1) The force between an electron and proton separated by a distance \( r \) is:
\[
F = 2.307 \times 10^{-28} \text{ N} \cdot \text{m}^2/\text{r}^2
\]
Calculate the work required to bring these particles from \( r = 8 \) to \( r = 0.5 \times 10^{-10} \) m, roughly, their average separation in a hydrogen atom.
\[
w = -\int F \, dr = 2.307 \times 10^{-28} \text{ N} \cdot \text{m}^2/\text{r}^2 \, dr \bigg|_{r = 0.5 \times 10^{-10} \text{ m}}^{r = 8 \text{ m}}
\]
\[
= -2.307 \times 10^{-28} \text{ N} \cdot \text{m}^2/0.5 \times 10^{-10} \text{ m} - (-2.307 \times 10^{-28} \text{ N} \cdot \text{m}^2/8 \text{ m})
\]
\[
= -4.614 \times 10^{-18} \text{ J}
\]
Energy is leaving the system as the system goes to lower energy. No work is required to be applied to reach this state of lower energy as there is no opposing force.

The ionization energy of the H atom is 1312 kJ/mol or about half of what we have calculated. This is due to the electron having kinetic and potential energy and we calculated the total energy.

2) A 200 kg brick is placed on a piston enclosing 5.00 moles of an ideal gas at 295 K and 1.0 atm. The piston’s area is 300 cm\(^2\). Calculate the work associated with this isothermal process and find the distance the piston moved.
\[
V = nRT/P = 5 \text{ mole} \times 8.205 \times 10^{-2} \text{ L} \cdot \text{atm/mol-K} \times 295 \text{ K} / 1 \text{ atm}
\]
\[
= 121 \text{ L} \quad \text{original volume}
\]
\[
P = 1 \text{ atm} + F/A = 1 + ma/A = 1 + 200 \text{ kg} \times 9.8 \text{ m/sec}^2/300 \text{ cm}^2 \times (1 \text{ m}^2/1 \times 10^4 \text{ cm}^2)
\]
\[
= 1 \text{ atm} + 65,333 \text{ kg} \cdot \text{m} \cdot \text{sec}^2 \quad \text{or Pa} \quad 1 \text{ atm} = 101,325 \text{ Pa}
\]
\[
= 1.64 \text{ atm} \quad \text{new pressure}
\]
\[
V = nRT/P + b = 5 \text{ mole} \times 8.205 \times 10^{-2} \text{ L} \cdot \text{atm/mol-K} \times 295 \text{ K} / 1.64 \text{ atm} + 0.2 \text{ L}
\]
\[
= 121.2 \text{ L} \quad \text{original volume, the gas occupies very little space.}
\]
\[
P = 1 \text{ atm} + F/A = 1 + ma/A = 1 + 200 \text{ kg} \times 9.8 \text{ m/sec}^2/300 \text{ cm}^2 \times (1 \text{ m}^2/1 \times 10^4 \text{ cm}^2)
\]
\[
= 1 \text{ atm} + 65,333 \text{ kg} \cdot \text{m} \cdot \text{sec}^2 \quad \text{or Pa} \quad 1 \text{ atm} = 101,325 \text{ Pa}
\]
\[
= 1.64 \text{ atm} \quad \text{new pressure This will be the same in both cases.}
\]
\[
V = nRT/P + b = 5 \text{ mole} \times 8.205 \times 10^{-2} \text{ L} \cdot \text{atm/mol-K} \times 295 \text{ K} / 1.64 \text{ atm} + 0.2 \text{ L}
\]
\[
= 74.5 \text{ L} \quad \text{final volume}
\]
\[
w = -nRT\ln(V_f/V_i) = -5 \text{ mol} \times 8.314 \text{ J/mol-K} \times 295 \text{ K} \times \ln(74.5/121)
\]
\[
= 5948 \text{ J}
\]
\[
\Delta V = 121 - 74.5 \text{ L} = 46.5 \text{ L} \quad \text{distance} = \Delta V/A = 46,500 \text{ cm}^3/300 \text{ cm}^2 = 155 \text{ cm}
\]

