

CHAPTER 2

1.
 - a) $q_p = \Delta H = 1 \text{ L} \times 0.9982 \text{ kg L}^{-1} \times 2447 \text{ kJ kg}^{-1} = \underline{2443 \text{ kJ}}$
 - b) $\Delta T = 2443 \text{ kJ} / (60 \text{ kg} \times 4.184 \text{ kJ K}^{-1} \text{ kg}^{-1}) = \underline{9.7 \text{ K}}$
 - c) $\text{C}_{12}\text{H}_{22}\text{O}_{11}(s) + 12\text{O}_2(g) \rightarrow 12 \text{CO}_2(g) + 11\text{H}_2\text{O}(l)$
 $\Delta H = 11(-285.83 \text{ kJ mol}^{-1}) + 12(-393.51 \text{ kJ mol}^{-1}) - (-2222.10 \text{ kJ mol}^{-1})$
 $= -5644 \text{ kJ mol}^{-1}$
 $M_{\text{sucrose}} = 342.31 \text{ g mol}^{-1}$
 $m_{\text{sucrose}} = \underline{2443 \text{ kJ} \times 342.31 \text{ g mol}^{-1} / 5644 \text{ kJ mol}^{-1} = 148.2 \text{ g}}$
2.
 - a) 1 kg of carbon is $(1.0 \text{ kg} \times 1000 \text{ g kg}^{-1}) / (12.011 \text{ g mol}^{-1}) = 83.3 \text{ mol}$
 $83.3 \text{ mol CO}_2 \times 8.3145 \text{ J mol}^{-1} \text{ K}^{-1} \times 298 \text{ K} / (10^5 \text{ Pa}) = 2.06 \text{ m}^3 \text{ CO}_2$
 $2.06 \text{ m}^3 \text{ CO}_2 / (0.000390 \text{ m}^3 \text{ CO}_2 / \text{m}^3 \text{ air}) = \underline{5292 \text{ m}^3 \text{ air}}$
 - b) $p = F/A = mg/A = 10^5 \text{ Pa}$. $m = Ap/g = 1 \text{ m}^2 \times 10^5 \text{ Pa} / (9.80662 \text{ m s}^{-2}) = 10197 \text{ kg}$
 $M_{\text{air}} = 0.8 \times 0.0280 \text{ kg mol}^{-1} + 0.2 \times 0.0320 \text{ kg mol}^{-1} = 0.0288 \text{ kg} / (\text{mol air})$
 $n_{\text{air}} = 10197 \text{ kg} / 0.0288 \text{ kg} / (\text{mol air}) = 354069 \text{ mol air}$
 $n_{\text{CO}_2} = 354069 \text{ mol air} \times 0.000390 \text{ mol CO}_2 / (\text{mol air}) = 138.09 \text{ mol CO}_2$
 $m_{\text{C}} = 0.012011 \text{ kg/mol C} \times 138.09 \text{ mol CO}_2 = \underline{1.659 \text{ kg C}}$
 - c) $1.659 \text{ kg C} / (1 \text{ kg y}^{-1}) = \underline{1.659 \text{ y}}$.
3.
 - a) $w = mgh = 10 \text{ kg} \times 9.81 \text{ m s}^{-2} \times 10 \text{ m} = \underline{981 \text{ J}}$
 - b) $k = F/(x - x_0) = 5.00 \text{ N} / (0.105 \text{ m} - 0.100 \text{ m}) = 1.00 \times 10^3 \text{ N m}^{-1}$
 $w = (k/2)(x - x_0)^2 = 1.00 \times 10^3 \text{ N m}^{-1} \times (0.01 \text{ m})^2 / 2 = 0.050 \text{ J}$
 $\Delta d/d_{\text{surface}} \times 100\% = \underline{1.2\%}$
 - c) $w = -p(V_2 - V_1) = -10^5 \text{ Pa} \times 0.002 \text{ m}^3 = \underline{-200 \text{ J}}$.
 - d) $w = -2 \times 10^{-4} \text{ J}$
 - e) $w = -nRT \ln(V_2/V_1) = -p_1 V_1 \ln(V_2/V_1) = -10^5 \text{ Pa} \times 10^{-3} \text{ m}^3 \times \ln 3 = \underline{-110 \text{ J}}$.
4.
 - a) $w = \int_0^{10} f dx = \int_0^{10} (20x + x^2) dx = \left[10x^2 + \frac{1}{3}x^3 \right]_0^{10} = (1000 + 333) \times 10^{-21} \text{ J} = \underline{1.333 \times 10^{-18} \text{ J}}$
 - b) $w = 1.333 \times 10^{-18} \text{ J} \times 6.022 \times 10^{23} \text{ mol}^{-1} = \underline{8.03 \times 10^5 \text{ J mol}^{-1}}$
5.
 - a) $p = \rho gh = 1025 \text{ kg m}^{-3} \times 9.80662 \text{ m s}^{-2} \times 2500 \text{ m} = 2.513 \times 10^7 \text{ Pa} = \underline{251.3 \text{ bar}}$
 - b) $\Delta V/V = -\kappa \Delta p = -(2.513 \times 10^7 \text{ Pa}) \times 4.9458 \times 10^{-10} \text{ Pa}^{-1} = \underline{-0.0124}$
 So the density **increases** by a factor of 0.0124, or 1.24 %
 - c) $p_1 V_1 / T_1 = p_2 V_2 / T_2$, so $V_2 = p_1 V_1 T_2 / (T_1 p_2) = 1 \text{ bar} \times 10 \text{ L} \times 277 \text{ K} / (293 \text{ K} \times 252.3 \text{ bar})$

