Chapter 2 problems:  1*, 3e**, 9***, 10b-e****, 15a,c, 16, 18, 19, 21#, 24, 28, 34c##

* Assume the hiker’s clothing absorbed 1.25 L of water in the rainstorm, and weighs 55 kg and the water evaporates at 10° C instead of what the text uses. Suppose the hiker had eaten only glucose that day instead of sucrose for part (c).
** use 37° C instead of 25° and expansion is from 3.0 L to 30.0 L
*** you will need to know that the molar Cv for an ideal diatomic gas = 2.5 R where R is the gas constant.
**** 10  d. you will need to remember what boiling means: liquid water evaporating into bubbles of water vapor because the vapor pressure of the water = the applied pressure on the surface of the liquid. (water will boil at exactly 298 K if in a partial vacuum such that the air pressure = 2536 Pa (from Table 2.2) (=.02536 bar =0.02569 atm.)

**** 10 e. note: "bomb" is short for bomb calorimeter, a steel container in which small amounts of explosive mixtures may be detonated safely to see how much heat is given off.
# Do this for sucrose instead of glucose. (Table A.7)
##  Use formamide instead of formaldehyde.

1. Note: we are just getting a rough estimate of the person’s temperature change because of the extreme approximations made. This is inconsistent with the detail being done by interpolating to get precise values of ΔHvap, etc., but I want you to be able to do this for a future problem where greater precision is needed.

Density at 10° C is interpolated from Table 2.2: density = 998.2 + (999.8-998.2)× 10/20 = 999.00 g/L

ΔHvap,m =44.91 - (44.91- 44.08)× 10/20 = 44.495 kJ/mol

kJ/mol

The cooling of the body begins at 37° C, so need to interpolate between 20 and 40 for Cp,m
Cp,m = 75.38 + (75.29-75.38)× 17/20 = 75.304 Jmol⁻¹K⁻¹

1.25 L × 995.2 g/L /18.016 g mol⁻¹ = 69.313 mol water

a) qp = ΔHvap = 45.325 kJ mol⁻¹ × 69.313 mol = +3084.1 kJ

b) 55 kg → 55000 g/18.016 g mol⁻¹ = 3052.84 mol water in person
Cp,person = 75.304 Jmol⁻¹K⁻¹ x 3052.84 mol =229.89 kJ K⁻¹

using the person's body as system, and q = -3129.69 kJ
ΔT = -3129.69 / 229.89 kJ K⁻¹ = -13.61 K

note: this is -13.6 x 1.8 = -24.5 F below normal = 74 F = severe hypothermia
(but is quite exaggerated do to assumption of instant evaporation, and assumption of all heat
from body. Much of the heat will come from the air in reality.)

c) Glucose C₆H₁₂O₆(s) + 6O₂ (g) → 6 CO₂(g) + 6H₂O (l)
ΔH₀ = 6(-393.51 kJ mol⁻¹) + 6(-285.83 kJ mol⁻¹) – (-1274.4 kJ mol⁻¹) - 0
= -2801.64 kJ mol⁻¹ of glucose
M_{glucose} = 180.156 g mol⁻¹
mass_{glucose} = 3084.1 kJ heat × 180.156 g mol⁻¹/2801.64 kJ mol⁻¹ = 198.32 g

3. e) \( w = -nRT\ln(V_2/V_1) \) (reversible, isothermal, ideal gas)
\( T = 37 + 273 = 310 \text{ K} \)
\( n = 1 \text{ bar} \times 2 \text{ L}/(0.083145 \text{ bar} \text{ L} \text{ mol}^{-1} \text{ K}^{-1} \times 310 \text{ K}) = 0.0745 \text{ mol} \)
\( w = -0.0745 \text{ mol} \times 8.3145 \text{ J} \text{ mol}^{-1} \times 323 \times \ln 5 = -322 \text{ J} \)
Or:
\( w = -p_1V_1\ln(V_2/V_1) = -10^5 \text{ Pa} \times 2 \times 10^{-3} \text{ m}^3 \times \ln 5 \times 1 \text{ J}/(\text{Pa} \text{ m}^3) = -322 \text{ J}. \)

9. a) \( \Delta U = \Delta H = 0 \) isothermal and ideal gas: \( n = 1 \text{ mol} \) \( T = 298 \) \( \text{p}_1 = 10 \text{ bar}; \text{p}_\text{ext} = 1 \text{ bar} \)
constant; \( V_2 = 10V_1 \)
\( V_1 = nRT/\text{p}_1 = 2.5 \text{ L} \)
\( V_2 = 25 \text{ L} \)
\( w_T = -\text{p}_\text{ext} (V_2 - V_1) = -1 \text{ bar} \times (25\text{L} - 2.5 \text{ L}) \times 100 \text{ J} \text{bar}^{-1} \text{L}^{-1} = -2250 \text{ J} \)
\( q = -w = +2250 \text{ J} \)