3) Repeat the previous problems using a hard sphere gas with \( b = 40 \text{ cm}^3/\text{mol} \).
Use the van der Waal expression with \( a = 0 \).
\[
V = nRT/P + b = 5 \text{ mole} \times 8.205 \times 10^{-2} \text{ L} \cdot \text{atm/mol-K} \times 295 \text{ K} / 1 \text{ atm} + 0.2 \text{ L}
\]
\[
= 121.2 \text{ L} \quad \text{original volume}
\]
\[
P = 1 \text{ atm} + F/A = 1 + ma/A = 1 + 200 \text{ kg} \times 9.8 \text{ m/sec}^2/300 \text{ cm}^2 \times (1 \text{ m}^2/1 \times 10^4 \text{ cm}^2)
\]
\[
= 1 \text{ atm} + 65,333 \text{ kg} \cdot \text{m} \cdot \text{sec}^2 \quad \text{or Pa} \quad 1 \text{ atm} = 101,325 \text{ Pa}
\]
\[
= 1.64 \text{ atm} \quad \text{new pressure This will be the same in both cases.}
\]
\[
V = nRT/P + b = 5 \text{ mole} \times 8.205 \times 10^{-2} \text{ L} \cdot \text{atm/mol-K} \times 295 \text{ K} / 1.64 \text{ atm} + 0.2 \text{ L}
\]
\[
= 74.7 \text{ L} \quad \text{final volume}
\]
\[
w = -nRT\ln(V_f/V_i) = -5 \text{ mol} \times 8.314 \text{ J/mol-K} \times 295 \text{ K} \times \ln(74.7/121.2)
\]
\[
= 5935 \text{ J} \quad \text{a change of less than 1 \%}
\]
\[
\Delta V = 121.2 - 74.7 \text{ L} = 46.5 \text{ L} \quad \text{distance} = \Delta V/A = 46,500 \text{ cm}^3/300 \text{ cm}^2 = 155 \text{ cm}
\]
4) An ideal gas at \( T = 200 \) K, \( P = 1 \) atm and \( V = 1 \) L is suddenly and irreversibly compressed by a constant external pressure of 10 atm. It is then expand reversibly back to the initial state. The entire process is isothermal. Calculate the total work for this process.

\[
n = \frac{PV}{RT} = 1 \text{ atm} \times 1 \text{ L} / \frac{8.205 \times 10^{-2} \text{ L-atm/mol-K}}{} \times 200 \text{ K} = 0.061 \text{ mol}
\]

\[
V = \frac{nRT}{P} = 0.061 \text{ mol} \times \frac{8.205 \times 10^{-2} \text{ L-atm/mol-K}}{} \times 200 \text{ K} / 10 \text{ atm} = 0.1 \text{ L}
\]

Irreversible Compression

\[
w - p_{\text{ex}}dV = 10 \text{ atm} \times (0.1 \text{ L} - 1.0 \text{ L}) = 9 \text{ L-atm} = 911.9 \text{ J}
\]

Reversible Expansion

\[
w = -nRT\ln\left(\frac{V_f}{V_i}\right) = -0.061 \text{ mol} \times 8.314 \text{ J/mol-K} \times 200 \text{ K} \times \ln(1.0 \text{ L}/0.1 \text{ L})
\]

\[
w = -233.6 \text{ J}
\]

We put 912 J in and get only 234 J out. The reversible process produces the most work out and is the most efficient in requiring work in. The difference between the magnitudes of the two processes, 678 J, is the inefficiency of the irreversible process.