$$= 0.0375 \text{ L. Density is reciprocally related to volume. } 10/0.0375 = 266.9 - 1 = 265.9 = \underline{26590\%}$$

6. $n_{\text{H}_2\text{O}} = 100 \text{ g}/(18.015 \text{ g mol}^{-1}) = 5.55 \text{ mol.}$
- a) $q = 5.55 \text{ mol} \times 75.4 \text{ J mol}^{-1} \text{ K}^{-1} \times 100 \text{ K} = \underline{4.19 \times 10^4 \text{ J}}$
- b) $q = n_{\text{H}_2\text{O}} \Delta_{\text{fus}} H = 5.55 \text{ mol} \times 6007 \text{ J mol}^{-1} = \underline{-3.33 \times 10^4 \text{ J}}$
- c) $q = n_{\text{H}_2\text{O}} \Delta_{\text{vap}} H = 5.55 \text{ mol} \times 40667 \text{ J mol}^{-1} = \underline{2.26 \times 10^5 \text{ J}}$
7. a) $V_1 = 1 \text{ mol} \times 8.3145 \text{ J mol}^{-1} \text{ K}^{-1} \times 300 \text{ K} / (10^5 \text{ Pa}) = 0.0249 \text{ m}^3$
 $V_2 = 1 \text{ mol} \times 8.3145 \text{ J mol}^{-1} \text{ K}^{-1} \times 600 \text{ K} / (10^5 \text{ Pa}) = 0.0499 \text{ m}^3$
 $w_p = -p(V_2 - V_1) = -10^5 \text{ Pa} \times (0.0499 - 0.0249) \text{ m}^3 = -2494 \text{ J}$
- b) $\Delta U = nC_{V,m} \Delta T = 1 \text{ mol} \times 20.8 \text{ J mol}^{-1} \text{ K}^{-1} \times 300 \text{ K} = \underline{6.24 \text{ kJ}}$
 $\Delta H = \Delta U + \Delta(pV) = 6.24 \text{ kJ} + 2.49 \text{ kJ} = \underline{8.73 \text{ kJ}}$
- c) $q_p = \Delta H = \underline{8.73 \text{ kJ}}$
8. a) The volume, $V = (4/3)\pi r^3 = 1.333 \times 3.142 \times (5 \times 10^{-7} \text{ m})^3 = 5.236 \times 10^{-19} \text{ m}^3$
 $m = V\rho = 5.236 \times 10^{-19} \text{ m}^3 \times 1000 \text{ kg m}^{-3} = \underline{5.236 \times 10^{-16} \text{ kg.}}$
- b) $M = mN_A = 5.236 \times 10^{-16} \text{ kg} \times 6.022 \times 10^{23} \text{ mol}^{-1} = \underline{3.153 \times 10^8 \text{ kg mol}^{-1} \text{ (kD)}}$
- c) $N_{\text{water}} = M/M_{\text{water}} = 3.153 \times 10^8 \text{ kg mol}^{-1} / 0.018 \text{ kg mol}^{-1} = \underline{1.752 \times 10^{10}}$
- d) $6378.1 \times 10^3 \text{ m} / (1 \times 10^{-6} \text{ m}) = \underline{6.3781 \times 10^{12}}$
- e) $A = 4\pi r^2 = 4 \times 3.142 \times (5 \times 10^{-7} \text{ m})^2 = \underline{3.142 \times 10^{-12} \text{ m}^2}$
- f) $3.142 \times 10^{-12} \text{ m}^2 / (0.50 \times 10^{-18} \text{ m}^2) = \underline{6.283 \times 10^6}$
9. a) $\Delta U = \Delta H = 0.$
 $w_{\text{T}} = p(V_2 - V_1) = p \times nRT(1/p_2 - 1/p_1)$
 $= 10^5 \text{ Pa} \times (1 \text{ mol})(8.3145 \text{ J K}^{-1} \text{ mol}^{-1})(298 \text{ K})[1/(105 \text{ Pa}) - 1/(106 \text{ Pa})]$
 $= \underline{2230 \text{ J}}$
 $q_{\text{T}} = -w_{\text{T}}$
- b) $q = 1 \text{ mol} \times (5/2) \times 8.3145 \text{ J mol}^{-1} \text{ K}^{-1} \times 75 \text{ K} = \underline{1559 \text{ J}}$
 $w = 0$
 $\Delta U = q$
 $\Delta H = \Delta U + nR\Delta T = 1559 \text{ J} + 1 \text{ mol} \times 8.3145 \text{ J mol}^{-1} \text{ K}^{-1} \times 75 \text{ K} = \underline{2183 \text{ J}}$
- c) $p = 1 \text{ bar} \times 373 \text{ K} / (298 \text{ K}) = 1.252 \text{ bar}$
- d) lower, because the system will do work against the surroundings.
10. a) $q = 0$, adiabatic.
 $w < 0$, expansion.
 $\Delta U = w < 0.$
 $\Delta H < 0.$
- b) $\Delta U = \Delta H = 0$ since $\Delta T = 0$

