

4 Thermochemistry

Problem numbers in italics indicate that the solution is included in the *Student Solutions Manual*.

Conceptual Problems

Q4.1 In calculating ΔH_R° at 285.15 K, only the ΔH_f° of the compounds that take part in the reactions listed in Tables 4.1 and 4.2 (Appendix B, Data Tables) are needed. Is this statement also true if you want to calculate ΔH_R° at 500. K?

No. At any temperature other than 298.15 K, the heat capacities of all elements and compounds that appear in the overall reaction enter into the calculation.

Q4.2 What is the point of having an outer water bath in a bomb calorimeter (see Figure 4.3), especially if its temperature is always equal to that of the inner water bath?

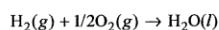
This water bath effectively isolates the calorimeter and the inner water bath from the rest of the universe. Because the temperatures of the water baths are the same, there is no heat flow between them. Because the container of the inner water bath has rigid walls, no work is done on the composite system consisting of the calorimeter and the inner water bath. Therefore, the calorimeter and inner water bath form an isolated composite system.

Q4.3 Is the following statement correct? If not rewrite it so that it is correct. The standard state of water is $\text{H}_2\text{O}(g)$.

The statement should read as follows: The standard reference state of water is $\text{H}_2\text{O}(l)$.

Q4.4 Does the enthalpy of formation of $\text{H}_2\text{O}(l)$ change if the absolute enthalpies of $\text{H}_2(g)$ and $\text{O}_2(g)$ are set equal to $100. \text{ kJ mol}^{-1}$ rather than to zero? Answer the same question for $\text{CO}_2(g)$. Will ΔH_R° for the reaction $\text{H}_2\text{O}(l) + \text{CO}_2(g) \rightarrow \text{H}_2\text{CO}_3(l)$ change as a result of this change in the enthalpy of formation of the elements?

The enthalpy of formation for a compound is defined as the change in enthalpy in the reaction in which the only reaction product is 1 mole of the compound in its standard reference state and the only reactants are the elements needed to form the product, each in its standard reference state. The relevant reaction for water formation is



$$\Delta H_R = \Delta H_f(\text{H}_2\text{O}(l)) = H(\text{H}_2\text{O}(l)) - H(\text{H}_2(g)) - 1/2H(\text{O}_2(g))$$

The H are absolute enthalpies which are not accessible through measurement because we can only measure changes in energy rather than absolute values of energy. Because $\Delta H_f(\text{H}_2\text{O}(l))$ is a quantity that is determined from experiment, it will not change if we choose to set the absolute enthalpies of $\text{H}_2(g)$ and $\text{O}_2(g)$ equal to 100 kJ mol^{-1} rather than to zero. However, the absolute enthalpy $H(\text{H}_2\text{O}(l)) = \Delta H_f(\text{H}_2\text{O}(l)) + H(\text{H}_2(g)) + 1/2H(\text{O}_2(g))$ will change in accordance with the previous equation. This change in $H(\text{H}_2\text{O}(l))$ has no practical significance because we can only measure changes in enthalpy and not absolute enthalpies. A similar argument can be made for $\text{CO}_2(g)$.

To demonstrate that the choice of absolute enthalpies for elements does not affect the reaction enthalpy, we express ΔH_R° for the reaction $\text{H}_2\text{O}(l) + \text{CO}_2(g) \rightarrow \text{H}_2\text{CO}_3(l)$ in terms of absolute enthalpies.

$$\begin{aligned}\Delta H_R^\circ &= H(\text{H}_2\text{CO}_3(l)) - H(\text{H}_2\text{O}(l)) - H(\text{CO}_2(g)) \\ &= \Delta H_f^\circ(\text{H}_2\text{CO}_3(l)) + H(\text{H}_2(g)) + 3/2H(\text{O}_2(g)) + H(\text{C}(\text{graphite})) \\ &\quad - (\Delta H_f^\circ(\text{H}_2\text{O}(l)) + H(\text{H}_2(g)) + 1/2H(\text{O}_2(g))) \\ &\quad - (\Delta H_f^\circ(\text{CO}_2(g)) + H(\text{C}(\text{graphite})) + H(\text{O}_2(g))) \\ &= \Delta H_f^\circ(\text{H}_2\text{CO}_3(l)) - \Delta H_f^\circ(\text{H}_2\text{O}(l)) - \Delta H_f^\circ(\text{CO}_2(g))\end{aligned}$$

It is seen that all the enthalpies for the elements have cancelled out.

- Q4.5** Why are elements included in the sum in Equation (4.20) when they are not included in calculating ΔH_R° at 298 K?
Although ΔH_f° for an element at any temperature is zero, ΔH_R at a temperature other than 298 K includes the enthalpy change associated with bringing the elements to that temperature from 298 K.
- Q4.6** Why are heat capacities of reactants and products required for calculations of ΔH_R° at elevated temperatures?
 ΔH_R° for a reaction at a temperature other than 298 K includes the enthalpy change associated with bringing the elements to that temperature from 298 K.
- Q4.7** Is the following statement correct? If not rewrite it so that it is correct. The superscript zero in ΔH_f° means that the reactions conditions are 298.15 K.
The superscript means that the pressure is 1 bar. Unless otherwise specified, it is generally safe to assume that $T = 298.15$ K.
- Q4.8** Why is it valid to add the enthalpies of any sequence of reactions to obtain the enthalpy of the reaction that is the sum of the individual reactions?
Because H is a state function, any path between the reactants and products, regardless of which intermediate products are involved, has the same value for ΔH .
- Q4.9** In a calorimetric study, the temperature of the system rises to 325 K before returning to its initial temperature of 298 K. Why doesn't this temperature rise affect your measurement of ΔH_R° at 298 K?
Because H is a state function, any path between the reactants and products, regardless of which intermediate temperatures are involved, has the same value for ΔH for given initial and final temperatures.
- Q4.10** Is the following statement correct? If not rewrite it so that it is correct. Because the reaction $\text{H}_2(g) + \text{O}_2(g) \rightarrow \text{H}_2\text{O}(l)$ is exothermic, the products are at a higher temperature than the reactants.
The statement is incorrect as written because the coupling of the system to the surroundings is not specified. The statement "Because the reaction $\text{H}_2(g) + \text{O}_2(g) \rightarrow \text{H}_2\text{O}(l)$ is exothermic, the products are at a higher temperature than the reactants if the reaction is carried out under adiabatic conditions."
- Q4.11** The reactants in the reaction $2\text{NO}(g) + \text{O}_2(g) \rightarrow 2\text{NO}_2(g)$ are initially at 298 K. Why is the reaction enthalpy the same if (a) the reaction is constantly kept at 298 K or (b) if the reaction temperature is not controlled and the heat flow to the surroundings is measured only after the temperature of the products is returned to 298 K?
Because H is a state function, any path between the reactants and products, regardless of which intermediate temperatures are involved, has the same value for ΔH for given initial and final temperatures.

Q4.12 What is the advantage of a differential scanning calorimeter over a bomb calorimeter in determining the enthalpy of fusion of a series of samples?

Measurements on all samples can be carried out simultaneously in a differential scanning calorimeter if care is taken that the samples do not mix with one another, whereas they must be done sequentially in a bomb calorimeter. However, the sensitivity of a differential scanning calorimeter is less than that of a bomb calorimeter.

Q4.13 You wish to measure the heat of solution of NaCl in water. Would the calorimetric technique of choice be at constant pressure or constant volume? Why?

Constant pressure calorimetry is the technique of choice because none of the reactants or products is gaseous, and it is therefore not necessary to contain the reaction. Constant pressure calorimetry is much easier to carry out than constant volume calorimetry.

Q4.14 Is the following statement correct? If not, rewrite it so that it is correct. Because the enthalpy of formations of elements is zero, $\Delta H_f^\circ(\text{O}(\text{g})) = 0$.

The formation enthalpy of a pure element is zero in its standard reference state at 298.15 K. For oxygen, the standard reference state is $\text{O}_2(\text{g})$, not $\text{O}(\text{g})$, so that $\Delta H_f^\circ(\text{O}_2(\text{g})) = 0$.

Q4.15 If the ΔH_f° for the chemical compounds involved in a reaction are available at a given temperature, how can ΔH_R° be calculated at another temperature?

$$\text{From Equation (4.19), } \Delta H_{R,T}^\circ = \Delta H_{R,298.15\text{K}}^\circ + \int_{298.15\text{K}}^T \Delta C_p(T') dT'$$

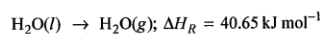
Q4.16 Is the following statement correct? If not, rewrite it so that it is correct. If ΔH_R° for a chemical reaction does not change appreciably with temperature, the heat capacities for reactants and products must be small.

The statement is not correct. If ΔH_R° for a chemical reaction does not change appreciably with temperature, the difference in the heat capacities of reactants and products must be small.

Q4.17 Under what conditions are ΔH and ΔU for a reaction involving gases and/or liquids or solids identical?

This is the case if $\Delta(PV) = 0$.

Q4.18 Dogs cool off in hot weather by panting. Write a chemical equation to describe this process and calculate ΔH_R° .



Q4.19 Is ΔH for breaking the first C—H bond in methane equal to the average C—H bond enthalpy in this molecule? Explain your answer.

No. The average bond enthalpy is the average of the enthalpies to dissociate $\text{CH}_4(\text{g})$, $\text{CH}_3(\text{g})$, $\text{CH}_2(\text{g})$, and $\text{CH}(\text{g})$.

Q4.20 Humans cool off through perspiration. How does the effectiveness of this process depend on the relative humidity?

Perspiration is only effective if the relative humidity is less than 100%. If the relative humidity is 100%, perspiration is completely ineffective as a cooling mechanism.