b) constant V heat from 298 to 373 K; \( C_{p,m} = 5/2 R \)
\( q = 1 \text{ mol} \times (5/2) \times 8.3145 \text{ J} \text{ mol}^{-1} \text{ K}^{-1} \times 75 \text{ K} = 1559 \text{ J} \)
\( w = 0 \) (constant V)
\( \Delta U = q \)
\( \Delta H = \Delta U + \Delta pV = \Delta U + nR\Delta T = 1559 \text{ J} + 1 \text{ mol} \times 8.3145 \text{ J} \text{ mol}^{-1} \text{ K}^{-1} \times 75 \text{ K} = 2183 \text{ J} \)
\( c) \text{p} = 1 \text{ bar} \times 373 \text{ K}/298 \text{ K} = 1.252 \text{ bar} \)
d) lower, because the system will do work against the surroundings.

10. a) \( q = 0 \), adiabatic.
\( w < 0 \), expansion.
\( \Delta U = w < 0 \).
\( \Delta H < 0 \) \( pV \) decreases because \( T \) decreases
b) \( \Delta U = \Delta H = 0 \) since \( \Delta T = 0 \)
\( w < 0 \), 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) \( q > 0 \), vaporization is endothermic.
\( w < 0 \), expansion against external pressure
\( \Delta H = q \) because \( p = p_{\text{ext}} = \text{constant} \) and no useful work
\( \Delta U = \Delta H - \Delta (pV) > 0 \); because \( \Delta H > > \Delta (pV) \equiv n_{\text{gas}}RT \)

e) \( q < 0 \), exothermic reaction.
\( w = 0 \), closed bomb, \( \Delta V = 0 \)
\( \Delta U = qV < 0 \).
\( \Delta H = \Delta U + \Delta (pV) < 0 \); \( \Delta (pV) = \Delta n_{\text{gas}}RT = - (n_{\text{H}_2} + n_{\text{O}_2})RT < 0 \) assuming \( \text{H}_2\text{O} \) is liquid;
but if there was only a small amount of \( \text{H}_2 \) and \( \text{O}_2 \) reacted, the \( \text{H}_2\text{O} \) could be gas;
\( \Delta (pV) \) is still negative because \( n_{\text{H}_2\text{O}} \) is < \( n_{\text{H}_2} + n_{\text{O}_2} \)

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
\( \Delta U = w > 0 \)
\( \Delta H = \Delta U = w > 0 \) because \( \Delta (pV) = 0 \), with negligible expansion of the system.

c) \( q = 0 \)
\( w = 0 \) no expansion against external pressure
\( \Delta U = 0 \)
\( \Delta H = 0 \) \( \Delta pV = 0 \) (all answers assume ideal gas behavior)

16. a) \( \Delta U = q + w \): always true for closed system. I accepted simply saying “always true” as correct.
b) Constant pressure (Publisher’s answer key was wrong)
correct answer is: \( p = p_{\text{ext}} = \text{constant} \), with only obligatory \( pV \) work (e.g., against atmosphere).
c) Enthalpy must be a linear function of temperature; or heat capacity is constant, \( \Delta H/\Delta T = dH/dT \). Each of these means the same thing.
d) Reactions of ideal gases at constant temperature, where \( \Delta (pV) = RT\Delta n \)
e) van der Waals equation is approximately true for all gases unless at very high pressure.
f) Constant $p_{\text{ext}}$ and $pV$ work only

18. $n = \frac{pV}{(RT)} = 1 \text{ bar} \times 0.5 \text{ L}/ (0.083145 \text{ JK}^{-1} \text{mol}^{-1} \times 293 \text{ K}) = 0.021 \text{ mol}$

or: $n = \frac{pV}{(RT)} = (10^5 \text{ Pa})(5\times10^{-4} \text{ m}^3)/(8.314 \text{ JK}^{-1} \text{mol}^{-1} \times 293 \text{ K}) = 0.021 \text{ mol}$

Per breath, $\Delta H = nC_{p,m}(T_2 - T_1) = 0.021 \text{ mol} \times (7/2) \times 8.3145 \text{ J mol}^{-1} \text{ K}^{-1} \times (310-293) \text{ K} = 10.4 \text{ J}$.

Per day, $10.4 \text{ J} \times 12 \text{ min}^{-1} \times 60 \text{ min hr}^{-1} \times 24 \text{ hr d}^{-1} = 180 \text{ kJ d}^{-1}$, 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 $-40^\circ \text{C}$, $T_2 - T_1 = 310 - 233 = 77 \text{ K}$ or about 4.5 times more energy will be lost through breathing = 7% of food energy, which begins to be significant.

19. a) $W = p \Delta V = 10^5 \text{ Pa} \times 5 \times 10^{-4} \text{ m}^3 = 50 \text{ J/breath}$ (another bad answer from Publisher)

$W = -p_{\text{ext}} \Delta V = -1 \text{ bar} \times 0.5 \text{ L} \times 100 \text{ J bar}^{-1} \text{ L}^{-1} = -10^5 \text{ Pa} \times 5 \times 10^{-4} \text{ m}^3 = -50 \text{ J/breath}$.