$$w < 0, \text{ expansion}$$

$$q = -w > 0$$

- c) $q = 0$, adiabatic.
 $w = 0$, expansion against zero pressure
 $\Delta U = w + q = 0$.
 $\Delta H = \Delta U + R\Delta T = 0$
- d) $q > 0$, heat of vaporization.
 $w < 0$, expansion against pressure
 $\Delta H = q_p > 0$.
 $\Delta U = \Delta H - \Delta(pV) > 0$; $\Delta H \gg \Delta(pV) \cong n_g RT$
- e) $q < 0$, exothermic reaction.
 $w = 0$, closed bomb, $\Delta V = 0$
 $\Delta U = q_V < 0$.
 $\Delta H = q_V + \Delta(pV) < 0$; $\Delta(pV) = -(n_{\text{H}_2} + n_{\text{O}_2})RT < 0$

11. a) $\Delta H = q_p = \underline{40.667 \text{ kJ}}$.
 $\Delta U = \Delta H - \Delta(pV) = \Delta H - \Delta(n_g RT) = 40667 \text{ J} - (1 \text{ mol} \times 8.3145 \text{ J mol}^{-1} \text{ K}^{-1} \times 373.15 \text{ K})$
 $= \underline{37.564 \text{ kJ}}$
 $w_p = p\Delta V = \Delta(n_g RT) = 1 \text{ mol} \times 8.3145 \text{ J mol}^{-1} \text{ K}^{-1} \times 373.15 \text{ K} = \underline{-3.103 \text{ kJ}}$

- b) $w = w_1 + w_2 = 0$, since $p_{\text{ex}} = 0$ in step 1 and $\Delta V = 0$ in step 2.
 $q = \Delta U = \underline{37.564 \text{ kJ}}$, path independent.
 $\Delta H = \underline{40.667 \text{ kJ}}$, path independent.