Numerical Problems

P4.1 Given the data in Table 4.1 (Appendix B, Data Tables) and the following information, calculate the single bond enthalpies and energies for Si—F, Si—Cl, C—F, N—F, O—F, H—F:

Substance	$\text{SiF}_4(\text{g})$	$\text{SiCl}_4(\text{g})$	$\text{CF}_4(\text{g})$	$\text{NF}_3(\text{g})$	$\text{OF}_2(\text{g})$	$\text{HF}(\text{g})$
$\Delta H_f^\circ(\text{kJ mol}^{-1})$	-1614.9	-657.0	-925	-125	-22	-271

The average single bond enthalpy Si—F is calculated as follows:



$$\text{Average Si—F bond enthalpy in SiF}_4 = \frac{2382 \text{ kJ mol}^{-1}}{4} = 596 \text{ kJ mol}^{-1}.$$

$$\begin{aligned} \Delta U^\circ &= \Delta H^\circ - \Delta nRT \\ &= 2382 \text{ kJ mol}^{-1} - 4 \times 8.314 \text{ J mol}^{-1} \text{ K}^{-1} \times 298.15 \text{ K} = 2372 \text{ kJ mol}^{-1} \end{aligned}$$

$$\text{Average Si—F bond energy in SiF}_4 = \frac{2372 \text{ kJ mol}^{-1}}{4} = 593 \text{ kJ mol}^{-1}.$$

Average single bond enthalpy in SiCl₄



$$\text{Average single bond enthalpy in SiCl}_4 = \frac{1592 \text{ kJ mol}^{-1}}{4} = 398 \text{ kJ mol}^{-1}.$$

$$\begin{aligned} \Delta U^\circ &= \Delta H^\circ - \Delta nRT \\ &= 1592 \text{ kJ mol}^{-1} - 4 \times 8.314 \text{ J mol}^{-1} \text{ K}^{-1} \times 298.15 \text{ K} = 1582 \text{ kJ mol}^{-1} \end{aligned}$$

$$\text{Average Si—Cl bond energy in SiCl}_4 = \frac{1582 \text{ kJ mol}^{-1}}{4} = 396 \text{ kJ mol}^{-1}.$$

Average single bond enthalpy in CF₄



$$\text{Average single bond enthalpy in CF}_4 = \frac{1959 \text{ kJ mol}^{-1}}{4} = 489 \text{ kJ mol}^{-1}.$$

$$\begin{aligned} \Delta U^\circ &= \Delta H^\circ - \Delta nRT \\ &= 1959 \text{ kJ mol}^{-1} - 4 \times 8.314 \text{ J mol}^{-1} \text{ K}^{-1} \times 298.15 \text{ K} = 1949 \text{ kJ mol}^{-1} \end{aligned}$$

$$\text{Average C—F bond energy in CF}_4 = \frac{1949 \text{ kJ mol}^{-1}}{4} = 487 \text{ kJ mol}^{-1}.$$

Average single bond enthalpy in NF_3 Average single bond enthalpy in $\text{NF}_3 = \frac{836 \text{ kJ mol}^{-1}}{3} = 279 \text{ kJ mol}^{-1}$.

$$\begin{aligned} \Delta U^\circ &= \Delta H^\circ - \Delta nRT \\ &= 836 \text{ kJ mol}^{-1} - 3 \times 8.314 \text{ J mol}^{-1} \text{ K}^{-1} \times 298.15 \text{ K} = 828 \text{ kJ mol}^{-1} \end{aligned}$$

Average N—F bond energy in $\text{NF}_3 = \frac{828 \text{ kJ mol}^{-1}}{3} = 276 \text{ kJ mol}^{-1}$.Average single bond enthalpy in OF_2 Average single bond enthalpy in $\text{OF}_2 = \frac{430 \text{ kJ mol}^{-1}}{2} = 215 \text{ kJ mol}^{-1}$.

$$\begin{aligned} \Delta U^\circ &= \Delta H^\circ - \Delta nRT \\ &= 430 \text{ kJ mol}^{-1} - 2 \times 8.314 \text{ J mol}^{-1} \text{ K}^{-1} \times 298.15 \text{ K} = 425 \text{ kJ mol}^{-1} \end{aligned}$$

Average O—F bond energy in $\text{OF}_2 = \frac{425 \text{ kJ mol}^{-1}}{2} = 213 \text{ kJ mol}^{-1}$.

Single bond enthalpy in HF

Single bond enthalpy in HF = 568 kJ mol⁻¹.

$$\begin{aligned} \Delta U^\circ &= \Delta H^\circ - \Delta nRT \\ &= 568 \text{ kJ mol}^{-1} - 1 \times 8.314 \text{ J mol}^{-1} \text{ K}^{-1} \times 298.15 \text{ K} = 565 \text{ kJ mol}^{-1} \end{aligned}$$

Average single bond energy in HF = 565 kJ mol⁻¹.

- P4.2** At 1000. K, $\Delta H_R^\circ = -123.77 \text{ kJ mol}^{-1}$ for the reaction $\text{N}_2(\text{g}) + 3\text{H}_2(\text{g}) \rightarrow 2\text{NH}_3(\text{g})$, with $C_{P,m} = 3.502 R$, $3.466 R$, and $4.217 R$ for $\text{N}_2(\text{g})$, $\text{H}_2(\text{g})$, and $\text{NH}_3(\text{g})$, respectively. Calculate ΔH_f° of $\text{NH}_3(\text{g})$ at 450. K from this information. Assume that the heat capacities are independent of temperature.

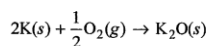
$$\Delta H_R^\circ(450. \text{ K}) = \Delta H_R^\circ(1000. \text{ K}) + \int_{1000. \text{ K}}^{450. \text{ K}} \Delta C_P(T) dT$$

For this problem, the heat capacities are assumed to be independent of T .

$$\begin{aligned} \Delta H_R^\circ(450. \text{ K}) &= \Delta H_R^\circ(1000. \text{ K}) + \Delta C_P \Delta T \\ &= -123.77 \text{ kJ mol}^{-1} + [2C_{P,m}(\text{NH}_3, \text{g}) - C_{P,m}(\text{N}_2, \text{g}) - 3C_{P,m}(\text{H}_2, \text{g})][-550. \text{ K}] \\ &= -123.77 \text{ kJ mol}^{-1} + 8.314 \text{ J mol}^{-1} \text{ K}^{-1} \times [2 \times 4.217 - 3.502 - 3 \times 3.466][-550. \text{ K}] \\ &= -98.775 \text{ kJ mol}^{-1} \end{aligned}$$

$$\Delta H_f^\circ(\text{NH}_3, \text{g}, 450. \text{ K}) = \frac{1}{2} \Delta H_R^\circ(450. \text{ K}) = -49.39 \text{ kJ mol}^{-1}$$

- P4.3** A sample of $\text{K}(s)$ of mass 2.740 g undergoes combustion in a constant volume calorimeter. The calorimeter constant is 1849 J K^{-1} , and the measured temperature rise in the inner water bath containing 1450. g of water is 1.60 K. Calculate ΔU_f° and ΔH_f° for K_2O .



$$\begin{aligned} \Delta U_f^\circ &= -\frac{M_s}{m_s} \left(\frac{m_{\text{H}_2\text{O}}}{M_{\text{H}_2\text{O}}} C_{H_2O,m} \Delta T + C_{\text{calorimeter}} \Delta T \right) \\ &= -\frac{39.098 \text{ g mol}^{-1}}{2.740 \text{ g}} \times \frac{2 \text{ mol K}}{1 \text{ mol reaction}} \times \left(\frac{1.450 \times 10^3 \text{ g}}{18.02 \text{ g mol}^{-1}} \times 75.3 \text{ J mol}^{-1} \text{ K}^{-1} \times 1.60^\circ \text{C} \right. \\ &\quad \left. + 1.849 \times 10^3 \text{ J}^\circ \text{C}^{-1} \times 1.60^\circ \text{C} \right) \\ &= -361 \text{ kJ mol}^{-1} \\ \Delta H_f^\circ &= \Delta U_f^\circ + \Delta nRT \\ &= -361 \text{ kJ mol}^{-1} - \frac{1}{2} \times 8.314 \text{ J K}^{-1} \text{ mol}^{-1} \times 298.15 \text{ K} = -362 \text{ kJ mol}^{-1} \end{aligned}$$

- P4.4** Calculate ΔH_f° for $\text{NO}(\text{g})$, at 975 K, assuming that the heat capacities of reactants and products are constant over the temperature interval at their values at 298.15 K.

$$\begin{aligned} \Delta H &= \Delta H_f^\circ(\text{NO}, \text{g}, 298.15 \text{ K}) + \int_{298.15}^{975} \Delta C_P \left(\frac{T}{\text{K}} \right) d \frac{T}{\text{K}} \\ \Delta C_P &= C_{P,m}(\text{NO}, \text{g}) - \frac{1}{2} C_{P,m}(\text{N}_2, \text{g}) - \frac{1}{2} C_{P,m}(\text{O}_2, \text{g}) \\ &= (29.86 - 0.5 \times 29.13 - 0.5 \times 29.38) \text{ J K}^{-1} \text{ mol}^{-1} \\ &= 0.605 \text{ J K}^{-1} \text{ mol}^{-1} \\ \Delta H &= \Delta H_f^\circ(\text{NO}, \text{g}, 298.15 \text{ K}) + \left[\int_{298.15}^{975} 0.605 d \frac{T}{\text{K}} \right] \text{ J mol}^{-1} \\ &= \Delta H_f^\circ(\text{NO}, \text{g}, 298.15 \text{ K}) + 0.327 \text{ kJ mol}^{-1} = 91.3 \text{ kJ mol}^{-1} + 0.409 \text{ kJ mol}^{-1} = 91.7 \text{ kJ mol}^{-1} \end{aligned}$$

- P4.5** The total surface area of the Earth covered by ocean is $3.35 \times 10^8 \text{ km}^2$. Carbon is fixed in the oceans via photosynthesis performed by marine plants according to the reaction $6\text{CO}_2(\text{g}) + 6\text{H}_2\text{O}(\text{l}) \rightarrow \text{C}_6\text{H}_{12}\text{O}_6(\text{s}) + 6\text{O}_2(\text{g})$. A lower range estimate of the mass of carbon fixed in the oceans is $44.5 \times 10^3 \text{ kg km}^2$ per year. Calculate the annual enthalpy change resulting from photosynthetic carbon fixation in the ocean per mole of C given the data above. Assume $P = 1 \text{ bar}$ and $T = 298 \text{ K}$.

$$\begin{aligned}\Delta H_R^\circ &= \Delta H_f^\circ(\text{C}_6\text{H}_{12}\text{O}_6, \text{s}) - 6\Delta H_f^\circ(\text{CO}_2, \text{g}) - 6\Delta H_f^\circ(\text{H}_2\text{O}, \text{l}) \\ &= -1273.1 \text{ kJ mol}^{-1} + 6 \times 393.5 \text{ kJ mol}^{-1} + 6 \times 285.8 \text{ kJ mol}^{-1} \\ &= 2802.7 \text{ kJ mol}^{-1}\end{aligned}$$

$$n_{\text{C, fixed}} = \frac{m_{\text{C, fixed}}}{M_{\text{C}}} = \frac{44.5 \times 10^3 \text{ kg km}^2 \text{ yr}^{-1}}{12.01 \times 10^{-3} \text{ kg mol}^{-1}} = 3.71 \times 10^3 \text{ mol km}^{-2} \text{ yr}^{-1}$$

We calculate the enthalpy change per mole of C using the above result:

$$\begin{aligned}\Delta H &= \frac{\Delta H_R^\circ}{6} = \frac{3.71 \times 10^3 \text{ mol km}^{-2} \text{ yr}^{-1} \times 2802.7 \text{ kJ mol}^{-1} \times 3.35 \times 10^8 \text{ km}^2}{6} \\ &= 5.80 \times 10^{17} \text{ kJ yr}^{-1}\end{aligned}$$

- P4.6** Derive a formula for $\Delta H_R^\circ(T)$ for the reaction $\text{CO}(\text{g}) + \frac{1}{2}\text{O}_2(\text{g}) \rightarrow \text{CO}_2(\text{g})$ assuming that the heat capacities of reactants and products do not change with temperature.