In 24 hr, $w = -50 \text{ J} \times 15000 \text{ d}^{-1} = -750 \text{ kJ}$

b) $w = mgh = -750 \text{ kJ}$ so $\frac{W}{gh} = 750 \text{ kJ} / (9.8 \text{ m s}^{-2} \times 100 \text{ m}) = 7.65 \text{ kg}$.

20. Sucrose

$\Delta H_{298}^\circ = 12\Delta_f H^\circ(\text{CO}_2, \text{g}) + 11\Delta_f H^\circ(\text{H}_2\text{O}, \text{l}) - \Delta_f H^\circ(\text{C}_12\text{H}_22\text{O}_11, \text{s}) - 12\Delta_f H^\circ(\text{O}_2, \text{g})$

$= [12(-393.509) + 11(-285.830) - (-2222.1) + 0] \text{ kJ mol}^{-1} = -5644.14 \text{ kJ mol}^{-1}$

24. a) $\Delta H_{298}^\circ = -74.81 - 0 - (-238.57) \text{ kJ mol}^{-1} = 163.76 \text{ kJ mol}^{-1}$

$\Delta U_{298}^\circ = -74.87 - 0 - (-238.57) \text{ kJ mol}^{-1} = 163.70 \text{ kJ mol}^{-1}$

b) $\Delta U^\circ = \Delta H^\circ - \Delta n_{\text{gases}}RT = 163.76 \text{ kJ mol}^{-1} - (3/2) (8.3145 \text{ J mol}^{-1} \text{K}^{-1} / 1000)(298 \text{ K}) = 160.0 \text{ kJ mol}^{-1}$

c) $\Delta H_{773}^0 = \int_7^{298} C_{p,m}(\text{CH}_3\text{OH}) \text{d}T + \Delta H_{298}^0 + \int_7^{773} C_{p,m}(\text{CH}_4) \text{d}T + \int_7^{773} \frac{1}{2} C_{p,m}(\text{O}_2) \text{d}T$

$= \Delta H_{298}^0 + \int_7^{773} \Delta C_{p,m} \text{d}T$

where $\Delta C_p = C_{p,m}(\text{CH}_4) + 0.5 C_{p,m}(\text{O}_2) - C_{p,m}(\text{CH}_3\text{OH})$
28. a) \[ \Delta_r H^\circ_{298} = \Delta_r H^\circ (\text{sucrose, s}) + 12 \Delta_r H^\circ (\text{O}_2, \text{g}) - 12 \Delta_r H^\circ (\text{CO}_2, \text{g}) - 11 \Delta_r H^\circ (\text{H}_2\text{O}, \text{l}) \]
\[ = -2222.1 + 0 - 12(-393.509) - 11(-285.830) \text{ kJmol}^{-1} \]
\[ = 5644.1 \text{ kJmol}^{-1} \]

b) 20 kg sucrose hectare$^{-1}$ hr$^{-1}$ = (5644.1 kJmol$^{-1}$) (0.3423 kgmol$^{-1}$)$^{-1}$ (20 kg)
\[ = 329,800 \text{ kJ h}^{-1} \times 1 \text{ h}/3600 \text{ s} = 91.6 \text{ kW hectare}^{-1} \]

c) Stored energy = [(91.6 kW)(10$^{-4}$ hectare m$^{-2}$)$^{-1}$ / 1kW m$^{-2}$] x 100
\[ = 0.92\% \]

34.c) \[ \text{C(graphite)} + 1.5\text{H}_2 (\text{g}) + 0.5\text{O}_2 (\text{g}) + 0.5\text{N}_2 \rightarrow \text{HCONH}_2 \]
\[ \Delta H^\circ = D(\text{C(graphite)}) + 1.5D(\text{H} - \text{H}) + 0.5\text{H} = \text{O} = \text{O} + 0.5\text{D}( \text{N} \equiv \text{N}) - D(\text{C} - \text{H}) - D(\text{C} = \text{O}) - D(\text{C} - \text{N}) - 2D(\text{N-H}) \]
\[ = 716.7 + 1.5 \times 436.0 + 0.5 \times 498.3 + 0.5 \times 498.3 - 411 - 709 - 303 - 2 \times 383 \]
\[ = -96.45 \text{ kJ mol}^{-1} \]

The value from Table A.7 = -186.2 kJmol$^{-1}$ for formamide (g). The purpose of bond dissociation tables is to give insight—not accurate numbers. Larger discrepancy is expected even for gases because bond dissociation energy is an idealized concept when applied to molecules with more than two atoms. The bonds are often not independent. The table values come from averaging the apparent bond energy from many molecules.

In this case, the amide bonds are not pure double bond and single bond, but are resonance hybrid bonds, perhaps accounting for the large discrepancy.