Answer 19: Works in Thermodynamics

19-1 Isothermal reversible expansion

We have 100/22.41=4.461 moles, and the final volume is

$$V_2 = \frac{P_1 V_1}{P_2} = \frac{10 \times 10}{1} = 100\ell \quad (1)$$

The work done by gas is

$$\begin{aligned} -w = q &= nRT \ln\frac{V_2}{V_1} \\ &= 4.461 \times 8.341 \times 273.2 \ln 10 \\ &= 23290\, joules \end{aligned} \quad (2)$$

19-2 Adiabatic reversible expansion

Notice that

$$\gamma = \frac{C_P}{C_V} = \frac{\frac{3}{2}R + R}{R} = \frac{5}{3} \quad (3)$$

Thus

$$\begin{aligned} V_2 &= \left(\frac{P_1}{P_2}\right)^{\frac{1}{2}} V_1 = (10)^{\frac{3}{5}} \times 10 \\ &= 39.8\ell \end{aligned} \quad (4)$$

and the final temperature is obtained from

$$\begin{aligned} T_2 &= \frac{P_2 V_2}{nR} = \frac{1 \times 39.81}{4.461 \times 0.08205} \\ &= 108.8^o K \end{aligned} \quad (5)$$

For adiabatic processes,

$q = 0$ and $\Delta E = q + w = w$

ie

$$w = \Delta E = n\overline{C}v\Delta T = -9141\, joules \quad (6)$$

19-3 Irreversible adiabatic expansion

Since q=0, we have

$$\Delta E = w = n\overline{C}_v (T_2 - T_1) \quad (7)$$

$$w = -P_2(V_2 - V_1) \quad (8)$$

and

$$-\frac{3}{2}nR(T_2 - 273.2) = (\frac{nRT_2}{1} - \frac{nR \times 273.2}{10}) \quad (9)$$

It follows that

$$T_2 = 174.8^o K \quad (10)$$

and

$$\Delta E = w = \frac{3}{2}nR(174.8 - 273.2) \\ = -5474\, joules \quad (11)$$

Answer 20: Kinetics — Atmosphere Chemistry

20-1

$$\frac{dP_{NO_2}}{dt} = -kP_{NO_2}^2$$

$$\frac{1}{P_{NO_2}} = \frac{1}{P_{NO_2}^0} + kt$$

where $P_{NO_2}^0$ devotes the initial pressure of NO_2

20-2 At $t = t_{1/2}$, $P_{NO_2} = \frac{1}{2}P_{NO_2}^0$

$$k = \frac{1}{P_{NO_2}^0 t_{1/2}}$$

or

$$k = \frac{1}{3 \times \frac{600}{760}} = 0.422 \text{ l / atm} \cdot \text{min}$$

Answer 21: Kinetics and Thermodynamics

21-1 In the beginning 4 min of the reaction,

$$\frac{d[B]}{dt} = k_1[A] \quad \text{............. (1)}$$

$$\frac{d[C]}{dt} = k_2[A] \quad \text{............. (2)}$$

(1) divided by (2) gives

$$\frac{d[B]}{d[C]} = \frac{k_1}{k_2} \qquad\qquad \frac{B}{C} = \frac{k_1}{k_2} = \frac{1}{0.1} = 10$$

21-2 When the reaction is complete, the system reaches thermal equilibrium.

$$\frac{[B]}{[A]} = \frac{k_1}{k_{-1}} \qquad \frac{[C]}{[A]} = \frac{k_2}{k_{-2}}$$

$$\frac{[B]}{[C]} = \frac{k_1/k_{-1}}{k_2/k_{-2}} = \frac{1/0.01}{0.1/0.0005} = \frac{100}{200} = \frac{1}{2}$$

21-3 A→C thermodynamic- controlled reaction process is favored when temperature increases. The system will reach thermal equilibrium more rapidly.

Answer 22: Phase Diagram

22-1 A: solid; B: solid, liquid, and gas states coexist; C: liquid and gas states coexist.

22-2 The negative slope of the solid/liquid line indicates the liquid state of water is denser than its solid state. Therefore, ice may not sink in its own liquid.

22-3 Clapeyron equation is expressed as

$$\frac{dP}{dT} = \frac{\Delta H}{T\Delta V} ,$$

where ΔH is molar enthalpy of water and ΔV is volume change. The phase diagram shows that the slope of dP/dT for the liquid-solid coexistence region is negative, indicating the volume expands when water freezes.

22-4 As pressure is lowered, liquid phase transforms directly to gas phase at the same temperature. Thus water may vaporize. At the same time, the process of water evaporation is endothermic as to make the surrounding cooled. The left water becomes frozen. The solid state will sublime until none is left, if the pump is left on.

22-5 The ice surface, exerted by a pressure more than one atm, turns to liquid state at 0 ^{o}C.