$$\begin{aligned}\Delta H_R(T) &= \Delta H_R(298.15 \text{ K}) + \Delta C_p \Delta T \\ &= \Delta H_f^\circ(\text{CO}_2(\text{g})) - \Delta H_f^\circ(\text{CO}(\text{g})) + \left[C_{p,m}(\text{CO}_2(\text{g})) - C_{p,m}(\text{CO}(\text{g})) - \frac{1}{2}C_{p,m}(\text{O}_2(\text{g})) \right] (\Delta T)\end{aligned}$$

- P4.7** Given the data in Table 4.3 and the data tables, calculate the bond enthalpy and energy of the following:

- The C—H bond in CH_4
- The C—C single bond in C_2H_6
- The C=C double bond in C_2H_4

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

- (a) $\text{CH}_4(\text{g}) \rightarrow \text{C}(\text{g}) + 4\text{H}(\text{g})$

$$\begin{aligned}\Delta H_R^\circ &= 4\Delta H_f^\circ(\text{H}, \text{g}) + \Delta H_f^\circ(\text{C}, \text{g}) - \Delta H_f^\circ(\text{CH}_4, \text{g}) \\ &= 4 \times 218.0 \text{ kJ mol}^{-1} + 716.7 \text{ kJ mol}^{-1} + 74.6 \text{ kJ mol}^{-1} \\ &= 1663 \text{ kJ mol}^{-1}\end{aligned}$$

$$\text{Average C—H bond enthalpy in } \text{CH}_4 = \frac{1663 \text{ kJ mol}^{-1}}{4} = 416 \text{ kJ mol}^{-1}.$$

$$\begin{aligned}\Delta U^\circ &= \Delta H^\circ - \Delta nRT \\ &= 1663 \text{ kJ mol}^{-1} - 3 \times 8.314 \text{ J mol}^{-1} \text{ K}^{-1} \times 298.15 \text{ K} = 1654 \text{ kJ mol}^{-1}\end{aligned}$$

$$\text{Average C—H bond energy in } \text{CH}_4 = \frac{1654 \text{ kJ mol}^{-1}}{4} = 413 \text{ kJ mol}^{-1}.$$

- (b) $\text{C}_2\text{H}_6(\text{g}) \rightarrow 2\text{C}(\text{g}) + 6\text{H}(\text{g})$

$$\begin{aligned}\Delta H_R^\circ &= 6\Delta H_f^\circ(\text{H}, \text{g}) + 2\Delta H_f^\circ(\text{C}, \text{g}) - \Delta H_f^\circ(\text{C}_2\text{H}_6, \text{g}) \\ &= 6 \times 218.0 \text{ kJ mol}^{-1} + 2 \times 716.7 \text{ kJ mol}^{-1} + 84.0 \text{ kJ mol}^{-1} \\ &= 2825 \text{ kJ mol}^{-1}\end{aligned}$$

$$\Delta H_R^\circ = 6 \times \text{C—H bond enthalpy} + \text{C—C bond enthalpy}$$

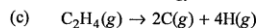
$$\text{C—C bond enthalpy} = 2825 \text{ kJ mol}^{-1} - 6 \times 416 \text{ kJ mol}^{-1} = 329 \text{ kJ mol}^{-1}$$

$$\Delta U^\circ = \Delta H^\circ - \Delta nRT$$

$$= 2825 \text{ kJ mol}^{-1} - 7 \times 8.314 \text{ J mol}^{-1} \text{ K}^{-1} \times 298.15 \text{ K} = 2808 \text{ kJ mol}^{-1}$$

$$\Delta U^\circ = 6 \times \text{C—H bond energy} + \text{C—C bond energy}$$

$$\text{C—C bond energy} = 2808 \text{ kJ mol}^{-1} - 6 \times 413 \text{ kJ mol}^{-1} \approx 329 \text{ kJ mol}^{-1}$$



$$\Delta H_R^\circ = 2\Delta H_f^\circ(\text{C}, \text{g}) + 4\Delta H_f^\circ(\text{H}, \text{g}) - \Delta H_f^\circ(\text{C}_2\text{H}_4, \text{g})$$

$$= 2 \times 716.7 \text{ kJ mol}^{-1} + 4 \times 218 \text{ kJ mol}^{-1} - 52.4 \text{ kJ mol}^{-1} = 2253 \text{ kJ mol}^{-1}$$

$$\Delta H_R^\circ = 4 \times \text{C—H bond enthalpy} + \text{C=C bond enthalpy}$$

$$\text{C=C bond enthalpy} = 2253 \text{ kJ mol}^{-1} - 4 \times 416 \text{ kJ mol}^{-1} = 589 \text{ kJ mol}^{-1}$$

$$\Delta U^\circ = \Delta H^\circ - \Delta nRT$$

$$= 2253 \text{ kJ mol}^{-1} - 5 \times 8.314 \text{ J mol}^{-1} \text{ K}^{-1} \times 298.15 \text{ K} = 2240 \text{ kJ mol}^{-1}$$

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

$$\text{C—C bond energy} = 2240 \text{ kJ mol}^{-1} - 4 \times 413 \text{ kJ mol}^{-1} = 588 \text{ kJ mol}^{-1}$$

P4.8 Use the following data at 298.15 K to complete this problem:

	ΔH_R° (kJ mol ⁻¹)
$\frac{1}{2}\text{H}_2(\text{g}) + \frac{1}{2}\text{O}_2(\text{g}) \rightarrow \text{OH}(\text{g})$	38.95
$\text{H}_2(\text{g}) + \frac{1}{2}\text{O}_2(\text{g}) \rightarrow \text{H}_2\text{O}(\text{g})$	-241.814
$\text{H}_2(\text{g}) \rightarrow 2\text{H}(\text{g})$	435.994
$\text{O}_2(\text{g}) \rightarrow 2\text{O}(\text{g})$	498.34

Calculate ΔH_R° for

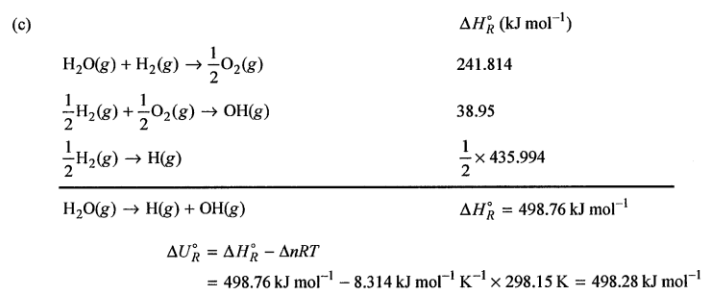
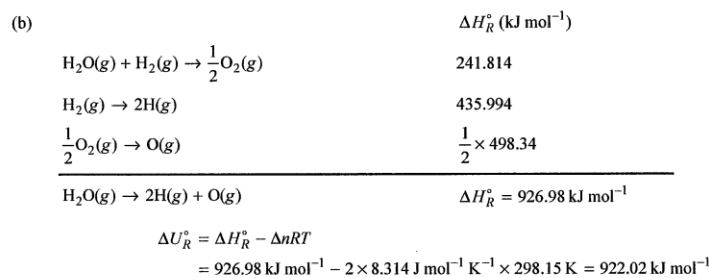
- $\text{OH}(\text{g}) \rightarrow \text{H}(\text{g}) + \text{O}(\text{g})$
- $\text{H}_2\text{O}(\text{g}) \rightarrow 2\text{H}(\text{g}) + \text{O}(\text{g})$
- $\text{H}_2\text{O}(\text{g}) \rightarrow \text{H}(\text{g}) + \text{OH}(\text{g})$

Assuming ideal gas behavior, calculate ΔH_R° and ΔU_R° for all three reactions.

(a)	ΔH_R° (kJ mol ⁻¹)
$\text{OH}(\text{g}) + \frac{1}{2}\text{H}_2(\text{g}) \rightarrow \frac{1}{2}\text{O}_2(\text{g})$	-38.95
$\frac{1}{2}\text{H}_2(\text{g}) \rightarrow \text{H}(\text{g})$	$\frac{1}{2} \times 435.994$
$\frac{1}{2}\text{O}_2(\text{g}) \rightarrow \text{O}(\text{g})$	$\frac{1}{2} \times 498.34$
<hr/>	<hr/>
$\text{OH}(\text{g}) \rightarrow \text{H}(\text{g}) + \text{O}(\text{g})$	$\Delta H_R^\circ = 428.22 \text{ kJ mol}^{-1}$

$$\Delta U_R^\circ = \Delta H_R^\circ - \Delta nRT$$

$$= 428.22 \text{ kJ mol}^{-1} - 8.314 \text{ J mol}^{-1} \text{ K}^{-1} \times 298.15 \text{ K} = 425.74 \text{ kJ mol}^{-1}$$



P4.9 Calculate the standard enthalpy of formation of $\text{FeS}_2(s)$ at 600. °C from the following data at 298.15 K. Assume that the heat capacities are independent of temperature.

Substance	Fe(s)	FeS ₂ (s)	Fe ₂ O ₃ (s)	S(rhombic)	SO ₂ (g)
ΔH_f° (kJ mol ⁻¹)			-824.2		-296.81
$C_{p,m}/R$	3.02	7.48		2.72	

You are also given that for the reaction $2\text{FeS}_2(s) + \frac{11}{2}\text{O}_2(g) \rightarrow \text{Fe}_2\text{O}_3(s) + 4\text{SO}_2(g)$, $\Delta H_R^\circ = -1655 \text{ kJ mol}^{-1}$.

$$2\text{FeS}_2(s) + \frac{11}{2}\text{O}_2(g) \rightarrow \text{Fe}_2\text{O}_3(s) + 4\text{SO}_2(g) \quad \Delta H_R^\circ = -1655 \text{ kJ mol}^{-1}$$

$$-1655 \text{ kJ mol}^{-1} = \Delta H_f^\circ(\text{Fe}_2\text{O}_3, s) + 4\Delta H_f^\circ(\text{SO}_2, g) - 2\Delta H_f^\circ(\text{FeS}_2, s)$$

$$\Delta H_f^\circ(\text{FeS}_2, s, 298 \text{ K}) = \frac{1655 \text{ kJ mol}^{-1} + \Delta H_f^\circ(\text{Fe}_2\text{O}_3, s) + 4\Delta H_f^\circ(\text{SO}_2, g)}{2}$$

$$= \frac{1655 - 824.2 - 4 \times 296.81 \text{ kJ mol}^{-1}}{2}$$

$$= -178.2 \text{ kJ mol}^{-1}$$

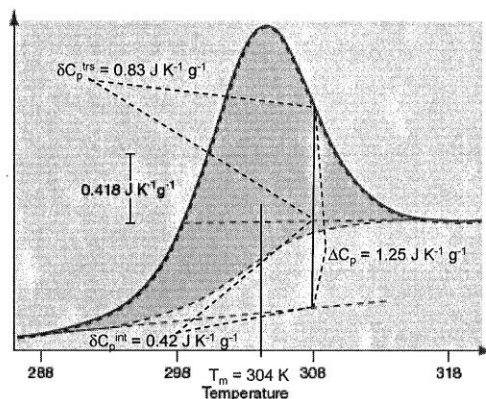
The enthalpy of formation at 600. °C is given by

$$\Delta H_f^\circ(\text{FeS}_2(s), 873 \text{ K}) - \Delta H_f^\circ(\text{FeS}_2(s), 298 \text{ K}) + \int_{298 \text{ K}}^{873 \text{ K}} \Delta C_p(T) dT$$

Because the heat capacities are assumed to be independent of T ,

$$\begin{aligned}\Delta H_f^\circ(\text{FeS}_2(s), 573 \text{ K}) &= \Delta H_f^\circ(\text{FeS}_2(s), 298 \text{ K}) + [C_{p,m}(\text{FeS}_2, s) - C_{p,m}(\text{Fe}, s) - 2C_{p,m}(\text{S}, s)][873 \text{ K} - 298 \text{ K}] \\ &= -178.2 \text{ kJ mol}^{-1} + 8.314 \text{ J K}^{-1} \text{ mol}^{-1} \times (7.48 - 3.02 - 2 \times 2.72) \times [873 \text{ K} - 298 \text{ K}] \\ &= -182.9 \text{ kJ mol}^{-1}\end{aligned}$$

P4.10 The following data are a DSC scan of a solution of a T4 lysozyme mutant. From the data determine T_m . Determine also the excess heat capacity ΔC_p at $T = 308 \text{ K}$. Determine also the intrinsic δC_p^{int} and transition δC_p^{trs} excess heat capacities $T = 308 \text{ K}$. In your calculations use the extrapolated curves, shown as dashed lines in the DSC scan.