5) For each of the following processes determine whether the amount of work done by the system on the surroundings is positive, negative or zero.

a) reversible melting of ice at 1 atm and 0 °C.

\[\Delta V < 0, \ p_{\text{ex}} > 0 \rightarrow w > 0\]

b) reversible adiabatic expansion of an ideal gas.

\[\Delta V > 0, \ p_{\text{ex}} > 0 \rightarrow w < 0\]

c) reversible isothermal expansion of an ideal gas.

\[\Delta V > 0, \ p_{\text{ex}} = 0 \rightarrow w = 0\]

d) adiabatic expansion of an ideal gas into a vacuum.

\[\Delta V > 0, \ p_{\text{ex}} > 0 \rightarrow w < 0\]

e) reversible heating of a perfect gas at constant pressure.

\[\Delta V > 0, \ p_{\text{ex}} > 0 \rightarrow w < 0\]

f) reversible cooling of a perfect gas at constant pressure.

\[\Delta V < 0, \ p_{\text{ex}} > 0 \rightarrow w > 0\]

g) reversible cooling of a perfect gas at constant volume.

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

Work done on surroundings by system is positive if \( w > 0 \).

Work done on surroundings by system is negative if \( w < 0 \).

\[\text{a) Ice is less dense than water. As the ice melts there is a contraction in volume.} \ \Delta V < 0, \ p_{\text{ex}} > 0 \rightarrow w > 0\]

\[\text{b) Gas expands against 1 atm.} \ \Delta V > 0, \ p_{\text{ex}} > 0 \rightarrow w < 0\]

\[\text{c) Gas expands against 1 atm.} \ \Delta V > 0, \ p_{\text{ex}} = 0 \rightarrow w = 0\]

\[\text{d) Gas expands against 0 atm.} \ \Delta V > 0, \ p_{\text{ex}} = 0 \rightarrow w = 0\]

\[\text{e) Gas expands against pressure.} \ \Delta V > 0, \ p_{\text{ex}} > 0 \rightarrow w < 0\]

\[\text{f) Gas contracts against pressure.} \ \Delta V < 0, \ p_{\text{ex}} > 0 \rightarrow w > 0\]

\[\text{g) No Volume change.} \ \Delta V = 0, \ p_{\text{ex}} > 0 \rightarrow w = 0\]

6) A way to increase the energy of a system is to raise its temperature. Another is to throw it, giving it a kinetic energy component. Another is to raise it in a gravitational field to increase its potential energy. Consider a 0.05 g rain droplet. Find a) the temperature increase and b) the velocity needed to increase this droplet’s energy by an amount equal to that corresponding to raising the droplet 1 km in the Earth’s gravitational field. The specific heat of water is 4.184 \( J/g-K \) and kinetic energy is given by \( E = \frac{1}{2}mv^2 \).

\[\text{Energy} = mgh = 0.05 \text{ g} \times (1 \text{ kg}/1000 \text{ g}) \times 9.8 \text{ m/sec}^2 \times 1000 \text{ m} = 0.49 \text{ J}\]

\[\Delta T = \frac{Q}{mc} = 0.49 \text{ J} / 0.05 \text{ g} \times 4.184 \text{ J/g-K} = 2.34 \text{ K}\]

\[v = \sqrt{2*E/m} = \sqrt{2*0.49 \text{ kg-m}^2/\text{sec}^2 / 0.05 \text{ g} \times (1 \text{ kg}/1000 \text{ g})} = 140 \text{ m/sec}\]
Chapter 2, Problem 3
A sample consisting of 1 mole of a monoatomic perfect gas \((C_v = 3/2 \, R)\) is taken through the cycle shown below.

![Diagram of gas cycle]

a) Determine the temperature at points 1, 2, & 3.
b) Calculate \(q\), \(w\), \(\Delta U\) and \(\Delta H\) for each step and the overall cycle. If a numerical answer cannot be obtained from the information given, then write in +, - 0 or ? as appropriate.