12. a) $q = nC_m(T_2 - T_1) = (1 \text{ mol})(38.0 \text{ J K}^{-1} \text{ mol}^{-1})(20 \text{ K}) = \underline{760 \text{ J}}$

b) $q = (1 \text{ mol})(6007 \text{ J mol}^{-1}) = \underline{6007 \text{ J}}$

c) Per degree temperature drop, 10 mol H₂O (*l*) loses

$$(10 \text{ mol})(75.4 \text{ J mol}^{-1} \text{ K}^{-1}) = 754 \text{ J K}^{-1}$$

$$760 \text{ J} + 6007 \text{ J} + (1 \text{ mol})(75.4 \text{ J K}^{-1} \text{ mol}^{-1})(T_f - 0) = (10 \text{ mol})(75.4 \text{ J K}^{-1} \text{ mol}^{-1})(20 - T_f)$$

$$T_f = \frac{(10)(75.4)(20) - 760 - 6007}{(11)(75.4)} = \underline{10.0^\circ\text{C}}$$

The final state is liquid.

13. a) $\Delta T = q_p / nC_{p,m} = -400 \text{ J} / (36.5 \text{ J K}^{-1} \text{ mol}^{-1} \times 1 \text{ mol}) = -11.0 \text{ K}$

$$T_f = 125.0 - 11.0 = \underline{114.0^\circ\text{C}}$$

There is no phase change, so

$$\Delta V = nR\Delta T / p = \frac{1 \text{ mol}(8.314 \text{ J K}^{-1} \text{ mol}^{-1})(-11.0 \text{ K})}{10^5 \text{ Pa}} = \underline{-9.1 \times 10^{-4} \text{ m}^3}$$

b) $\Delta T = -400 \text{ J} / (1 \text{ mol} \times 75.95 \text{ J mol}^{-1} \text{ K}^{-1}) = -5.27 \text{ }^\circ\text{C}$
 $T_f = 100 - 5.27 = \underline{94.73^\circ\text{C}}$
 $V_f(l) = (18 \text{ g}) / (0.96 \text{ g mL}^{-1}) = \underline{18.75 \text{ mL}}$. No phase change; ΔV is negligible for the liquid water.

c) $\Delta n_g = (-400 \text{ J}) / (40,657 \text{ J mol}^{-1}) = \underline{-9.84 \times 10^{-3} \text{ mol}}$
 Δn_g mol water vapor will condense to liquid
 No temperature change
 $\Delta V = \Delta n RT / p = (-9.84 \times 10^{-3} \text{ mol})(8.314 \text{ J mol}^{-1} \text{ K}^{-1})(373 \text{ K}) / (10^5 \text{ Pa})$
 $\Delta V = \underline{-3.05 \times 10^{-4} \text{ m}^3}$

d) Part (a), because it has the greatest ΔV ; $w > 0$.

14. $V = 5.8 - 2 \times \exp[100(0.002)] = \underline{3.36 \text{ L}}$
 At 1.005 bar, $V = 5.8 - 2 \times \exp[100(-0.005)] = \underline{4.59 \text{ L}}$
 $\Delta n = 10^5 \text{ Pa} \times (4.59 - 3.36) \times 10^{-3} \text{ m}^3 / (8.3145 \text{ J mol}^{-1} \text{ K}^{-1} \times 310 \text{ K}) = \underline{0.0477 \text{ mol}}$

15. a) $q = 0$, thermally insulated
 $w = 0$, assuming no volume change because decrease in volume of hot copper equals increase in cool copper.
 $\Delta U = 0$, energy is conserved.
 $\Delta H = 0$

b) $q = 0$, thermally insulated
 $w = 0$, mechanical work done on the system
 $\Delta U = w > 0$
 $\Delta H = 0$ because $\Delta pV = 0$, with negligible expansion of the system.

c) $q = 0$
 $w = 0$
 $\Delta U = 0$
 $\Delta H = 0$ (all answers assume ideal gas behavior)

16. a) First Law of Thermodynamics – no restrictions
 b) Constant pressure process with no non- pV work.
 c) Enthalpy is a linear function of temperature (heat capacity is constant). i.e. $\Delta H / \Delta T = dH/dT$.
 d) Reactions in ideal gases at constant temperature, where $\Delta(pV) = RT\Delta n$
 e) van der Waals gas.
 f) Constant p_{ex} .