P4.11 At 298 K , $\Delta H_R^\circ = 131.28 \text{ kJ mol}^{-1}$ for the reaction $\text{C}(\text{graphite}) + \text{H}_2\text{O}(\text{g}) \rightarrow \text{CO}(\text{g}) + \text{H}_2(\text{g})$, with $C_{p,m} = 8.53, 33.58, 29.12$, and $28.82 \text{ J K}^{-1} \text{ mol}^{-1}$ for graphite, $\text{H}_2\text{O}(\text{g})$, $\text{CO}(\text{g})$, and $\text{H}_2(\text{g})$, respectively. Calculate ΔH_R° at $240.^\circ\text{C}$ from this information. Assume that the heat capacities are independent of temperature.

$$\Delta H_R^\circ(513 \text{ K}) = \Delta H_R^\circ(298 \text{ K}) + \int_{298 \text{ K}}^{513 \text{ K}} \Delta C_p(T) dT$$

For this problem, it is assumed that the heat capacities are independent of T .

$$\begin{aligned}\Delta H_R^\circ(513 \text{ K}) &= \Delta H_R^\circ(298 \text{ K}) + [C_{p,m}(\text{H}_2, \text{g}) + C_{p,m}(\text{CO}, \text{g}) - C_{p,m}(\text{C}, \text{graphite}) - C_{p,m}(\text{H}_2\text{O}, \text{g})]\Delta T \\ &= 131.28 \text{ kJ mol}^{-1} + [28.82 + 29.12 - 8.53 - 33.58] \text{ J mol}^{-1} \text{ K}^{-1} \times 215 \text{ K} \\ &= 134.68 \text{ kJ mol}^{-1}\end{aligned}$$

P4.12 Consider the reaction $\text{TiO}_2(\text{s}) + 2 \text{C}(\text{graphite}) + 2 \text{Cl}_2(\text{g}) \rightarrow 2 \text{CO}(\text{g}) + \text{TiCl}_4(\text{l})$ for which $\Delta H_R^\circ_{298 \text{ K}} = -80. \text{ kJ mol}^{-1}$. Given the following data at 25°C , (a) calculate ΔH_R° at 135.8°C , the boiling point of TiCl_4 , and (b) calculate ΔH_f° for $\text{TiCl}_4(\text{l})$ at 25°C :

Substance	$\text{TiO}_2(\text{s})$	$\text{Cl}_2(\text{g})$	$\text{C}(\text{graphite})$	$\text{CO}(\text{g})$	$\text{TiCl}_4(\text{l})$
$\Delta H_f^\circ(\text{kJ mol}^{-1})$	-945			-110.5	
$C_{p,m}(\text{J K}^{-1} \text{ mol}^{-1})$	55.06	33.91	8.53	29.12	145.2

Assume that the heat capacities are independent of temperature.

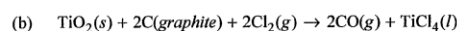
- Calculate ΔH_R° at 135.8°C, the boiling point of TiCl_4 .
- Calculate ΔH_f° for $\text{TiCl}_4(l)$ at 25°C.

Assume that the heat capacities are independent of temperature.

$$(a) \quad \Delta H_R^\circ(409.0 \text{ K}) = \Delta H_R^\circ(298 \text{ K}) + \int_{298 \text{ K}}^{409.0 \text{ K}} \Delta C_{P,m} dT$$

In this case, the heat capacities are assumed to be independent of T.

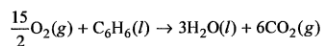
$$\begin{aligned} \Delta H_R^\circ(409.0 \text{ K}) &= \Delta H_R^\circ(298 \text{ K}) + \Delta C_{P,m}[409.0 \text{ K} - 298 \text{ K}] \\ &= -80. \text{ kJ mol}^{-1} + [C_{P,m}(\text{TiCl}_4, l) + 2C_{P,m}(\text{CO}, g) - C_{P,m}(\text{TiO}_2, s) \\ &\quad - 2C_{P,m}(\text{graphite}, s) - 2C_{P,m}(\text{Cl}_2, g)][409.0 \text{ K} - 298 \text{ K}] \\ &= -80. \text{ kJ mol}^{-1} + [145.2 + 2 \times 29.12 - 55.06 - 2 \times 8.53 - 2 \times 33.91][409.0 \text{ K} - 298 \text{ K}] \\ &= -73.0 \text{ kJ mol}^{-1} \end{aligned}$$



$$\begin{aligned} \Delta H_R^\circ &= -80. \text{ kJ mol}^{-1} = 2\Delta H_f^\circ(\text{CO}, g) + \Delta H_f^\circ(\text{TiCl}_4, l) - \Delta H_f^\circ(\text{TiO}_2, s) \\ \Delta H_f^\circ(\text{TiCl}_4, l) &= \Delta H_f^\circ(\text{TiO}_2, s) - 2\Delta H_f^\circ(\text{CO}, g) - 80. \text{ kJ mol}^{-1} \\ &= -945 \text{ kJ mol}^{-1} + 2 \times 110.5 \text{ kJ mol}^{-1} - 80. \text{ kJ mol}^{-1} \\ &= -804 \text{ kJ mol}^{-1} \end{aligned}$$

P4.13 Calculate ΔH_R° and ΔU_R° for the oxidation of benzene (g). Also calculate

$$\frac{\Delta H_R^\circ - \Delta U_R^\circ}{\Delta H_R^\circ}$$



From the data tables,

$$\begin{aligned} \Delta H_{\text{combustion}}^\circ &= 3\Delta H_f^\circ(\text{H}_2\text{O}, l) + 6\Delta H_f^\circ(\text{CO}_2, g) - \Delta H_f^\circ(\text{C}_6\text{H}_6, l) \\ &= -3 \times 285.8 \text{ kJ mol}^{-1} - 6 \times 393.5 \text{ kJ mol}^{-1} - 49.1 \text{ kJ mol}^{-1} \\ &= -3268 \text{ kJ mol}^{-1} \end{aligned}$$

$$\begin{aligned} \Delta U_R^\circ &= \Delta H_R^\circ - \Delta nRT = -3268 \text{ kJ mol}^{-1} + 1.5 \times 8.314 \text{ J K}^{-1} \text{ mol}^{-1} \times 298.15 \text{ K} \\ &= -3264 \text{ kJ mol}^{-1} \end{aligned}$$

$$\frac{\Delta H_R^\circ - \Delta U_R^\circ}{\Delta H_R^\circ} = \frac{-3268 \text{ kJ mol}^{-1} + 3264 \text{ kJ mol}^{-1}}{-3268 \text{ kJ mol}^{-1}} = 0.0122$$

P4.14 Several reactions and their standard reaction enthalpies at 298.15 K are given here:

	ΔH_R° (kJ mol ⁻¹)
$\text{CaC}_2(s) + 2\text{H}_2\text{O}(l) \rightarrow \text{Ca}(\text{OH})_2(s) + \text{C}_2\text{H}_2(g)$	-127.9
$\text{Ca}(s) + \frac{1}{2}\text{O}_2(g) \rightarrow \text{CaO}(s)$	-635.1
$\text{CaO}(s) + \text{H}_2\text{O}(l) \rightarrow \text{Ca}(\text{OH})_2(s)$	-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 .

	ΔH_R° (kJ mol^{-1})
$Ca(OH)_2(s) + C_2H_2(g) \rightarrow CaC_2(s) + 2H_2O(l)$	+127.9
$CaO(s) + H_2O(l) \rightarrow Ca(OH)_2(s)$	-65.2
$2CO_2(g) + H_2O(l) \rightarrow C_2H_2(s) + \frac{5}{2}O_2(s)$	1299.58
$2C(s) + 2O_2(g) \rightarrow 2CO_2(g)$	$2 \times (-393.51)$
$Ca(s) + \frac{1}{2}O_2(g) \rightarrow CaO(s)$	-635.1
$2C(s) + Ca(s) \rightarrow CaC_2(s)$	$\Delta H_f^\circ = -59.8$ kJ mol^{-1}

P4.15 Benzoic acid, 1.35 g, is reacted with oxygen in a constant volume calorimeter to form $H_2O(l)$ and $CO_2(g)$ at 298 K. The mass of the water in the inner bath is 1.55×10^3 g. The temperature of the calorimeter and its contents rises 2.76 K as a result of this reaction. Calculate the calorimeter constant.

$$\Delta U_{\text{combustion}} = \Delta H_{\text{combustion}} - \Delta nRT$$

For the reaction $C_6H_5COOH(s) + \frac{15}{2}O_2(g) \rightarrow 7CO_2(g) + 3H_2O(l)$, $\Delta n = -\frac{1}{2}$.

$$\Delta U_{\text{combustion}} = -3227. \text{ kJ mol}^{-1} + \frac{1}{2} \times 8.3145 \text{ J mol}^{-1} \text{ K}^{-1} \times 298.15 \text{ K} = -3226 \text{ kJ mol}^{-1}$$

$$C_{\text{calorimeter}} = \frac{\frac{m_s}{M_s} \Delta U_R - \frac{m_{H_2O}}{M_{H_2O}} C_{H_2O,m} \Delta T}{\Delta T}$$

$$= \frac{\frac{1.35 \text{ g}}{122.13 \text{ g mol}^{-1}} \times 3226 \times 10^3 \text{ J mol}^{-1} - \frac{1.550 \times 10^3 \text{ g}}{18.02 \text{ g mol}^{-1}} \times 75.3 \text{ J mol}^{-1} \text{ K}^{-1} \times 2.76^\circ\text{C}}{2.76^\circ\text{C}}$$

$$= 6.64 \times 10^3 \text{ J }^\circ\text{C}^{-1}$$

P4.16 The total surface area of Asia consisting of forest, cultivated land, grass land, and desert is 4.46×10^7 km^2 . Every year, the mass of carbon fixed by photosynthesis by vegetation covering this land surface according to the reaction $6CO_2(g) + 6H_2O(l) \rightarrow C_6H_{12}O_6(s) + 6O_2(g)$ is about 455×10^3 kg km^{-2} . Calculate the annual enthalpy change resulting from photosynthetic carbon fixation over the land surface per mole of carbon given the data above. Assume $P = 1$ bar and $T = 298$ K.