\[ a) \quad T_1 = \frac{P_1 V_1}{n R} = 1.00 \text{ atm} \times \frac{22.44 \text{ L}}{1 \text{ mole}} \times \frac{0.082 \text{ L-atm/K-mole}}{1 \text{ mole}} = 274 \text{ K} \]

\[ T_2 = 1.00 \text{ atm} \times \frac{44.88 \text{ L}}{1 \text{ mole}} \times \frac{0.082 \text{ L-atm/K-mole}}{1 \text{ mole}} = 547 \text{ K} \]

\[ T_3 = 0.50 \text{ atm} \times \frac{44.88 \text{ L}}{1 \text{ mole}} \times \frac{0.082 \text{ L-atm/K-mole}}{1 \text{ mole}} = 274 \text{ K} \]

\[ b) \ 1 \to 2 \]
\[ w = -\frac{\partial \hat{p}}{\partial V} \Delta V = -1.00 \text{ atm} \times (44.88 \text{ L} - 22.44 \text{ L}) \times (101.3 \text{ J/L-atm}) = -2.27 \text{ kJ} \]
\[ \Delta H = C_p \Delta T = \frac{5}{2} R \times (547 - 274) = 5.67 \text{ kJ} \]
\[ \Delta U = \Delta H - \Delta (PV) = \Delta H - P \Delta V = 5.67 - 2.27 \text{ kJ} = 3.40 \text{ kJ} \]
\[ q = \Delta U - w = 3.40 - (-2.27) \text{ kJ} = 5.67 \text{ kJ} \]

\[ 2 \to 3 \]
\[ w = 0 \text{ kJ} \]
\[ \Delta U = C_v \Delta T = \frac{3}{2} R \times (274 - 547) = -3.4 \text{ kJ} \]
\[ q = \Delta U - w = -3.4 \text{ kJ} \]
\[ \Delta H = \Delta U + \Delta (PV) = \Delta U + V \Delta P \]
\[ \Delta H = -3.4 \text{ kJ} + 44.88 \text{ L} \times (0.5 - 1.0 \text{ atm}) \times (101.3 \text{ J/L-atm}) = -5.67 \text{ kJ} \]

\[ 3 \to 1 \]
\[ w = -\frac{\partial \hat{p}}{\partial V} \Delta V = -nRT \ln \left( \frac{V_f}{V_i} \right) = -1.58 \text{ kJ} \]
\[ \Delta H = C_p \Delta T = 0 \text{ kJ} \]
\[ \Delta U = C_v \Delta T = 0 \text{ kJ} \]
\[ q = \Delta U - w = +1.58 \text{ kJ} \]

Overall
\[ \Delta H = 5.67 + (-5.67) + 0.0 = 0.0 \text{ kJ} \quad \Delta U = 3.40 + (-3.40) + 0.0 = 0.0 \text{ kJ} \]
\[ w = -2.27 + 0 + (-1.58) = -3.85 \text{ kJ} \]
\[ q = 5.67 + (-3.40) + 1.58 = +3.85 \text{ kJ} \]

\(\Delta U\) & \(\Delta H\) are state functions. They should not change for a cycle in which the final & initial states are the same. \(w\) & \(q\) have to balance according to the 1st Law.
Problem 27
When a system is taken from state A to state B along the path ACB 80 J of heat flows into the system and the system does 30 J of work. a) How much heat flows into the system along path ADB if the work done is 10 J? b) When the system is returned from state B to state A along the curved path, the work done on the system is 20 J. Does the system absorb or liberate heat and how much? c) If \( U(D) - U(A) = 40 \) J find the heat absorbed in the processes AD and DB.

\( \Delta U = q + w = 80 + -30 = 50 \) J between states A & B.
\( q = \Delta U - w = 50 - -10 = 60 \) J of heat for path ADB
b) \( q = \Delta U - w = -50 + 20 = -30 \) J of heat released for curved path BA.
c) \( \Delta U(A \rightarrow B) = 50 \) & \( \Delta U(A \rightarrow D) = 40 \) so \( \Delta U(D \rightarrow B) = 10 \) J.
for D\( \rightarrow \)B w = 0 as no change in volume occurs, \( q = \Delta U = 10 \) J for A\( \rightarrow \)D \( q = 50 \) J using results from part A.