17. $c = C_{p,m}/M = 75.4 \text{ J mol}^{-1} \text{ K}^{-1}/(0.018 \text{ kg mol}^{-1}) = 4189 \text{ J/K}$.
 So 4 kJ/hr corresponds to almost 1° K per hour. It's probably best to limit moon walks to two hours, since 2°C (3.6 F) above normal is a substantial fever.
18. $n = pV/RT = (10^5 \text{ Pa})(5 \times 10^{-4} \text{ m}^3)/(8.314 \text{ J K}^{-1} \text{ mol}^{-1})(293 \text{ K}) = 0.021 \text{ mol}$
 Per breath, $\Delta H = nC_{p,m}(T_2 - T_1) = 0.021 \text{ mol} \times 3.5 \times 8.3145 \text{ J mol}^{-1} \text{ K}^{-1} \times 17.15 \text{ K} = 10.2 \text{ J}$.
 Per day, $10.2 \text{ J} \times 12 \text{ min}^{-1} \times 60 \text{ min hr}^{-1} \times 24 \text{ hr d}^{-1} = 177 \text{ kJ d}^{-1}$, representing about 1.5% of food energy.
 Metabolic heat = $80 \text{ kg} \times 4 \text{ kJ h}^{-1} \text{ kg}^{-1} \times 24 \text{ h} = 7.68 \text{ kJ d}^{-1}$, or 0.06% of food energy. At outside temperatures of -40°C, 4.5 × more energy will be lost through breathing; 7% of food energy begins to be significant.
19. a) $w = p\Delta V = 10^5 \text{ Pa} \times 5 \times 10^{-4} \text{ m}^3 = 50 \text{ J/breath}$.
 In 24 hr, $w = 50 \text{ J} \times 15000 \text{ d}^{-1} = \underline{750 \text{ kJ}}$
 b) $w = mgh = 750 \text{ kJ}$ so $m = w/gh = 750 \text{ kJ}/(9.8 \text{ m s}^{-2} \times 100 \text{ m}) = \underline{765 \text{ kJ}}$.
20. By convention, lower case symbols are specific (per kilogram) rather than molar quantities
- $$m_{\text{water}} c_{p,m,\text{water}} (T_f - 55) \text{ K} + m_{\text{ice}} c_{p,m,\text{ice}} \times 10 \text{ K} + (m_{\text{ice}}) \Delta_{\text{fus}} h + m_{\text{ice}} c_{p,m,\text{water}} (T_f - 0) \text{ K} = 0$$
- $$0.100 \text{ kg} \times 4.184 \text{ kJ K}^{-1} \text{ kg}^{-1} \times (T_f - 55) \text{ K} + 0.010 \text{ kg} \times 2.11 \text{ kJ K}^{-1} \text{ kg}^{-1} (10 \text{ K})$$
- $$+ 0.010 \text{ kg} \times 333.4 \text{ kJ kg}^{-1} + 0.010 \text{ kg} \times 4.184 \text{ kJ K}^{-1} \text{ kg}^{-1} \times T_f \text{ K} = 0$$
- $$0.4184T_f - 23.01 + 0.211 + 3.334 + 0.04184T_f = 0$$
- $$T_f = \frac{19.47}{0.460} = \underline{42.3^\circ\text{C}}$$
21. $\Delta H_{298}^\circ = 6\Delta_f H^\circ(\text{CO}_2, g) + 6\Delta_f H^\circ(\text{H}_2\text{O}, l) - \Delta_f H^\circ(\text{C}_6\text{H}_{12}\text{O}_6, s) - 6\Delta_f H^\circ(\text{O}_2, g)$
 $= [6(-393.509) + 6(-285.830) - (-1274.4) - 0] \text{ kJ mol}^{-1} = \underline{-2801.6 \text{ kJ mol}^{-1}}$
22. a) $q_p = \Delta H = 2\Delta_f H^\circ(\text{ethanol}, l) + 2\Delta_f H^\circ(\text{CO}_2, g) - \Delta_f H^\circ(\text{glucose}, s)$
 $= [2(-276.98) + 2(-393.509) - (-1274.4)] \text{ kJ mol}^{-1} = \underline{-66.6 \text{ kJ}}$
 b) This represents 2.4% of the heat available from the complete combustion.
23. $\Delta_r H^\circ = \Delta_f H^\circ(\text{H}_2\text{O}, l) + \frac{1}{2} \Delta_f H^\circ(\text{O}_2, g) - \Delta_f H^\circ(\text{H}_2\text{O}_2, aq)$

$$\Delta_r H^\circ = [(-285.830) + 0 - (-191.17)] \text{ kJ mol}^{-1} = -94.66 \text{ kJ mol}^{-1}$$

