Tutorial 2 – Questions from Atkins 8th Edition Chapters 2 and 9

Discussion Questions

2.1 Provide mechanical and molecular definitions of work and heat

2.2 Consider the reversible expansion of a perfect gas. Provide a physical interpretation for the fact that pV^γ = constant for an adiabatic change, whereas pV = constant for an isothermal change.

2.4 Explain the significance of a physical observable being a state function and compile a list of as many state functions as you can identify.

9.1 Discuss the physical origin of quantization energy for a particle confined to moving inside a 1 dimensional box or ring.

9.2 Discuss the correspondence principle and provide two examples.

Exercises

2.13a When 3.0 mol O_2 is heated at a constant pressure of 3.25atm, its temperature increases from 260K to 285K. Given that the molar heat capacity of O_2 at constant pressure is 29.4 K^{-1} mol^{-1}, calculate q, delta H and delta U.

2.19a When 120 mg of naphthalene $C_{10}H_8$ (s) was burned in a bomb calorimeter the temperature rose by 3.05K. (I) Calculate the calorimeter constant.

9.1a Calculate the energy separations in joules, kilojoules per mole, electronvolts and reciprocal centimetres between the levels (a) n=2 and n=1 (b) n=6 and n=5 of an electron in a box of 1.0nm.

9.6a Consider a particle in a cubic box. What is the degeneracy of the level that has an energy three times that of the lowest level.

9.8a Calculate the zero-point energy of a harmonic oscillator consisting of a particle of mass 2.33×10^{-26}kg and force constant 155 N m^{-1}.

Group	D	E
1	2.1	9.1
2	2.2	9.6
3	2.4	9.8
4	9.1	2.19
5	9.2	2.13

Discussion Questions

2.1 Work

mechanical: work is the appication of force through a distance.
• measured in Joules

$w = -\vec{f} \cdot \vec{d}$
$= -fd\cos\theta$

• Force & distance are both vectors, work is scalar

• The Force is to calculate work is the force applied in the direction of the displacement.

molecular: transfer of energy resulting in orderly motion of molecules in the system

Heat:

mechanical: • measured as a difference when the system changes states through some non-adiabatic process.

• Formal defn. heat is the difference between the adiabatic & non adiabatic work through the same change in state.

• Less Formal: heat is the form of energy exchanged when two bodies of different temperature are in thermal contact.

molecular: transfer of energy resulting in disorderly motion of molecules in the system.

2.2 $pV^{\gamma} = \text{constant}$ adiabatic $p \propto \frac{1}{V^{\gamma}}$

$pV = \text{constant}$ isothermal $p \propto \frac{1}{V}$

Adiabatic: no heat flows into the system so the temp. decreases as the system does work (expands)

Isothermal: heat enters the system to maintain a constant temp. while the work is being done.

Since the temperature also changes along with the volume for the adiabatic process the pressure must decrease faster.

$\therefore p \propto \frac{1}{V^{\gamma}}$ where $\gamma > 1$; pV^{γ} $\gamma = \frac{C_{pm}}{C_{Vm}}$

In the isothermal process temperature is not affected and the pressure depends only on the volume

$p \propto \frac{1}{V}$

2.4 State function: Changes are independant of the path taken therefore when calculating differences for these observables any convienient path may be chosen.

Some examples are:

temperature, volume, pressure, energy, heat capacity, amount,

9.1 In quantum mechanics particles have wave characteristics.
For a particle to exist the waves representing it must not experience destructive interference when reflected by a barrier (or it would no longer exist)

$\therefore$ (1) $\lambda = \frac{2}{n} \times L$ where L is the length of the path & n is a positive integer

(2) $\lambda = \frac{h}{p}$ & (3) $E = \frac{p^2}{2m}$

Sub (1) & (2) into (3) to get

$E = \frac{n^2h^2}{8mL^2}$, since n is an integer E is quantized.

See 9.6 for same process but particle on a ring.

9.2

Correspondence principle: at very large quantum numbers quantum mechanics merges with classical mechanics.

Example: particle in a box at room temperature

The quantum numbers are very large, corresponding to the average energy of the gas molecules ($\frac{1}{2}kT$ per degree of freedom). The separation of energy levels is small so the energy is essentially continuous

Harmonic oscillator behaves as a classical system at large values for n. Figure 9.26 of the text (see $v = 20$ graph) shows the probability distributions approaching the classical model

(E)

Exercises

2.13a) Given:

p = constant = 3.25 atm
T_1 = 260 K
T_2 = 285 K
$\Delta T = 25\,K$
$C_{p,m}$ = 29.4 J K^{-1} mol^{-1}

Want:
q, ΔH, ΔU

$q_p = n C_{p,m} (\Delta T)$

$q_p = 29.4\,J K^{-1} mol^{-1} (25\,K) \cdot 3.0\,mol$

$q_p = 2205\,J = 2.2\,kJ$

$\Delta H = q_p = 2.2\,kJ$

$\Delta U = \Delta H - \Delta pV$ assume perfect gas

$\Delta U = \Delta H - nR\Delta T$

$\Delta U = 2205\,J - (3.00\,mol \times 8.314\,J K^{-1} mol^{-1} \times 25\,K)$

$\Delta U = 2205\,J - 623.6\,J$

$\Delta U = 1581\,J$ or $\boxed{1.6\,kJ}$

2.19 a)

<u>Given</u>

$m = 120\,mg$

$M_{C_{10}H_8} = 128.2\,g/mol$

$\Delta T = 3.05K$

<u>Want</u>

Calorimeter constant.