Answer 23: Standard Deviation in One-Dimensional Quantum Mechanics

23-1 average speed <v>:

$$<v>=\int_0^\infty vF(v)dv = 4\pi\left(\frac{M}{2\pi RT}\right)^{3/2}\int_0^\infty \exp\left(\frac{-Mv^2}{2RT}\right)v^3 dv$$

$$=\sqrt{\frac{8RT}{\pi M}}=\sqrt{\frac{8x8.31x300}{3.14x0.032}} = 4.45 \text{ x } 10^2 \text{ ms}^{-1}$$

standard deviation σ_v:

$$<v^2>=\int_0^\infty vF(v)dv = 4\pi\left(\frac{M}{2\pi RT}\right)^{3/2}\int_0^\infty \exp\left(\frac{-Mv^2}{2RT}\right)v^4 dv$$

$$=\frac{3RT}{M}=\frac{3x8.31x300}{0.032}=2.33 \text{ x } 10^5 \text{ m}^2\text{s}^{-2}$$

$$\sigma_v = \sqrt{<v^2> - <v>^2} = \sqrt{2.33x10^5 - (4.45x10^2)^2} = 1.87 \text{ x } 10^2 \text{ ms}^{-1}$$

23-2 average position <x>:

$$<x>=\int_{-\infty}^\infty \varphi^* x\varphi dx = \frac{1}{\sqrt{2\pi}}\int_{-\infty}^\infty x\exp(-\frac{x^2}{2})dx = 0$$

standard deviation σ_x:

$$<x^2>=\int_{-\infty}^\infty \varphi^* x^2\varphi dx = \frac{1}{\sqrt{2\pi}}\int_{-\infty}^\infty x^2\exp(-\frac{x^2}{2})dx = 1$$

$$\sigma_x = \sqrt{<x^2> - <x>^2} = 1.$$

23-3
$$<p> = \int_{-\infty}^\infty \varphi^*(-i\frac{h\partial}{2\pi\partial x})\varphi dx = \int_{-\infty}^\infty \frac{ihxe^{-x^2/2}}{4\pi\sqrt{2\pi}}dx = 0$$

$$<p^2>=\int_{-\infty}^\infty \varphi^*(-\frac{h^2\partial^2}{4\pi^2\partial x^2})\varphi dx = \frac{h^2}{16\pi^2}$$

$$\sigma_p = \sqrt{<p^2> - <p>^2} = \frac{h}{4\pi}$$

23-4
$$\sigma_x\sigma_p = \frac{h}{4\pi}$$

Answer 24: A Particle in 2-D Box Quantum Mechanics

24-1 $E_{1,1} = 2E_0$

$E_{1,2} = E_{2,1} = 5E_0$

$E_{2,2} = 8E_0$

$E_{1,3} = E_{3,1} = 10E_0$

$E_{2,3} = E_{3,2} = 13E_0$

$E_{1,4} = E_{4,1} = 17E_0$

$E_{3,3} = 18E_0$

$E_{2,4} = E_{4,2} = 20E_0$

$E_{3,4} = E_{4,3} = 25E_0$

$E_{1,5} = E_{5,1} = 26E_0$

where $E_0 = h^2 / 8\ mL^2$

24-2 The total number of electrons in the highest occupied energy level is 4.

24-3 Ground state is diamagnetic.

24-4 The longest-wavelength excitation energy is ΔE = (25-20) E_0, where

$$E_0 = (6.63\times10^{-34}\ \text{Js})^2 / [8 \cdot 9.11\times10^{-31}\ \text{kg} \cdot (1\times10^{-9}\ \text{m})^2] = 6.02\times10^{-20}\ \text{J} \quad (1)$$

$$\Delta E = (25\text{-}20)\ E_0 = 3.01\times10^{-19}\ \text{J} \quad (2)$$

The wavelength is

$$\lambda = \text{hc} / \Delta E = [6.63\times10^{-34}\ \text{Js} \cdot 3\times10^{8}] / 3.01\times10^{-19} = 660\ \text{nm} \quad (3)$$

Answer 25: Spectrum Analysis

25-1 $\Lambda = 355.00 / 2\ \sin 60.00^\circ = 204.96$

$\lambda_{DFDL} = 2 \times 1.40 \times 204.96 = 573.89$ nm

Answer 26: Time-of-Flight Mass Spectrometer

26-1 (a)

$$\nu = [(2 \times 1 \times 1.6022\times10^{-19}\ \text{C} \times 20000\ \text{V}) / (12362 \times 1.6605\times10^{-27}\ \text{kg})]^{½}$$

ν =17669.5 m/s

26-2 (c)

t = 1.00 m / 17669.5 m/s = 56.59 μs

Answer 27: Enzyme Catalysis

27-1 $A = \varepsilon bC$; $\Delta C = \Delta A / \Delta\varepsilon b$; $\Delta mol = \Delta C \times V$ (volume)

$[0.1 / ((27.7-9.2) \times 10^{3})] \times 5 \times 10^{-3} = 2.7 \times 10^{-8}$ mol/sec

27-2 Four electrons are needed to reduce one molecule of oxygen, therefore, the oxygen consuming rate is $2.7 \times 10^{-8} / 4 = 6.75 \times 10^{-9}$ mol/sec

27-3 By definition, the turnover number equals 6.75×10^{-9} (mol/sec) / (2.7×10^{-9} M x 5×10^{-3} L). Therefore, oxidase has a turnover number of 500.

Practical Problems

Answer 30: Identification of Unknown Solutions （II）

1. Use the indicator to find out NaOH, HCl, and H_2SO_4 (confirmed by Pb^{2+})
2. Find out the Na_2S by the odor, and use it to find Cd^{2+} and Zn^{2+} (by precipitation. and color).
3. By electrolysis of the four solutions remained, KI solution can be found by the trace of yellowish brown (I_2) formed in the anode.
4. The color of I_2 will be disappeared by $Na_2S_2O_3$ solution.
5. The concentration of unknown solution is about 0.5 M (mol/L)