Problem 31
In biological cells that have a plentiful supply of \( O_2 \), glucose is oxidized to \( CO_2 \) and \( H_2O \) by a process called aerobic oxidation. Muscle cells may be deprived of \( O_2 \) during vigorous exercise and in that case one molecule of glucose is converted to two molecules of lactic acid (\( CH_3CH(OH)COOH \)) by a process called anaerobic glycolysis. a) When 0.3212 g of glucose was burned in a bomb calorimeter of calorimeter constant 641 J/K the temperature rose by 7.793 K. Calculate i) the standard molar enthalpy of combustion, ii) the standard internal energy of combustion and iii) the standard enthalpy of formation of glucose. b) What is the biological advantage (in kJ/mol of energy released as heat) of complete aerobic oxidation compared with anaerobic glycolysis to lactic acid?

a) \( C_6H_{12}O_6 + 6 O_2 \rightarrow 6 CO_2 + 6 H_2O \)
\( \Delta H^{\circ}_{\text{com}} = \frac{641 J/K \times 7.793 J/K}{0.3212 g \times 180 g} = -2,800 \) kJ/mol
\( \Delta U^{\circ}_{\text{com}} = \Delta H^{\circ}_{\text{com}} - \Delta (PV) = \Delta H^{\circ}_{\text{com}} - RT\Delta n = -2800 \text{kJ/mol} - 8.314 J/K-mol \times 298K \times 6 \)
\( \Delta U^{\circ}_{\text{com}} = -2815 \) kJ/mol
\( \Delta H^{\circ}_{f}(C_6H_{12}O_6) = -((\Delta H^{\circ}_{\text{com}}(C_6H_{12}O_6) - 6 \Delta H^{\circ}_{f}(CO_2) - \Delta H^{\circ}_{f}(H_2O)) \)
\( = -((-2,800 \text{kJ/mol} - 6 \text{mol} \times -394 \text{kJ/mol} - 6 \text{mol} \times -286 \text{kJ/mol}) = -1,280 \) kJ/mol
b) \( \Delta H^{\circ}(\text{anaerobic}) = -\Delta H^{\circ}_{f}(C_6H_{12}O_6) + 2*\Delta H^{\circ}_{f}(C_2H_6O_3) \)
\( = -(-1280 \text{kJ/mol}) + 2(-694 \text{kJ/mol}) \)
\( = -108 \text{kJ/mol} \)
28x more energy is released in aerobic oxidation of glucose compared to anaerobic oxidation of glucose.
Problem 32

Geological conditions are sometimes so extreme that quantities neglected in normal laboratory experiments take on an overriding importance. For example, consider the formation of diamond under geophysically typical conditions. The density of graphite is 2.27 g/cm$^3$ and that of diamond is 3.52 g/cm$^3$ at a certain temperature and 500 kbar. By how much does $\Delta_{\text{trs}} U$ differ for $\Delta_{\text{trs}} H$ for the graphite to diamond transition?

$$\Delta_{\text{trs}} H = \Delta_{\text{trs}} U + \Delta(PV)$$

$\Delta_{\text{trs}} H = \Delta_{\text{trs}} U + P\Delta V + V\Delta P$ transition occurs under constant $P = 500$ kbar

$$\Delta V = ((1/2.27)\text{cm}^3/\text{g} - (1/3.52)\text{cm}^3/\text{g}) \times 12 \text{ g/mol} = 1.88 \text{ cm}^3/\text{mol} = 1.88 \times 10^{-6} \text{ m}^3/\text{mol}$$

$$\Delta_{\text{trs}} H - \Delta_{\text{trs}} U = + P\Delta V = 500 \text{ kbar} \times 10^5 \text{ Pa/bar} \times 1.88 \times 10^{-6} \text{ m}^3/\text{mol} = 94,000 \text{ Pa} \cdot \text{m}^3/\text{mol}$$

$$\Delta_{\text{trs}} H - \Delta_{\text{trs}} U = 94 \text{ kJ/mol}$$