible fragmentation of a large alkyl radical into smaller radicals and alkenes. Use the following data to compute the standard reaction enthalpies for three possible fates of the *tert*-butyl radical, namely, (a) *tert*-$C_4H_9 \rightarrow$ *sec*-C_4H_9, (b) *tert*-$C_4H_9 \rightarrow C_3H_6 + CH_3$, (c) *tert*-$C_4H_9 \rightarrow C_2H_4 + C_2H_5$.

Species:	C_2H_5	*sec*-C_4H_9	*tert*-C_4H_9	CH_3
$\Delta_f H^\circ/(\mathrm{kJ\ mol^{-1}})$	+121.0	+67.5	+51.3	+149.4

a) $\mathrm{tert-C_4H_9 \rightarrow sec-C_4H_9}$

$$\Delta H^\circ_{reaction} = \Delta H^\circ_f(sec - C_4H_9) - \Delta H^\circ_f(tert - C_4H_9)$$
$$= 67.5\ \mathrm{kJ}\ mol^{-1} - 51.3\ kJ\ mol^{-1} = 16.2\ kJ\ mol^{-1}$$

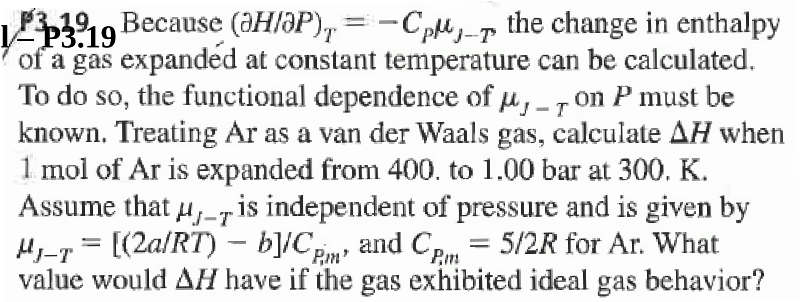
b) $\mathrm{tert-C_4H_9 \rightarrow C_3H_6 + CH_3}$

$$\Delta H^\circ_{reaction} = \Delta H^\circ_f(CH_3) + \Delta H^\circ_f(C_3H_6) - \Delta H^\circ_f(tert - C_4H_9)$$
$$= 149.4\ \mathrm{kJ}\ mol^{-1} + 53.3\ \mathrm{kJ}\ mol^{-1} - 51.3\ kJ\ mol^{-1}$$
$$= 103.4\ kJ\ mol^{-1}$$

c) $\mathrm{tert-C_4H_9 \rightarrow C_2H_4 + C_2H_5}$

$$\Delta H^\circ_{reaction} = \Delta H^\circ_f(C_2H_5) + \Delta H^\circ_f(C_2H_4) - \Delta H^\circ_f(tert - C_4H_9)$$
$$= 121.0\ \mathrm{kJ}\ mol^{-1} + 52.4\ \mathrm{kJ}\ mol^{-1} - 51.3\ kJ\ mol^{-1}$$
$$= 122.1\ kJ\ mol^{-1}$$

10. Engel – P3.19



P3.19 Because $(\partial H/\partial P)_T = -C_P\mu_{J-T}$, the change in enthalpy of a gas expanded at constant temperature can be calculated. To do so, the functional dependence of μ_{J-T} on P must be known. Treating Ar as a van der Waals gas, calculate ΔH when 1 mol of Ar is expanded from 400. to 1.00 bar at 300. K. Assume that μ_{J-T} is independent of pressure and is given by $\mu_{J-T} = [(2a/RT) - b]/C_{P,m}$, and $C_{P,m} = 5/2R$ for Ar. What value would ΔH have if the gas exhibited ideal gas behavior?

$$\Delta H_m = -\int_{p_i}^{p_f} C_{p,m}\,\mu_{J\text{-}T}\,dp \approx -C_{p,m}\,\mu_{J\text{-}T}(p_f - p_i)$$

$$= -C_{p,m}\frac{1}{C_{p,m}}\left(\frac{2\times(0.1355\,\mathrm{m^6\ Pa\ mol^{-2}})}{(8.314472\,\mathrm{J\ mol^{-1}\ K^{-1}})\times(300\,\mathrm{K})} - 0.03201\times10^{-3}\ \mathrm{m^3\ mol^{-1}}\right)$$

$$\times(1.00\times10^5\ \mathrm{Pa} - 400\times10^5\ \mathrm{Pa}) \underline{= 3.06\times10^3\ \mathrm{J}}$$

For an ideal gas, $\Delta H_m = 0$, because $\mu_{J\text{-}T} = 0$ for and ideal gas.