A temperature rise of 0.02 °C requires $(0.02 \text{ °C})(4.184 \text{ kJ kg}^{-1})(1 \text{ kg L}^{-1}) = 0.0837 \text{ kJ L}^{-1}$

$$\text{Minimum detectable concentration} = \frac{0.0837 \text{ kJ L}^{-1}}{94.66 \text{ kJ mol}^{-1}} = \underline{8.84 \times 10^{-4} \text{ M}}$$

24. a) $\Delta H^\circ_{298} = [(-74.81) + 0 - (-238.57)] \text{ kJ mol}^{-1} = \underline{163.76 \text{ kJ mol}^{-1}}$

b) $\Delta U^\circ = \Delta H^\circ - \Delta n_{\text{gases}} RT$
 $= 163.76 \text{ kJ mol}^{-1} - \frac{3}{2} \left(8.3145 \text{ J mol}^{-1} \text{ K}^{-1} / 1000 \right) (298 \text{ K}) = \underline{160.04 \text{ kJ mol}^{-1}}$

c) $\Delta H^\circ_{773} = \Delta H^\circ_{298} + \int_{298}^{773} \Delta C_p dT$ where
 $\Delta C_p = C_{p,m}(\text{CH}_4) + \frac{1}{2} C_{p,m}(\text{O}_2) - C_{p,m}(\text{CH}_3\text{OH})$

25. $\Delta_r H^\circ_{298} = \Delta_f H^\circ(\text{urea}, s) + 3\Delta_f H^\circ(\text{CO}_2, g) + 3\Delta_f H^\circ(\text{H}_2\text{O}, l) - 2\Delta_f H^\circ(\text{glycine}, s)$
 $\Delta_r H^\circ_{298} = [(-333.17) + 3(-393.509) + 3(-285.83) - 2(-537.2)] \text{ kJ mol}^{-1}$
 $= \underline{-1296.8 \text{ kJ mol}^{-1}}$

26 a) $\Delta_r H^\circ_{298} = [2(-276.98) + 2(-393.509) - (-1274.4)] \text{ kJ mol}^{-1} = \underline{-66.6 \text{ kJ mol}^{-1}}$

b) $\Delta_r H^\circ_{298} = [2(-484.1) + 2(-393.509) + 2(-285.830) - (-1274.4)] \text{ kJ mol}^{-1}$
 $= \underline{-1052.5 \text{ kJ mol}^{-1}}$

c) $\Delta H^\circ_{298} = \underline{-2801.6 \text{ kJ mol}^{-1}}$ (see Prob. 21)

27. a) From problem 26 a)
 $\Delta_r H^\circ_{353} = \Delta_r H^\circ_{298} + \Delta T \Delta_r C_p$
 $= -66.6 \text{ kJ mol}^{-1} + (353 - 298) \text{ K} (2 \times 111.5 + 2 \times 37.1 - 219.2) \text{ J mol}^{-1} \text{ K}^{-1}$
 $= -62.3 \text{ kJ mol}^{-1}$

b) From problem 26 b)
 $\Delta_r H^\circ_{353} =$
 $-1052.5 \text{ kJ mol}^{-1} + (353 - 298) \text{ K} (2 \times 123.5 + 2 \times 75.4 + 2 \times 37.1 - 219.2 - 2 \times 29.4) \text{ J mol}^{-1} \text{ K}^{-1}$
 $= -1041.8 \text{ kJ mol}^{-1}$

28. a)
$$\Delta_r H^\circ_{298} = \Delta_f H^\circ(\text{sucrose}, s) + 12\Delta_f H^\circ(\text{O}_2, g) - 12\Delta_f H^\circ(\text{CO}_2, g) - 11\Delta_f H^\circ(\text{H}_2\text{O}, l)$$

$$= [(-2222.1) + 0 - 12(-393.509) - 11(-285.830)] \text{ kJ mol}^{-1}$$

$$= \underline{5644.1 \text{ kJ mol}^{-1}}$$

b)
$$20 \text{ kg sucrose ha}^{-1} \text{ hr}^{-1} = (5644.1 \text{ kJ mol}^{-1}) (0.3423 \text{ kg mol}^{-1})^{-1} (20 \text{ kg})$$