$$\begin{aligned} \Delta H_R &= \Delta H_f^\circ(C_6H_{12}O_6(s)) - 6\Delta H_f^\circ(H_2O(l)) - 6\Delta H_f^\circ(CO_2(g)) \\ &= -1273.1 \text{ kJ mol}^{-1} + 6 \times 393.5 \text{ kJ mol}^{-1} + 6 \times 285.5 \text{ kJ mol}^{-1} \\ &= 2802.7 \text{ kJ mol}^{-1} \end{aligned}$$

The number of moles of fixed carbon is:

$$n_{C, \text{fixed}} = \frac{m_{C, \text{fixed}}}{M_C} = \frac{(4.55 \times 10^5 \text{ kg km}^{-2} \text{ year}^{-1})}{(12.01 \times 10^{-3} \text{ kg mol}^{-1})} = 3.786 \times 10^7 \text{ mol km}^{-2} \text{ year}^{-1}$$

We calculate the enthalpy change per mole of C using the above result:

$$\begin{aligned}\Delta H &= \frac{\Delta H_R}{6} = \frac{(3.786 \times 10^7 \text{ mol km}^{-2} \text{ year}^{-1}) \times (2802 \text{ kJ mol}^{-1}) \times (4.46 \times 10^7 \text{ km}^2)}{6} \\ &= 7.89 \times 10^{17} \text{ kJ year}^{-1}\end{aligned}$$

P4.17 Calculate ΔH_R° and ΔU_R° at 298.15 K for the following reactions:

- $4\text{NH}_3(\text{g}) + 6\text{NO}(\text{g}) \rightarrow 5\text{N}_2(\text{g}) + 6\text{H}_2\text{O}(\text{g})$
- $2\text{NO}(\text{g}) + \text{O}_2(\text{g}) \rightarrow 2\text{NO}_2(\text{g})$
- $\text{TiCl}_4(\text{l}) + 2\text{H}_2\text{O}(\text{l}) \rightarrow \text{TiO}_2(\text{s}) + 4\text{HCl}(\text{g})$
- $2\text{NaOH}(\text{aq}) + \text{H}_2\text{SO}_4(\text{aq}) \rightarrow \text{Na}_2\text{SO}_4(\text{aq}) + 2\text{H}_2\text{O}(\text{l})$. Assume complete dissociation of NaOH, H_2SO_4 , and Na_2SO_4 .
- $\text{CH}_4(\text{g}) + \text{H}_2\text{O}(\text{g}) \rightarrow \text{CO}(\text{g}) + 3\text{H}_2(\text{g})$
- $\text{CH}_3\text{OH}(\text{g}) + \text{CO}(\text{g}) \rightarrow \text{CH}_3\text{COOH}(\text{l})$

(a) $4\text{NH}_3(\text{g}) + 6\text{NO}(\text{g}) \rightarrow 5\text{N}_2(\text{g}) + 6\text{H}_2\text{O}(\text{g})$

$$\begin{aligned}\Delta H_R^\circ &= 5\Delta H_f^\circ(\text{N}_2, \text{g}) + 6\Delta H_f^\circ(\text{H}_2\text{O}, \text{g}) - 4\Delta H_f^\circ(\text{NH}_3, \text{g}) - 6\Delta H_f^\circ(\text{NO}, \text{g}) \\ &= 0 - 6 \times 241.8 \text{ kJ mol}^{-1} + 4 \times 45.9 \text{ kJ mol}^{-1} - 6 \times 91.3 \text{ kJ mol}^{-1} \\ &= -1815.0 \text{ kJ mol}^{-1} \\ \Delta U_R^\circ &= \Delta H_R^\circ - \Delta nRT \\ &= -1815.0 \text{ kJ mol}^{-1} - 8.314 \text{ J K}^{-1} \text{ mol}^{-1} \times 298.15 \text{ K} = -1817.5 \text{ kJ mol}^{-1}\end{aligned}$$

(b) $2\text{NO}(\text{g}) + \text{O}_2(\text{g}) \rightarrow 2\text{NO}_2(\text{g})$

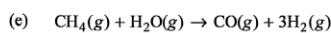
$$\begin{aligned}\Delta H_R^\circ &= 2\Delta H_f^\circ(\text{NO}_2, \text{g}) - \Delta H_f^\circ(\text{O}_2, \text{g}) - 2\Delta H_f^\circ(\text{NO}, \text{g}) \\ &= 2 \times 33.2 \text{ kJ mol}^{-1} - 0 - 2 \times 91.3 \text{ kJ mol}^{-1} \\ &= -116.2 \text{ kJ mol}^{-1} \\ \Delta U_R^\circ &= \Delta H_R^\circ - \Delta nRT \\ &= -116.2 \text{ kJ mol}^{-1} + 8.314 \text{ J K}^{-1} \text{ mol}^{-1} \times 298.15 \text{ K} = -113.7 \text{ kJ mol}^{-1}\end{aligned}$$

(c) $\text{TiCl}_4(\text{l}) + 2\text{H}_2\text{O}(\text{l}) \rightarrow \text{TiO}_2(\text{s}) + 4\text{HCl}(\text{g})$

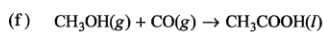
$$\begin{aligned}\Delta H_R^\circ &= \Delta H_f^\circ(\text{TiO}_2, \text{s}) + 4\Delta H_f^\circ(\text{HCl}, \text{g}) - \Delta H_f^\circ(\text{TiCl}_4, \text{l}) - 2\Delta H_f^\circ(\text{H}_2\text{O}, \text{l}) \\ &= -944 - 4 \times 92.3 \text{ kJ mol}^{-1} + 804.2 \text{ kJ mol}^{-1} + 2 \times 285.8 \text{ kJ mol}^{-1} \\ &= 62.6 \text{ kJ mol}^{-1} \\ \Delta U_R^\circ &= \Delta H_R^\circ - \Delta nRT \\ &= 62.6 \text{ kJ mol}^{-1} - 4 \times 8.314 \text{ J K}^{-1} \text{ mol}^{-1} \times 298.15 \text{ K} = 52.7 \text{ kJ mol}^{-1}\end{aligned}$$

- (d) $2\text{NaOH}(\text{aq}) + \text{H}_2\text{SO}_4(\text{aq}) \rightarrow \text{Na}_2\text{SO}_4(\text{aq}) + 2\text{H}_2\text{O}(\text{l})$
 Assume that $\text{NaOH}(\text{aq})$ and $\text{H}_2\text{SO}_4(\text{aq})$ are completely dissociated.
 The overall reaction is $2\text{OH}^-(\text{aq}) + 2\text{H}^+(\text{aq}) \rightarrow 2\text{H}_2\text{O}(\text{l})$.

$$\begin{aligned}\Delta H_R^\circ &= 2\Delta H_f^\circ(\text{H}_2\text{O}, l) - 2\Delta H_f^\circ(\text{H}^+, aq) - 2\Delta H_f^\circ(\text{OH}^-, aq) \\ &= -2 \times 285.8 \text{ kJ mol}^{-1} - 0 + 2 \times 230.0 \text{ kJ mol}^{-1} \\ &= -111.6 \text{ kJ mol}^{-1} \\ \Delta U_R^\circ &= \Delta H_R^\circ - \Delta nRT \\ &= -111.6 \text{ kJ mol}^{-1} - 0 = -111.6 \text{ kJ mol}^{-1}\end{aligned}$$



$$\begin{aligned}\Delta H_R^\circ &= \Delta H_f^\circ(\text{CO}, g) + 3\Delta H_f^\circ(\text{H}_2, g) - \Delta H_f^\circ(\text{CH}_4, g) - \Delta H_f^\circ(\text{H}_2\text{O}, g) \\ &= -110.5 \text{ kJ mol}^{-1} + 0 + 74.6 \text{ kJ mol}^{-1} + 241.8 \text{ kJ mol}^{-1} \\ &= 205.9 \text{ kJ mol}^{-1} \\ \Delta U_R^\circ &= \Delta H_R^\circ - \Delta nRT \\ &= 205.9 \text{ kJ mol}^{-1} - 2 \times 8.3145 \text{ J K}^{-1} \text{ mol}^{-1} \times 298.15 \text{ K} = 200.9 \text{ kJ mol}^{-1}\end{aligned}$$



$$\begin{aligned}\Delta H_R^\circ &= \Delta H_f^\circ(\text{CH}_3\text{COOH}, l) - \Delta H_f^\circ(\text{CH}_3\text{OH}, g) - \Delta H_f^\circ(\text{CO}, g) \\ &= -484.3 \text{ kJ mol}^{-1} + 201.0 \text{ kJ mol}^{-1} + 110.5 \text{ kJ mol}^{-1} \\ &= -172.8 \text{ kJ mol}^{-1} \\ \Delta U_R^\circ &= \Delta H_R^\circ - \Delta nRT \\ &= -172.8 \text{ kJ mol}^{-1} + 2 \times 8.3145 \text{ J K}^{-1} \text{ mol}^{-1} \times 298.15 \text{ K} = -167.8 \text{ kJ mol}^{-1}\end{aligned}$$

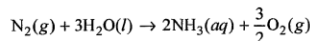
P4.18 A sample of $\text{Na}_2\text{SO}_4(s)$ is dissolved in 225 g of water at 298 K such that the solution is 0.325 molar in Na_2SO_4 . A temperature rise of 0.146°C is observed. The calorimeter constant is $330. \text{ J K}^{-1}$. Calculate the enthalpy of solution of Na_2SO_4 in water at this concentration. Compare your result with that calculated using the data in Table 4.1 (Appendix B, Data Tables).

$$\begin{aligned}0 &= \frac{m_s}{M_s} \Delta H_{\text{solution},m} + \frac{m_{\text{H}_2\text{O}}}{M_{\text{H}_2\text{O}}} C_{\text{H}_2\text{O},m} \Delta T + C_{\text{calorimeter}} \Delta T \\ \Delta H_{\text{solution},m} &= - \left(\frac{225 \text{ g}}{18.02 \text{ g mol}^{-1}} \times 75.3 \text{ J K}^{-1} \text{ mol}^{-1} \times 0.146^\circ\text{C} + 330. \text{ J K}^{-1} \times 0.146^\circ\text{K} \right) \\ &= -2.52 \times 10^3 \text{ J mol}^{-1} \\ \Delta H_{\text{solution},m} &= 2\Delta H_{\text{solution},m}(\text{Na}^+, aq) + \Delta H_{\text{solution},m}(\text{SO}_4^{2-}, aq) - \Delta H_f(\text{Na}_2\text{SO}_4, s) \\ &= -2 \times 240.1 \times 10^3 \text{ J mol}^{-1} - 909.3 \times 10^3 \text{ J mol}^{-1} + 1387.1 \times 10^3 \text{ J mol}^{-1} \\ &= -2.4 \times 10^3 \text{ J mol}^{-1}\end{aligned}$$

$$\text{The relative error is } \frac{-2.52 \text{ kJ mol}^{-1} + 2.4 \text{ kJ mol}^{-1}}{-2.4 \text{ kJ mol}^{-1}} = 5.1\%$$

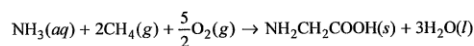
P4.19 Nitrogen is a vital component of proteins and nucleic acids, and thus is necessary for life. The atmosphere is composed of roughly 80% N_2 , but most organisms cannot directly utilize N_2 for biosynthesis. Bacteria capable of “fixing” nitrogen (i.e., converting N_2 to a chemical form [such as NH_3] which 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 bacteria that live in the plant's roots. Assume that the hypothetical reaction for fixing nitrogen biologically is



- a. Calculate the standard enthalpy change for the biosynthetic fixation of nitrogen at $T = 298 \text{ K}$. For $\text{NH}_3(\text{aq})$, ammonia dissolved in aqueous solution, $\Delta H_f^\circ = -80.3 \text{ kJ mol}^{-1}$.