11. Engel – P3.22

Use the relation $(\partial U/\partial V)_T = T(\partial P/\partial T)_V - P$ and the cyclic rule to obtain an expression for the internal pressure, $(\partial U/\partial V)_T$, in terms of P, β, T, and κ.

$$\left(\frac{\partial \mathrm{U}}{\partial \mathrm{V}}\right)_{\mathrm{T}} = \mathrm{T}\left(\frac{\partial \mathrm{p}}{\partial \mathrm{T}}\right)_{\mathrm{V}} - \mathrm{p} = -\mathrm{T}\frac{\left(\frac{\partial \mathrm{V}}{\partial \mathrm{T}}\right)_{\mathrm{p}}}{\left(\frac{\partial \mathrm{V}}{\partial \mathrm{p}}\right)_{\mathrm{T}}} - \mathrm{p} = \mathrm{T}\frac{\mathrm{V}\beta}{\mathrm{V}\kappa} - \mathrm{p} = \underline{\mathrm{T}\frac{\beta}{\kappa} - \mathrm{p}}$$

12. Engel – P4.8

P4.8) Calculate $\Delta H^{\circ}_{reaction}$ at 650 K for the reaction $4NH_3(g) + 6NO(g) \rightarrow 5N_2(g) + 6H_2O(g)$ using the temperature dependence of the heat capacities from the data tables.

$$\Delta \mathrm{H}_{\mathrm{f}}^{\circ}(650\,\mathrm{K}) = \Delta \mathrm{H}_{\mathrm{f}}^{\circ}(298.15\,\mathrm{K}) + \int_{298.15\mathrm{K}}^{650} \Delta \mathrm{C}_{\mathrm{p}}\left(\frac{\mathrm{T}}{\mathrm{K}}\right) \mathrm{d}\frac{\mathrm{T}}{\mathrm{K}}$$

$$\Delta \mathrm{C}_{\mathrm{p}} = 5\,\mathrm{C}_{\mathrm{p,m}}(\mathrm{N}_2,\mathrm{g}) + 6\,\mathrm{C}_{\mathrm{p,m}}(\mathrm{H}_2\mathrm{O},\mathrm{g}) - 4\,\mathrm{C}_{\mathrm{p,m}}(\mathrm{NH}_3,\mathrm{g}) - 6\,\mathrm{C}_{\mathrm{p,m}}(\mathrm{NO},\mathrm{g})$$

$$= \begin{bmatrix} (5\times 30.81 + 6\times 33.80 - 4\times 29.29 - 6\times 33.58) \\ -(5\times 0.01187 + 6\times 0.00795 - 4\times 0.01103 - 6\times 0.02593)\frac{\mathrm{T}}{\mathrm{K}} \\ +(5\times 2.3968 + 6\times 2.8228 - 4\times 4.2446 - 6\times 5.3326)\frac{\mathrm{T}}{\mathrm{K}} \\ -(5\times 1.0176 + 6\times 1.3115 - 4\times 2.7706 - 6\times 2.7744)\frac{\mathrm{T}}{\mathrm{K}} \end{bmatrix} \mathrm{J\,K^{-1}\,mol^{-1}}$$

$$\int_{298.15\,\mathrm{K}}^{650} \Delta \mathrm{C}_{\mathrm{p}}\left(\frac{\mathrm{T}}{\mathrm{K}}\right) \mathrm{d}\frac{\mathrm{T}}{\mathrm{K}} = \left[38.21 + 0.00441\frac{\mathrm{T}}{\mathrm{K}} - 2.0053\times 10^{-4}\frac{\mathrm{T}^2}{\mathrm{K}^2} + 1.4772\times 10^{-8}\frac{\mathrm{T}^3}{\mathrm{K}^3}\right] \mathrm{J\,K^{-1}\,mol^{-1}}$$

$$\int_{298.15\,\mathrm{K}}^{650} \left[\left(38.21 + 0.00441\frac{\mathrm{T}}{\mathrm{K}} - 2.0053\times 10^{-4}\frac{\mathrm{T}^2}{\mathrm{K}^2} + 1.4772\times 10^{-8}\frac{\mathrm{T}^3}{\mathrm{K}^3}\right)\mathrm{d}\frac{\mathrm{T}}{\mathrm{K}}\right] \mathrm{J\,mol^{-1}}$$