$C = \frac{|q|}{\Delta T}$

Reaction is: $*\ \Delta n_{(g)} = 10 - 12 = -2$

$$C_{10}H_{8\,(s)} + \boxed{12O_{2\,(g)}} \rightarrow \boxed{10CO_{2\,(g)}} + 4H_2O_{(l)}$$

Note: bomb calorimeter gives $q_v = n\Delta_c U°$

$$\Delta_c U° = \Delta_c H° - \Delta n_g RT$$

From table 2.5, data section $\Delta_c H° = -5157\,kJmol^{-1}$

$T \neq \Delta T$, T is assumed to be room temp, (298K) bc this is the approximate starting temperature

$$\Delta_c U° = -5157\,kJmol^{-1} - (-2mol \cdot 8.3\times10^{-3}\,kJK^{-1}mol^{-1} \cdot 298K)$$

$$\Delta_c U° = -5157\,kJmol^{-1} + 4.95\,kJmol^{-1}$$

$$\Delta_c U° = -5152\,kJ\,mol^{-1}$$

$$q_v = n\Delta_c U = \left(\frac{120\times10^{-3}g}{128.2\,g/mol}\right) \times -5152\,kJmol^{-1}$$

$$q_v = -4.822\,kJ$$

$$C = \frac{|q|}{\Delta T} = \frac{4.822\,kJ}{3.05\,K} = 1.58\,kJK^{-1}$$

9.1 a)

$$E = \frac{n^2 h^2}{8 m_e L^2}$$

where $L = 1.0 \times 10^{-9}$ m (1.0 nm)
$m_e = 9.109 \times 10^{-31}$ kg
$h = 6.626 \times 10^{-34}$ J·s

$$\frac{h^2}{8 m_e L^2} = \frac{(6.626 \times 10^{-34} \text{ J.s})^2}{8 \cdot 9.109 \times 10^{-31} \text{kg} \cdot (1.0 \times 10^{-9} \text{m})^2} = 6.025 \times 10^{-20} \text{ J}$$

units: $J = kg \frac{m^2}{s^2}$ so: $\frac{\frac{kg^2 m^4 \cdot s^2}{s^4}}{kg \cdot m^2} = \frac{kg\, m^2}{s^2}$

a) $E_2 - E_1 = (2^2 - 1^2)(6.025 \times 10^{-20} J) = 1.81 \times 10^{-19} J$

electronvolts: $1.81 \times 10^{-19} J \times \frac{1 eV}{1.602 \times 10^{-19} J} = 1.13 eV$

cm^{-1}: $1.81 \times 10^{-19} J \times \frac{1 cm^{-1}}{1.986 \times 10^{-23} J} = 9.1 \times 10^{3} cm^{-1}$

$kJ mol^{-1}$: $1.13 eV \times \frac{96.485 kJ mol^{-1}}{1 eV} = 109 kJ mol^{-1}$

b) $E_6 - E_5 = (6^2 - 5^2)(6.025 \times 10^{-20} J) = 6.6275 \times 10^{-19} J$

$eV = 4.1 eV$, $cm^{-1} = 3.3 \times 10^{4} cm^{-1}$,

$kJ mol^{-1} = 396 kJ mol^{-1}$

9.6a) Energy $E = (n_1^2 + n_2^2 + n_3^2) \times \frac{h^2}{8mL^2}$

lowest level is $E_{111} = (1+1+1) \times \frac{h^2}{8mL^2}$

$= \frac{3h^2}{8mL^2}$

3x lowest level is $3E_{111} = \frac{9h^2}{8mL^2}$

which n_1, n_2 & n_3 make $n_1^2 + n_2^2 + n_3^2 = 9$?

$(n_1, n_2, n_3) = (1,2,2)$ or $(2,1,2)$ or $(2,2,1)$

So the degeneracy is 3.

9.8a) $E = (v + \frac{1}{2}) \hbar\omega$ where $\omega = \left(\frac{k}{m}\right)^{1/2}$

zero point energy $v = 0$ (E_0)

$E_0 = \frac{1}{2}\hbar\omega$
$= \frac{1}{2}\hbar\left(\frac{k}{m}\right)^{1/2}$

$m = 2.33 \times 10^{-26}$ kg
$k = 155 Nm^{-1}$
$\hbar = 1.055 \times 10^{-34}$ Js

$= (\frac{1}{2}) \times (1.055 \times 10^{-34} Js)\left(\frac{155 Nm^{-1}}{2.33 \times 10^{-26} kg}\right)^{1/2}$

$E_0 = 4.3 \times 10^{-21}$