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



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

- c. Calculate the standard enthalpy change for the synthesis of glycine from nitrogen, oxygen, and methane.

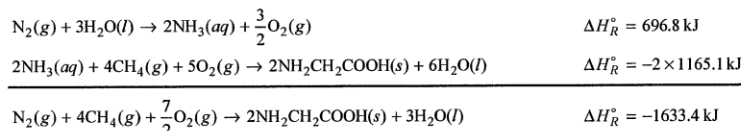
- (a) The enthalpy change for the reaction $\text{N}_2(\text{g}) + 3\text{H}_2\text{O}(\text{l}) \rightarrow 2\text{NH}_3(\text{aq}) + \frac{3}{2}\text{O}_2(\text{g})$ is:

$$\begin{aligned}\Delta H_R^\circ(298 \text{ K}) &= 2 \times \Delta H_f^\circ(\text{NH}_3, \text{aq}) - 3 \times \Delta H_f^\circ(\text{H}_2\text{O}, \text{l}) \\ &= 2 \times (-80.3 \text{ kJ mol}^{-1}) + (-3) \times (-285.8 \text{ kJ mol}^{-1}) = 696.8 \text{ kJ mol}^{-1}\end{aligned}$$

- (b) The enthalpy change for the reaction $\text{NH}_3(\text{aq}) + 2\text{CH}_4(\text{g}) + \frac{5}{2}\text{O}_2(\text{g}) \rightarrow \text{NH}_2\text{CH}_2\text{COOH}(\text{s}) + 3\text{H}_2\text{O}(\text{l})$ is:

$$\begin{aligned}\Delta H_R^\circ(298 \text{ K}) &= 3\Delta H_f^\circ(\text{H}_2\text{O}, \text{l}) + \Delta H_f^\circ(\text{NH}_2\text{CH}_2\text{COOH}, \text{s}) - 2\Delta H_f^\circ(\text{CH}_4, \text{g}) - \Delta H_f^\circ(\text{NH}_3, \text{aq}) \\ &= 3 \times (-285.8 \text{ kJ mol}^{-1}) + (-537.2 \text{ kJ mol}^{-1}) - 2 \times (-74.6 \text{ kJ mol}^{-1}) - (-80.3 \text{ kJ mol}^{-1}) \\ &= -1165.1 \text{ kJ mol}^{-1}\end{aligned}$$

- (c) To calculate the enthalpy for the reaction producing glycine we use:



Therefore, the enthalpy per mole of glycine is:

$$\Delta H_R^\circ \text{ per mole glycine} = \frac{(-1633.4 \text{ kJ})}{2} = -816.7 \text{ kJ mol}^{-1}$$

P4.20 If 3.365 g of ethanol, $\text{C}_2\text{H}_5\text{OH}(\text{l})$, is burned completely in a bomb calorimeter at 298.15 K, the heat produced is 99.472 kJ.

- a. Calculate $\Delta H_{\text{combustion}}^\circ$ for ethanol at 298.15 K.
b. Calculate ΔH_f° of ethanol at 298.15 K.

The reaction is $\text{C}_2\text{H}_5\text{OH}(\text{l}) + 3\text{O}_2(\text{g}) \rightarrow 3\text{H}_2\text{O}(\text{l}) + 2\text{CO}_2(\text{g})$.

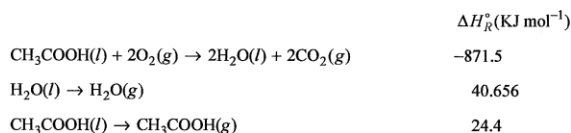
$$\begin{aligned}\Delta H_R &= 2\Delta H_f^\circ(\text{CO}_2, \text{g}) + 3\Delta H_f^\circ(\text{H}_2\text{O}, \text{l}) - \Delta H_f^\circ(\text{C}_2\text{H}_5\text{OH}, \text{l}) \\ \Delta H_f^\circ(\text{C}_2\text{H}_5\text{OH}, \text{l}) &= -\Delta H_R + 2\Delta H_f^\circ(\text{CO}_2, \text{g}) + 3\Delta H_f^\circ(\text{H}_2\text{O}, \text{l})\end{aligned}$$

$$\Delta U_R = \frac{\text{Energy}}{m_{\text{ethanol}}/M_{\text{ethanol}}} = \frac{-99472 \text{ J}}{3.365 \text{ g}/46.07 \text{ g mol}^{-1}} = -1362 \text{ kJ mol}^{-1}$$

$$\Delta H_R = \Delta U_R + \Delta nRT = -1362 \text{ kJ mol}^{-1} - R \times 298 \text{ K} = -1364 \text{ kJ mol}^{-1}$$

$$\begin{aligned}\Delta H_f^\circ(\text{C}_2\text{H}_5\text{OH}, l) &= -\Delta H_R + 2\Delta H_f^\circ(\text{CO}_2, g) + 3\Delta H_f^\circ(\text{H}_2\text{O}, l) \\ &= 1364 \text{ kJ mol}^{-1} - 2 \times 393.5 \text{ kJ mol}^{-1} - 3 \times 285.8 \text{ kJ mol}^{-1} = -280.0 \text{ kJ mol}^{-1}\end{aligned}$$

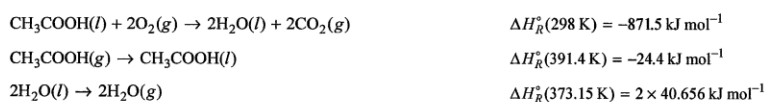
P4.21 From the following data, calculate $\Delta H_{R,391.4\text{K}}^\circ$ for the reaction $\text{CH}_3\text{COOH}(g) + 2\text{O}_2(g) \rightarrow 2\text{H}_2\text{O}(g) + 2\text{CO}_2(g)$:



Values for ΔH_R° for the first two reactions are at 298.15 K, and for the third reaction at 391.4 K.

Substance	CH ₃ COOH(l)	O ₂ (g)	CO ₂ (g)	H ₂ O(l)	H ₂ O(g)
$C_{P,m}/R$	14.9	3.53	4.46	9.055	4.038

The desired overall reaction can be related to the individual reactions for which the data are given as follows:



To obtain $\Delta H_R^\circ(391.4 \text{ K})$, all individual reaction enthalpies must be calculated at 391.4 K.

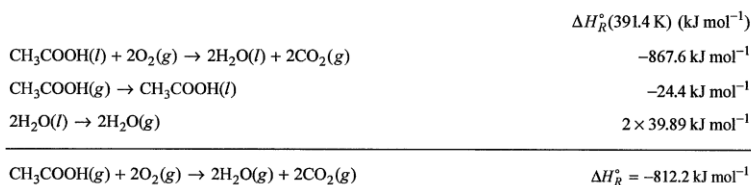
For the reaction $2\text{H}_2\text{O}(l) \rightarrow 2\text{H}_2\text{O}(g)$

$$\begin{aligned}\Delta H_R^\circ(391.4 \text{ K}) &= \Delta H_R^\circ(373.15 \text{ K}) + [C_{P,m}\text{H}_2\text{O}(g) - C_{P,m}\text{H}_2\text{O}(l)]\Delta T \\ &= 40.65 \text{ kJ mol}^{-1} + 8.314 \text{ J K}^{-1} \text{ mol}^{-1} [4.038 - 9.055] \times [391.4 \text{ K} - 373.15 \text{ K}] \\ &= 39.89 \text{ kJ mol}^{-1}\end{aligned}$$

For the reaction $\text{CH}_3\text{COOH}(l) + 2\text{O}_2(g) \rightarrow 2\text{H}_2\text{O}(l) + 2\text{CO}_2(g)$

$$\begin{aligned}\Delta H_R^\circ(391.4 \text{ K}) &= \Delta H_R^\circ + \Delta C_P \Delta T \\ &= -871.5 \text{ kJ mol}^{-1} + 8.314 \text{ J mol}^{-1} \text{ K}^{-1} \\ &\quad [2 \times 4.46 + 2 \times 9.055 - 14.9 - 2 \times 3.53] \times [391.4 \text{ K} - 298 \text{ K}] \\ &= -867.6 \text{ kJ mol}^{-1}\end{aligned}$$

The table above can now be rewritten with all enthalpy values given at 391.4 K.



P4.22 A 0.1429 g sample of sucrose, $\text{C}_{12}\text{H}_{22}\text{O}_{11}$, is burned in a bomb calorimeter. In order to produce the same temperature rise in the calorimeter as the reaction, 2353 J must be expended.

- a. Calculate ΔU and ΔH for the combustion of 1 mole of sucrose.

- b. Using the data tables and your answer to (a), calculate ΔH_f° for sucrose.
- c. The rise in temperature of the calorimeter and its contents as a result of the reaction is 1.743 K. Calculate the heat capacity of the calorimeter and its contents.