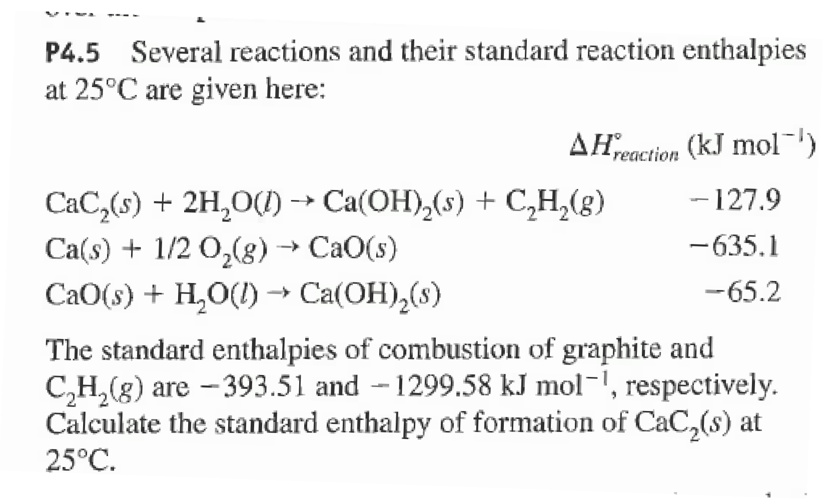
$$= (13.444 - 0.736 - 16.585 + 0.630)\ \mathrm{kJ\,mol^{-1}} \quad = \quad -1.775\ \mathrm{kJ\,mol^{-1}}$$

$$\Delta \mathrm{H}_{\mathrm{f}}^{\circ}(298.15\,\mathrm{K}) = 5\,\Delta \mathrm{H}_{\mathrm{f}}^{\circ}(\mathrm{N}_2,\mathrm{g}) + 6\,\Delta \mathrm{H}_{\mathrm{f}}^{\circ}(\mathrm{H}_2\mathrm{O},\mathrm{g}) - 4\,\Delta \mathrm{H}_{\mathrm{f}}^{\circ}(\mathrm{NH}_3,\mathrm{g}) - 6\,\Delta \mathrm{H}_{\mathrm{f}}^{\circ}(\mathrm{NO},\mathrm{g})$$

$$\Delta \mathrm{H}_{\mathrm{f}}^{\circ}(298.15\,\mathrm{K}) = 6\times(-241.8\,\mathrm{kJ\,mol^{-1}}) + 4\times(45.9\,\mathrm{kJ\,mol^{-1}}) + 6\times(-91.3\,\mathrm{kJ\,mol^{-1}}) = -1814\,\mathrm{kJ\,mol^{-1}}$$

$$\Delta \mathrm{H}_{\mathrm{f}}^{\circ}(650\,\mathrm{K}) = (-1814\ \mathrm{kJ\,mol^{-1}}) + (-1.775\ \mathrm{kJ\,mol^{-1}})\ \ \underline{=\ \ -1812\ \mathrm{kJ\,mol^{-1}}}$$

13. Engel – P4.5



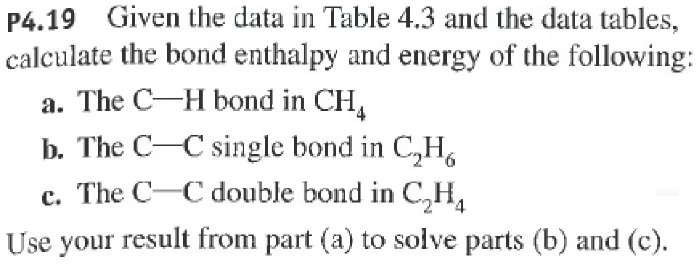
P4.5 Several reactions and their standard reaction enthalpies at 25°C are given here:

	$\Delta H^{\circ}_{reaction}$ (kJ mol^{-1})
$CaC_2(s) + 2H_2O(l) \rightarrow Ca(OH)_2(s) + C_2H_2(g)$	−127.9
$Ca(s) + 1/2\ O_2(g) \rightarrow CaO(s)$	−635.1
$CaO(s) + H_2O(l) \rightarrow Ca(OH)_2(s)$	−65.2

The standard enthalpies of combustion of graphite and $C_2H_2(g)$ are −393.51 and −1299.58 kJ mol^{-1}, respectively. Calculate the standard enthalpy of formation of $CaC_2(s)$ at 25°C.