$$= 329,800 \text{ kJ h}^{-1} = \underline{91.6 \text{ kW ha}^{-1}}$$

c)
$$\text{Stored energy} = [(91.6 \text{ kW hectare}^{-1})(10^{-4} \text{ hectare m}^{-2})/1 \text{ kW m}^{-2}] 100$$

$$= \underline{0.92\%}$$

29. a)
$$\text{H}_2(g) + \frac{1}{2}\text{O}_2(g) \rightarrow \text{H}_2\text{O}(l)$$

$$\Delta_r H^\circ_{298} = \Delta_f H^\circ(\text{H}_2\text{O}, l) = (-285.830 \text{ kJ mol}^{-1}) / (2.016 \text{ g H}_2 \text{ mol}^{-1})$$

$$= \underline{-141.8 \text{ kJ (g H}_2)^{-1}}$$

b)
$$\text{C}_8\text{H}_{18}(g) + \frac{25}{2}\text{O}_2(g) \rightarrow 8\text{CO}_2(g) + 9\text{H}_2\text{O}(l)$$

$$\Delta_r H^\circ_{298} = [-(-208.45) - 0 + 8(-393.509) + 9(-285.830)] / (114 \text{ g C}_8\text{H}_{18} / \text{mol})$$

$$= \underline{-48.35 \text{ kJ (g C}_8\text{H}_{18})^{-1}}$$

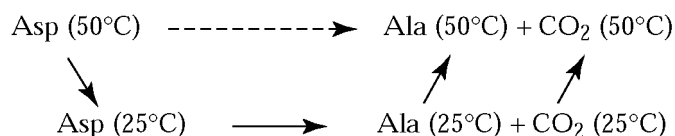
c)
$$\Delta_r H^\circ_{298}(\text{H}_2) / \Delta_r H^\circ_{298}(\text{C}_8\text{H}_{18}) = -141.8 / -48.35 = \underline{2.9}$$

Thus H₂ is nearly 3 times more energetic as a fuel than octane on a weight basis.

30. a)
$$\Delta_r H^\circ = \Delta_f H^\circ(\text{Ala}) + \Delta_f H^\circ(\text{CO}_2) - \Delta_f H^\circ(\text{Asp})$$

$$= [(-562.7) + (-393.509) - (-973.37)] \text{ kJ mol}^{-1}$$

$$= \underline{17.2 \text{ kJ mol}^{-1}}, \text{ absorbed}$$



Heat capacities needed

$$\Delta_r H^\circ_{323} = \Delta_r H^\circ_{298} + \Delta_r C_{p,m} (50 - 25)$$

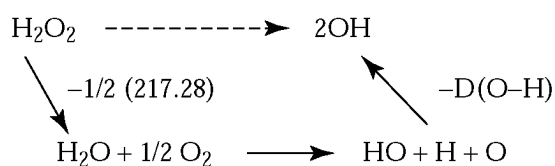
$$\text{where } \Delta_r C_{p,m} = C_{p,m}(\text{Ala}) + C_{p,m}(\text{CO}_2) - C_{p,m}(\text{Asp})$$

31. To measure $\Delta_r H_{298}^\circ$ the reactants could be put into a calorimeter at 25 °C and a small amount of an enzyme catalyst added. The heat evolved per mole at constant pressure is $\Delta_r H_{298}^\circ$. To estimate $\Delta_r U_{298}^\circ$ the volume change of the reaction must be determined. The change in volume can be measured in a dilatometer, or partial molal volumes can be used to calculate the change in volume. For practical purposes the volume change is negligible, since no gases are involved, and $\Delta_r U_{298}^\circ = \Delta_r H_{298}^\circ$.

32. a) $(22 \text{ kWh d}^{-1})(3600 \text{ kJ (kWh)}^{-1}) = \underline{7.92 \times 10^4 \text{ kJ d}^{-1}}$

b) $(1 \text{ kW m}^{-2})(0.1)(5 \text{ h}) = 0.5 \text{ kWh m}^{-2}$
 $A = (22 \text{ kWh}) / (0.5 \text{ kWh m}^{-2}) = \underline{44 \text{ m}^2}$