The reaction is $C_{12}H_{22}O_{11}(s) + 12O_2(g) \rightarrow 11H_2O(l) + 12CO_2(g)$.

$$\Delta H_R = 12\Delta H_f^\circ(CO_2, g) + 11\Delta H_f^\circ(H_2O, l) - \Delta H_f^\circ(C_{12}H_{22}O_{11}, s)$$

$$\Delta H_f^\circ(C_{12}H_{22}O_{11}, s) = -\Delta H_R + 12\Delta H_f^\circ(CO_2, g) + 11\Delta H_f^\circ(H_2O, l)$$

$$\Delta U_R = \frac{\text{Energy}}{m_{\text{sucrose}}/M_{\text{sucrose}}} = \frac{-2353 \text{ J}}{0.1429 \text{ g}/342.3 \text{ g mol}^{-1}} = -5.635 \times 10^3 \text{ kJ mol}^{-1}$$

$$\Delta H_R = \Delta U_R + \Delta nRT = -5635 \text{ kJ mol}^{-1}$$

$$\begin{aligned} \Delta H_f^\circ(C_{12}H_{22}O_{11}, l) &= -\Delta H_R + 12\Delta H_f^\circ(CO_2, g) + 11\Delta H_f^\circ(H_2O, l) \\ &= 5635 \text{ kJ mol}^{-1} - 12 \times 393.5 \text{ kJ mol}^{-1} - 11 \times 285.8 \text{ kJ mol}^{-1} \\ &= -2.231 \times 10^3 \text{ kJ mol}^{-1} \end{aligned}$$

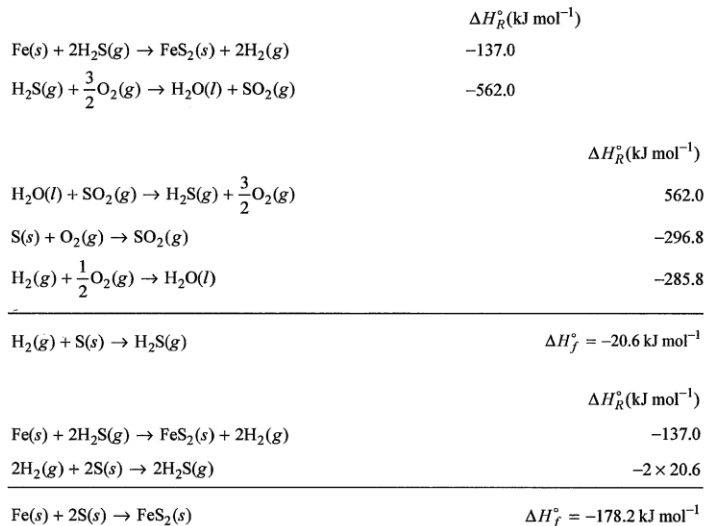
$$\text{Calorimeter constant} = \frac{|\text{Energy}|}{\Delta T} = \frac{2353 \text{ J}}{1.743 \text{ K}} = 1.350 \times 10^3 \text{ J K}^{-1}$$

- P4.23 Calculate ΔH_R° at 675 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. Compare your result with ΔH_R° at 298.15 K. Is the difference large or small? Why?

$$\begin{aligned} \Delta H_R^\circ(675 \text{ K}) &= \Delta H_R^\circ(298.15 \text{ K}) + \int_{298.15}^{675} \Delta C_p \left(\frac{T}{K} \right) d \frac{T}{K} \\ \Delta C_p &= 5C_{p,m}(N_2, g) + 6C_{p,m}(H_2O, g) - 4C_{p,m}(NH_3, g) - 6C_{p,m}(NO, g) \\ &= \left[\begin{aligned} &(5 \times 30.81 + 6 \times 33.80 - 4 \times 29.29 - 6 \times 33.58) \\ &- (5 \times 0.01187 + 6 \times 0.00795 + 4 \times 0.01103 - 6 \times 0.02593) \frac{T}{K} \\ &+ (5 \times 2.3968 + 6 \times 2.8228 - 4 \times 4.2446 - 6 \times 5.3326) \times 10^{-5} \frac{T^2}{K^2} \\ &- (5 \times 1.0176 + 6 \times 1.3115 - 4 \times 2.7706 - 6 \times 2.7744) \times 10^{-8} \frac{T^3}{K^3} \end{aligned} \right] \text{J K}^{-1} \text{mol}^{-1} \\ &= \left[38.21 + 0.00441 \frac{T}{K} - 2.0053 \times 10^{-4} \frac{T^2}{K^2} + 1.4772 \times 10^{-7} \frac{T^3}{K^3} \right] \text{J K}^{-1} \text{mol}^{-1} \\ \int_{298.15}^{675} \Delta C_p \left(\frac{T}{K} \right) d \frac{T}{K} &= \left[\int_{298.15}^{675} \left(38.21 + 0.00441 \frac{T}{K} - 2.0053 \times 10^{-4} \frac{T^2}{K^2} + 1.4772 \times 10^{-7} \frac{T^3}{K^3} \right) d \frac{T}{K} \right] \text{J mol}^{-1} \\ &= (14.400 + 0.8086 - 18.78 + 7.374) \text{kJ mol}^{-1} = 3.80 \text{ kJ mol}^{-1} \\ \Delta H_R^\circ(298.15 \text{ K}) &= 5\Delta H_f^\circ(N_2, g) + 6\Delta H_f^\circ(H_2O, g) - 4\Delta H_f^\circ(NH_3, g) - 6\Delta H_f^\circ(NO, g) \\ \Delta H_R^\circ(298.15 \text{ K}) &= -6 \times 241.8 \text{ kJ mol}^{-1} + 4 \times 45.9 \text{ kJ mol}^{-1} - 6 \times 91.3 \text{ kJ mol}^{-1} = -1815 \text{ kJ mol}^{-1} \\ \Delta H_R^\circ(675 \text{ K}) &= -1815 \text{ kJ mol}^{-1} + 3.80 \text{ kJ mol}^{-1} = -1811 \text{ kJ mol}^{-1} \end{aligned}$$

The difference is small, not because the heat capacities of reactants and products are small, but because the difference in heat capacities of reactants and products is small.

P4.24 From the following data at 298.15 K as well as data in Table 4.1 (Appendix B, Data Tables), calculate the standard enthalpy of formation of $\text{H}_2\text{S}(\text{g})$ and of $\text{FeS}_2(\text{s})$:



P4.25 Using the protein DSC data in Problem P4.10, calculate the enthalpy change between the $T = 288 \text{ K}$ and $T = 318 \text{ K}$. Give your answer in units of kJ per mole. Assume the molecular weight of the protein is 14,000. grams. [Hint: You can perform the integration of the heat capacity by estimating the area under the DSC curve and above the dotted baseline in Problem 4.10. This can be done by dividing the area up into small rectangles and summing the areas of the rectangles.] Comment on the accuracy of the method.

There are approximately 624 squares in the yellow area. On the horizontal axis, 1 square = 0.50 K. On the vertical axis, 1 square = $0.0418 \text{ J K}^{-1} \text{ g}^{-1}$. We obtain:

$$\Delta H_m = 624 \times 0.50 \text{ K} \times 0.0418 \text{ J K}^{-1} \text{ g}^{-1} \times 14,000. \text{ g mol}^{-1} = 1.8 \times 10^2 \text{ kJ mol}^{-1}$$

The method is reasonably accurate because the number of squares can be counted quite accurately.

P4.26 Given the following heat capacity data, calculate ΔH_f° of $\text{CO}_2(\text{g})$ at 525 K.

Substance	$C(\text{graphite})$	$\text{O}_2(\text{g})$	$\text{CO}_2(\text{g})$
$C_{P,m} / \text{J mol}^{-1} \text{ K}^{-1}$	8.52	28.8	37.1

$$\begin{aligned} \Delta H_R^\circ(525 \text{ K}) &= \Delta H_f^\circ(298.15 \text{ K}) + \int_{298.15}^{525} \Delta C_P \left(\frac{T}{\text{K}} \right) d \frac{T}{\text{K}} = \Delta C_P \Delta T \\ \Delta C_P &= C_{P,m}(\text{CO}_2, \text{g}) - C_{P,m}(\text{C, graphite}) - C_{P,m}(\text{O}_2, \text{g}) \\ &= [37.1 - 8.52 - 28.8] \text{ J K}^{-1} \text{ mol}^{-1} \\ &= -0.22 \text{ J K}^{-1} \text{ mol}^{-1} \end{aligned}$$

$$\begin{aligned}\Delta C_p \Delta T &= -0.22 \text{ J K}^{-1} \text{ mol}^{-1} \times 226.85 \text{ K} = -49.9 \text{ J mol}^{-1} \\ \Delta H_f^\circ(525 \text{ K}) &= \Delta H_f^\circ(298.15 \text{ K}) + \Delta C_p \Delta T \\ &= -393.5 \text{ kJ mol}^{-1} - 49.9 \text{ J mol}^{-1} = -393.6 \text{ kJ mol}^{-1}\end{aligned}$$

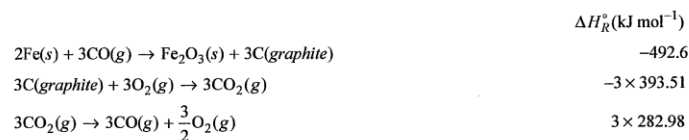
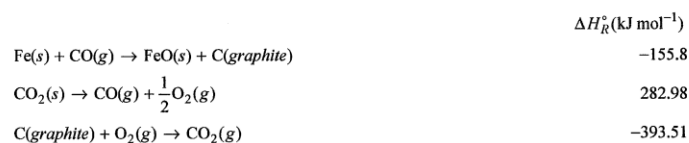
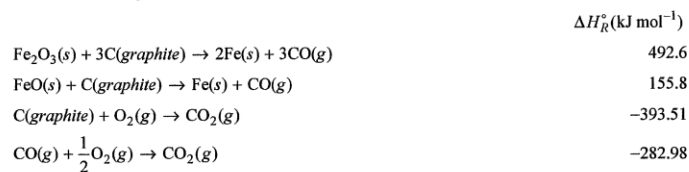
- P4.27** Calculate ΔH for the process in which $\text{Cl}_2(\text{g})$ initially at 298.15 K at 1 bar is heated to 690. K at 1 bar. Use the temperature-dependent heat capacities in the data tables. How large is the relative error if the molar heat capacity is assumed to be constant at its value of 298.15 K over the temperature interval?

$$\begin{aligned}\Delta H &= \int_{298.15}^{690} C_{p,m} \left(\frac{T}{\text{K}} \right) d \frac{T}{\text{K}} \\ &= \int_{298.15}^{690} \left[22.85 + 0.06543 \frac{T}{\text{K}} - 1.2517 \times 10^{-4} \frac{T^2}{\text{K}^2} + 1.1484 \times 10^{-7} \frac{T^3}{\text{K}^3} \right] d \frac{T}{\text{K}} \text{ J K}^{-1} \text{ mol}^{-1} \\ &= (8954 + 12668 - 12601 + 6281) \text{ J mol}^{-1} = 15.3 \text{ kJ mol}^{-1}\end{aligned}$$

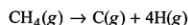
If it is assumed that the heat capacity is constant at its value at 298 K,

$$\begin{aligned}\Delta H^\circ &\approx \int_{298.15}^{690} (33.95) d \frac{T}{\text{K}} \text{ J K}^{-1} \text{ mol}^{-1} = 13.3 \text{ kJ mol}^{-1} \\ \text{Error} &= 100 \times \frac{15.3 \text{ kJ mol}^{-1} - 13.3 \text{ kJ mol}^{-1}}{15.3 \text{ kJ mol}^{-1}} = 13.1\%\end{aligned}$$

- P4.28** From the following data at 298.15 K calculate the standard enthalpy of formation of $\text{FeO}(\text{s})$ and of $\text{Fe}_2\text{O}_3(\text{s})$:



- P4.29** Calculate the average C—H bond enthalpy in methane using the data tables. Calculate the percent error in equating the average C—H bond energy in Table 4.3 with the bond enthalpy.



$$\begin{aligned}\Delta H_R^\circ &= 4\Delta H_f^\circ(\text{H}, g) + \Delta H_f^\circ(\text{C}, g) - \Delta H_f^\circ(\text{CH}_4, g) \\ &= 4 \times 218.0 \text{ kJ mol}^{-1} + 716.7 \text{ kJ mol}^{-1} + 74.6 \text{ kJ mol}^{-1} = 1663 \text{ kJ mol}^{-1}\end{aligned}$$

$$\text{Average Bond Enthalpy} = \frac{1663 \text{ kJ mol}^{-1}}{4} = 415.8 \text{ kJ mol}^{-1}$$

$$\text{Relative Error} = 100 \times \frac{415.8 \text{ kJ mol}^{-1} - 411 \text{ kJ mol}^{-1}}{415.8 \text{ kJ mol}^{-1}} = 1.2\%$$

- P4.30** Use the average bond energies in Table 4.3 to estimate ΔU for the reaction $\text{C}_2\text{H}_4(g) + \text{H}_2(g) \rightarrow \text{C}_2\text{H}_6(g)$. Also calculate ΔU_R° from the tabulated values of ΔH_f° for reactant and products (Appendix B, Data Tables). Calculate the percent error in estimating ΔU_R° from the average bond energies for this reaction.