$Ca(OH)_2\ (s) + C_2H_2\ (g) \longrightarrow CaC_2\ (s) + 2\,H_2O(\ell)$	$127.9\ kJ\ mol^{-1}$
$CaO\ (s) + H_2O\ (\ell) \longrightarrow Ca(OH)_2\ (s)$	$-65.2\ kJ\ mol^{-1}$
$3\,CO_2\ (g) + H_2O\ (\ell) \longrightarrow C_2H_2\ (s) + \frac{5}{2}O_2\ (g)$	$1299.58\ kJ\ mol^{-1}$
$2\,C\ (s) + 2\,O_2\ (g) \longrightarrow 2\,CO_2\ (g)$	$2 \times (-393.51 kJ\ mol^{-1})$
$C\ (s) + \frac{1}{2}O_2\ (g) \longrightarrow CaO\ (s)$	$-635.1\ kJ\ mol^{-1}$
$2\,C\ (s) + Ca\ (s) \longrightarrow CaC_2\ (s)$	$\Delta H^{\circ}_{f} = -59.8\ kJ\ mol^{-1}$

14. Engel – P4.19



P4.19 Given the data in Table 4.3 and the data tables, calculate the bond enthalpy and energy of the following:

- **a.** The C—H bond in CH_4
- **b.** The C—C single bond in C_2H_6
- **c.** The C—C double bond in C_2H_4

Use your result from part (a) to solve parts (b) and (c).

a) $CH_4\ (g) \longrightarrow C\ (g) + 4\,H\ (g)$

$$\Delta H^{\circ}_{reaction} = 4\,\Delta H^{\circ}_{f}(H,g) + \Delta H^{\circ}_{f}(C,g) - \Delta H^{\circ}_{f}(CH_4,g)$$
$$= (4)\times(218.0\ kJ\ mol^{-1}) - (-716.7\ kJ\ mol^{-1}) + (74.6\ kJ\ mol^{-1}) = 1663.3\ kJ\ mol^{-1}$$

The average C-H bond enthalpy is then:

$$\Delta H^{bond}_{avrg} = \frac{(1663.30\ kJ\ mol^{-1})}{4} \underline{= 415.8\ kJ\ mol^{-1}}$$

And the average C-H bond free energy:

$$\Delta U^\circ_{\text{reaction}} = \Delta H^\circ_{\text{reaction}} - \Delta n\ R\ T = \left(1663.3\ \text{kJ mol}^{-1}\right) - (3) \times \left(8.314472\ \text{J K}^{-1}\ \text{mol}^{-1}\right) \times (298.15\ \text{K})$$
$$= 1655.9\ \text{kJ mol}^{-1}$$

$$\Delta U^{\text{bond}}_{\text{avrg}} = \frac{\left(1655.9\ \text{kJ mol}^{-1}\ \text{kJ mol}^{-1}\right)}{4} \underline{= 414.0\ \text{kJ mol}^{-1}}$$

b) $C_2H_6\,(g) \longrightarrow 2\,C\,(g) + 6\,H\,(g)$

$$\Delta H^\circ_{\text{reaction}} = 6\,\Delta H^\circ_f\,(H, g) + 2\,\Delta H^\circ_f\,(C, g) - \Delta H^\circ_f\,(C_2H_6, g)$$
$$= (6) \times \left(218.0\ \text{kJ mol}^{-1}\right) + (2) \times \left(716.7\ \text{kJ mol}^{-1}\right) - \left(-84.0\ \text{kJ mol}^{-1}\right) = 2825.4\ \text{kJ mol}^{-1}$$

$$\Delta H^\circ_{\text{reaction}} = 6 \times \text{C - H bond enthalpy} + \text{C - C bond enthalpy}$$

$$\text{C-C bond enthalpy} = \left(2825.4\ \text{kJ mol}^{-1}\right) - 6 \times \left(416.0\ \text{kJ mol}^{-1}\right)\ \ \underline{=\ \ 329\ \text{kJ mol}^{-1}}$$

$$\Delta U^\circ_{\text{reaction}} = \Delta H^\circ_{\text{reaction}} - \Delta n\ R\ T = \left(2825.4\ \text{kJ mol}^{-1}\right) - (7) \times \left(8.314472\ \text{J K}^{-1}\ \text{mol}^{-1}\right) \times (298.15\ \text{K})$$
$$= 2808.0\ \text{kJ mol}^{-1}$$