33. a) $\Delta_r H_{298}^\circ = 2\Delta_f H^\circ(\text{H}_2\text{O}, g) + \Delta_f H^\circ(\text{O}_2, g) - \Delta_f H^\circ(\text{H}_2\text{O}_2, g)$
 $= [2(-241.818) + 0 - 2(-133.18)] \text{ kJ mol}^{-1} = \underline{-217.28 \text{ kJ mol}^{-1}}$



b) $+ D(\text{OH}) + 1/2 D(\text{O}_2)$

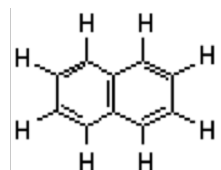
$$D(\text{O}-\text{O}) = -1/2(217.28) + 1/2(498.3) = \underline{140.5 \text{ kJ mol}^{-1}}$$

c) $\Delta_r H_{298}^\circ = [2(-285.830) + 0 - 2(-191.17)] \text{ kJ mol}^{-1} = \underline{-189.32 \text{ kJ mol}^{-1}}$

d) Heat evolved = $1/2(189.32 \text{ kJ (mol H}_2\text{O}_2)^{-1})(0.01 \text{ mol kg}^{-1}) = 0.947 \text{ kJ kg}^{-1}$
 Temperature rise = $(0.947 \text{ kJ kg}^{-1}) / (4.18 \text{ kJ K}^{-1} \text{ kg}^{-1}) = 0.226 \text{ K}$
 Final temperature 25.226°C

34. a) $8 \text{ C}(\text{graphite}) + 9 \text{ H}_2(g) \rightarrow \text{C}_8\text{H}_{18}(g)$
 $\Delta_f H^\circ = [8(716.7) + 9(436.0) - 7(359) - 18(411)] \text{ kJ mol}^{-1} = \underline{-253 \text{ kJ mol}^{-1}}$
 Published value = $-208.45 \text{ kJ mol}^{-1}$

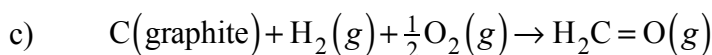
Chief discrepancy lies in using average bond dissociation energies for D(C—C) and D(C—H)



$$\begin{aligned}\Delta_f H^\circ &= 10\Delta_f H^\circ(\text{C}) + 4D(\text{H}-\text{H}) - 6D(\text{C}-\text{C}) - 5D(\text{C}=\text{C}) - 8D(\text{C}-\text{H}) \\ &= [10(716.7) + 4(436.0) - 6(359) - 5(611) - 8(411)] \text{ kJ mol}^{-1} \\ &= \underline{414 \text{ kJ mol}^{-1}}\end{aligned}$$

Published value $150.96 \text{ kJ mol}^{-1}$

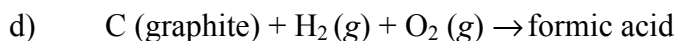
Chief discrepancy arises from neglect of resonance energy.



$$\begin{aligned}\Delta_f H^\circ &= \Delta_f H^\circ(\text{C}) + D(\text{H}-\text{H}) + \frac{1}{2}D(\text{O}_2) - 2D(\text{C}-\text{H}) - D(\text{C}=\text{O}) \\ &= 716.7 + 436.0 + 498.3/2 - 2(411) - 709 = \underline{-129 \text{ kJ mol}^{-1}}\end{aligned}$$

Published value $-115.90 \text{ kJ mol}^{-1}$

Chief discrepancy arises from use of average bond dissociation energies.



$$\begin{aligned}\Delta_f H^\circ &= \Delta_f H^\circ(\text{C}) + D(\text{H}-\text{H}) + D(\text{O}_2) - D(\text{C}-\text{H}) - D(\text{C}=\text{O}) - D(\text{C}-\text{O}) - D(\text{O}-\text{H}) \\ &= 716.7 + 436.0 + 498.3 - 411 - 709 - 361 - 452 \\ &= \underline{-282 \text{ kJ mol}^{-1}}\end{aligned}$$

Published value $-424.76 + 46.15 = -378.61 \text{ kJ mol}^{-1}$

Chief discrepancy comes from neglect of hydrogen bonding.

35. The steric repulsion can be estimated by the enthalpy change for the process
cis-2-butene \rightarrow *trans*-2-butene

$$\Delta_r H^\circ_{298} = -11.1 \text{ kJ mol}^{-1} - (-7.0 \text{ kJ mol}^{-1}) = -4.1 \text{ kJ mol}^{-1}$$

by which we see that the *trans* form has the lower enthalpy by 4.1 kJ/mol.