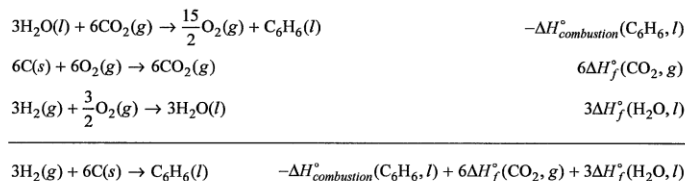
$$\begin{aligned}\Delta U_R &= -[(\text{C—C bond energy} + 6\text{C—H bond energy}) - \text{H—H bond energy} \\ &\quad - (\text{C=C bond energy} - 4\text{C—H bond energy})]\end{aligned}$$

$$\begin{aligned}\Delta U_R &= -[(346 \text{ kJ mol}^{-1} + 6 \times 411 \text{ kJ mol}^{-1}) - 432 \text{ kJ mol}^{-1} - (602 \text{ kJ mol}^{-1} \\ &\quad - 4 \times 411 \text{ kJ mol}^{-1})] = -134 \text{ kJ mol}^{-1}\end{aligned}$$

Using the data tables,

$$\begin{aligned}\Delta H_R^\circ(298.15 \text{ K}) &= \Delta H_f^\circ(\text{C}_2\text{H}_6, g) - \Delta H_f^\circ(\text{C}_2\text{H}_4, g) - \Delta H_f^\circ(\text{H}_2, g) \\ \Delta H_R^\circ(298.15 \text{ K}) &= -84.0 \text{ kJ mol}^{-1} - 52.4 \text{ kJ mol}^{-1} = -136.4 \text{ kJ mol}^{-1} \\ \Delta U_R^\circ(298.15 \text{ K}) &= \Delta H_R^\circ(298.15 \text{ K}) - \Delta nRT \\ &= -136.4 \text{ kJ mol}^{-1} + 8.314 \text{ J mol}^{-1} \text{ K}^{-1} \times 298.15 \text{ K} = -133.9 \text{ kJ mol}^{-1} \\ \text{Relative Error} &= 100 \times \frac{+134 \text{ kJ mol}^{-1} - 133.9 \text{ kJ mol}^{-1}}{-133.9 \text{ kJ mol}^{-1}} \approx 0\%\end{aligned}$$

- P4.31** Use the tabulated values of the enthalpy of combustion of benzene and the enthalpies of formation of $\text{CO}_2(g)$ and $\text{H}_2\text{O}(l)$ to determine ΔH_f° for benzene.

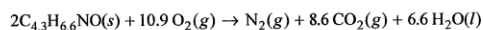
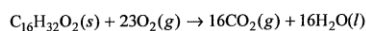
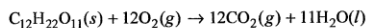


$$\begin{aligned}\Delta H_f^\circ(\text{C}_6\text{H}_6, l) &= 3268 \text{ kJ mol}^{-1} - 6 \times 393.5 \text{ kJ mol}^{-1} - 3 \times 285.8 \text{ kJ mol}^{-1} \\ &= 49.6 \text{ kJ mol}^{-1}\end{aligned}$$

- P4.32** Compare the heat evolved at constant pressure per mole of oxygen in the combustion of sucrose ($\text{C}_{12}\text{H}_{22}\text{O}_{11}$) and palmitic acid ($\text{C}_{16}\text{H}_{32}\text{O}_2$) with the combustion of a typical protein, for which the empirical formula is $\text{C}_4.3\text{H}_{6.6}\text{NO}$. Assume for the protein that the combustion yields $\text{N}_2(g)$, $\text{CO}_2(g)$, and $\text{H}_2\text{O}(l)$. Assume that the

enthalpies for combustion of sucrose, palmitic acid, and a typical protein are 5647 kJ mol^{-1} , $10,035 \text{ kJ mol}^{-1}$, and 22.0 kJ g^{-1} , respectively. Based on these calculations, determine the average heat evolved per mole of oxygen consumed, assuming combustion of equal moles of sucrose, palmitic acid, and protein.

We need the chemical equations to determine the moles of oxygen consumed for sucrose, palmitic acid, and protein:



Now we convert the enthalpy for the combustion of protein:

$$\Delta H_{\text{combustion}}(\text{protein}) = (22.0 \text{ kJ g}^{-1}) \times (88.31 \text{ g mol}^{-1}) = 1942.8 \text{ kJ mol}^{-1}$$

The average heat evolved per mole of oxygen is then:

$$\Delta H_{\text{combustion}}(\text{sucrose}) = \frac{(5647 \text{ kJ mol}^{-1})}{(12)} = 470.6 \text{ kJ mol}^{-1}$$

$$\Delta H_{\text{combustion}}(\text{palmitic acid}) = \frac{(10035 \text{ kJ mol}^{-1})}{(23)} = 436.3 \text{ kJ mol}^{-1}$$

$$\Delta H_{\text{combustion}}(\text{protein}) = \frac{(1942.8 \text{ kJ mol}^{-1})}{\left(\frac{10.9}{2}\right)} = 356.5 \text{ kJ mol}^{-1}$$

P4.33 A camper stranded in snowy weather loses heat by wind convection. The camper is packing emergency rations consisting of 58% sucrose, 31% fat, and 11% protein by weight. Using the data provided in Problem P4.32 and assuming the fat content of the rations can be treated with palmitic acid data and the protein content similarly by the protein data in Problem P4.32, how much emergency rations must the camper consume in order to compensate for a reduction in body temperature of 3.5 K ? Assume the heat capacity of the body equals that of water. Assume the camper weighs 67 kg . State any additional assumptions.

At constant pressure $q = \Delta H$. The composition of the emergency rations means that 1 kg of the rations contains the following number of moles of sucrose, fat, and protein:

$$n_{\text{sucrose}} = \frac{m}{M} = \frac{(0.58 \text{ kg})}{(342.3 \text{ g mol}^{-1})} = 1.694 \text{ mol}$$

$$n_{\text{fat}} = \frac{m}{M} = \frac{(0.31 \text{ kg})}{(256.43 \text{ g mol}^{-1})} = 1.209 \text{ mol}$$

$$n_{\text{protein}} = \frac{m}{M} = \frac{(0.11 \text{ kg})}{(88.30 \text{ g mol}^{-1})} = 1.246 \text{ mol}$$

Therefore, the enthalpy of combustion for 1 kg of rations is:

$$\begin{aligned} \Delta H_{\text{combustion}, 1 \text{ kg}}^{\circ} &= (1.694 \text{ mol}) \times (-5647 \text{ kJ mol}^{-1}) + (1.209 \text{ mol}) \times (-10035 \text{ kJ mol}^{-1}) \\ &\quad + (1.246 \text{ mol}) \times (-22 \text{ kJ mol}^{-1}) = -24120 \text{ kJ} \end{aligned}$$

The heat the stranded camper loses is given by:

$$\begin{aligned} q_{\text{lost}} &= n_{\text{H}_2\text{O}} C_{p,m} \Delta T = \frac{m_{\text{H}_2\text{O}}}{M_{\text{H}_2\text{O}}} \times C_{p,m} \times \Delta T = \frac{(67 \text{ kg})}{(18.01 \text{ g mol}^{-1})} \times (75.3 \text{ J K}^{-1} \text{ mol}^{-1}) \times (3.5 \text{ K}) \\ &= 980 \text{ kJ} \end{aligned}$$

Finally, the mass of rations that needs to be consumed to produce the lost amount of heat assuming the body consists of 90% water is then:

$$m_{\text{rations}} = 0.9 \times \frac{(1 \text{ kg}) \times (980 \text{ kJ})}{(24120 \text{ kJ})} = 49 \text{ g}$$

P4.34 In order to get in shape for mountain climbing, an avid hiker with a mass of 60. kg ascends the stairs in the world's tallest structure, the 828 m tall Burj Khalifa in Dubai, United Arab Emirates. Assume that she eats energy bars on the way up and that her body is 25% efficient in converting the energy content of the bars into the work of climbing. How many energy bars does she have to eat if a single bar produces 1.08×10^3 kJ of energy upon metabolizing?

$$\begin{aligned} E_{\text{potential}} &= mgh \\ &= 60. \text{ kg} \times 9.80 \text{ m s}^{-2} \times 828 \text{ m} = 4.87 \times 10^2 \text{ kJ} \\ E_{\text{metabolic}} &= \frac{E_{\text{potential}}}{0.25} = \frac{4.87 \times 10^2 \text{ kJ}}{0.25} = 1.95 \times 10^3 \text{ kJ} \\ N_{\text{bars}} &= \frac{E_{\text{metabolic}}}{\text{Energy per bar}} = \frac{1.95 \times 10^3 \text{ kJ}}{1.08 \times 10^3 \text{ kJ bar}^{-1}} = 1.8 \text{ bars} \end{aligned}$$

P4.35 We return to the 60. kg hiker of P4.34, who is climbing the 828 m tall Burj Khalifa in Dubai. If the efficiency of converting the energy content of the bars into the work of climbing is 25%, the remaining 75% of the energy released through metabolism is heat released to her body. She eats two energy bars and a single bar produces 1.08×10^3 kJ of energy upon metabolizing. Assume that the heat capacity of her body is equal to that for water. Calculate her temperature at the top of the structure. Is your result reasonable? Can you think of a mechanism by which her body might release energy to avoid a temperature increase?

$$\begin{aligned} \text{Energy leading to increase in } T &= 2 \text{ bars} \times 1.08 \times 10^3 \text{ kJ bar}^{-1} \times 0.75 \\ &= 1.62 \times 10^3 \text{ kJ} \end{aligned}$$

$$\text{Increase in } T = \frac{\text{energy}}{nC_{p,m}} = \frac{1.62 \times 10^3 \text{ kJ}}{\frac{60. \text{ kg}}{18.02 \text{ g mol}^{-1}} \times 75.3 \text{ J mol}^{-1} \text{ K}^{-1}} = 6.5^\circ \text{C}$$

A possible mechanism to release energy is perspiration. The evaporation of 0.72 L of water would dissipate the required amount of energy.