$$\Delta U^\circ_{\text{reaction}} = 6 \times \text{C - H bond energy} + \text{C - C bond energy}$$

$$\text{C-C bond energy} = \left(2808\ \text{kJ mol}^{-1}\right) - 6 \times \left(414.0\ \text{kJ mol}^{-1}\right)\ \ \underline{\approx\ \ 324.0\ \text{kJ mol}^{-1}}$$

c) $C_2H_4\,(g) \longrightarrow 2\,C\,(g) + 4\,H\,(g)$

$$\Delta H^\circ_{\text{reaction}} = 4\ \Delta H^\circ_f\,(H,g) + 2\ \Delta H^\circ_f\,(C,g) - \Delta H^\circ_f\,(C_2H_4,g)$$
$$= (4) \times \left(218.0\ \text{kJ mol}^{-1}\right) + (2) \times \left(716.7\ \text{kJ mol}^{-1}\right) - \left(52.4\ \text{kJ mol}^{-1}\right) = 2253\ \text{kJ mol}^{-1}$$

$$\Delta H^\circ_{\text{reaction}} = 4 \times \text{C - H bond enthalpy} + \text{C = C bond enthalpy}$$

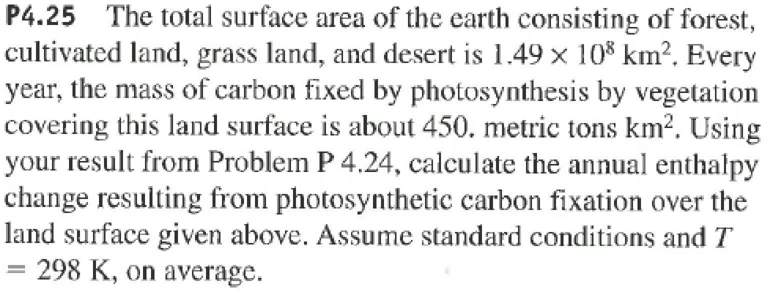
$$\text{C = C bond enthalpy} = \left(2253\ \text{kJ mol}^{-1}\right) - 4 \times \left(416.0\ \text{kJ mol}^{-1}\right)\ \ \underline{=\ \ 589\ \text{kJ mol}^{-1}}$$

$$\Delta U^\circ_{\text{reaction}} = \Delta H^\circ_{\text{reaction}} - \Delta n\ R\ T = \left(2253\ \text{kJ mol}^{-1}\right) - (5) \times \left(8.314472\ \text{J K}^{-1}\ \text{mol}^{-1}\right) \times (298.15\ \text{K})$$
$$= 2240\ \text{kJ mol}^{-1}$$

$$\Delta U^\circ_{\text{bond}} = 4 \times \text{C - H bond energy} + \text{C = C bond energy}$$

$$\text{C = C bond nergy} = \left(2240\ \text{kJ mol}^{-1}\right) - 4 \times \left(414.0\ \text{kJ mol}^{-1}\right)\ \ \underline{\approx\ \ 588\ \text{kJ mol}^{-1}}$$

15. Engel – P4.25



P4.25 The total surface area of the earth consisting of forest, cultivated land, grass land, and desert is 1.49×10^8 km^2. Every year, the mass of carbon fixed by photosynthesis by vegetation covering this land surface is about 450. metric tons km^2. Using your result from Problem P 4.24, calculate the annual enthalpy change resulting from photosynthetic carbon fixation over the land surface given above. Assume standard conditions and T = 298 K, on average.

The number of moles of fixed carbon is:

$$n_{\mathrm{C,fixed}} = \frac{m_{\mathrm{C,fixed}}}{M_{\mathrm{C}}} = \frac{\left(450000\ \mathrm{kg\ km^{-2}\ year^{-1}}\right)}{\left(12.01\times10^{-3}\ \mathrm{kg\ mol^{-1}}\right)} = 3.747\times10^{7}\ \mathrm{mol\ km^{-2}\ year^{-1}}$$

With the result from P4.24 we obtain:

$$\Delta H = \frac{\Delta H^{\circ}_{\mathrm{reaction}}}{6} = \frac{\left(3.747\times10^{7}\ \mathrm{mol\ km^{-2}\ year^{-1}}\right)\times\left(2802\ \mathrm{kJ\ mol^{-1}}\right)\times\left(1.49\times10^{8}\ \mathrm{km^{2}}\right)}{6}$$

$$\underline{= 2.60\times10^{18}\ \mathrm{kJ\ year^{-1}}}$$