Homework 2 Solutions

1. (i) $v_{mean} = 0.921 \times v_{rms} = 0.921\left(\frac{3RT}{M}\right)^{1/2}$

$v_{mean}(H_2)$ = 0.921(3x8.31447 J K^{-1} mol^{-1}x293.15 K / 2x10^{-3} kg mol^{-1})$^{1/2}$ = 1754 m s^{-1}
$v_{mean}(Hg)$ = 0.921(3x8.31447 J K^{-1} mol^{-1}x293.15 K / 200.6x10^{-3} kg mol^{-1})$^{1/2}$ = 175.8 m s^{-1}
$v_{mean}(H_2) / v_{mean}(Hg) = 10$
(ii) E_k(mean) = (3/2) RT – independent of a molecular mass – the ratio of mean translational energies of H_2 and Hg is 1.

2. We use numerical integration of the Maxwell-Boltzmann distribution function by calculating the area of a rectangle with the base of 210 – 200 = 10 m s^{-1} and the height of f(205 m s^{-1}) in the middle of the range.

$f(v) = 4\pi\left(\frac{M}{2\pi RT}\right)^{3/2} v^2 e^{-Mv^2/2RT}$ = 6.87x10^{-4} m^{-1} s

probability = $f(v)\Delta v$ = 6.87 x10^{-3}

3. (i) $v_{rms} = \left(\frac{3RT}{M}\right)^{1/2}$ = 510.8 m s^{-1} $\quad v_{mean} = 0.921 \times v_{rms}$= 470.5 m s^{-1}

(ii) $\lambda = \frac{RT}{2^{1/2} N_A \sigma p} = \frac{RT}{2^{1/2} N_A \left(\pi d^2\right) p}$ =58.6 nm

(iii) $z = \frac{v_{rms}}{\lambda}$ = 8.72x10^{-9} s^{-1}

4. (a) $w = -p_{ex}\Delta V$
p_{ex} = (200 Torr) × (133.32 Pa / 1 Torr) = 2.6664×10^4 Pa
ΔV = 3.3 L = 3.3×10^{-3} m^3
w = -(2.6664×10^4 Pa) × (3.3×10^{-3} m^3) = **-88 J**
(b) $w = -nRT \ln(V_f/V_i)$
n = 4.50 g / 16.04 g mol^{-1} = 0.2805 mol
V_f = (12.7 + 3.3) L = 16.0 L
w = -(0.2805 mol) × (8.3145 J K^{-1} mol^{-1}) × (310 K) × ln(16.0 L / 12.7 L) = **-167 J**

5. Calculate the final pressure:
$p_i/T_i = p_f/T_f$ $\quad p_f = p_iT_f/T_i$ = (1 atm) × (400 K) / (300 K) = **1.333 atm**
$\Delta U = nC_{V,m}\Delta T$ = (1 mol) × (3/2) × (8.3145 J K^{-1} mol^{-1}) × (400 K – 300 K) = **1247 J**
The process takes place at a constant volume. Therefore, $\boldsymbol{w = 0}$

$q = \Delta U - w = \mathbf{1247\ J}$

6. $C_V = q_V / \Delta T = 229\ \mathrm{J} / 2.55\ \mathrm{K} = 89.8\ \mathrm{J\ K^{-1}}$

The molar heat capacity at constant volume is therefore

$C_{V,\mathrm{m}} = 89.8\ \mathrm{J\ K^{-1}} / 3.0\ \mathrm{mol} = \mathbf{29.93\ J\ K^{-1}\ mol^{-1}}$

For a perfect gas $C_{p,\mathrm{m}} - C_{V,\mathrm{m}} = \mathrm{R}$, or

$C_{p,\mathrm{m}} = C_{V,\mathrm{m}} + \mathrm{R} = (29.93 + 8.31)\ \mathrm{J\ K^{-1}\ mol^{-1}} = \mathbf{38.24\ J\ K^{-1}\ mol^{-1}}$

7.

The reaction is

$$\mathrm{Zn} + 2\mathrm{H}^+ \rightarrow \mathrm{Zn}^{2+} + \mathrm{H}_2$$

so it liberates 1 mol $\mathrm{H_2(g)}$ for every 1 mol Zn used. Work at constant pressure is

$$\begin{aligned} w &= -p\Delta V = -pV_{\mathrm{gas}} = -nRT = -\left(\frac{5.0\ \mathrm{g}}{65.4\ \mathrm{g\ mol^{-1}}}\right) \\ &\quad \times (8.3145\ \mathrm{J\,K^{-1}\,mol^{-1}}) \times (23 + 273)\ \mathrm{K} \\ &= \boxed{-188\ \mathrm{J}} \end{aligned}$$

8.

$$\begin{aligned} \Delta H &= q_p = C_p\Delta T = nC_{p,\mathrm{m}}\Delta T = (2.0\ \mathrm{mol}) \times (37.11\ \mathrm{J\,K^{-1}\,mol^{-1}}) \times (277 - 250)\ \mathrm{K} \\ &= \boxed{2.0 \times 10^3\ \mathrm{J\,mol^{-1}}} \end{aligned}$$

$$\Delta H = \Delta U + \Delta(pV) = \Delta U + nR\Delta T \quad \text{so} \quad \Delta U = \Delta H - nR\Delta T$$

$$\begin{aligned} \Delta U &= 2.0 \times 10^3\ \mathrm{J\,mol^{-1}} - (2.0\ \mathrm{mol}) \times (8.3145\ \mathrm{J\,K^{-1}\,mol^{-1}}) \times (277 - 250)\ \mathrm{K} \\ &= \boxed{1.6 \times 10^3\ \mathrm{J\,mol^{-1}}} \end{aligned}$$

9. $\mathrm{d}w = -p\mathrm{d}V$ $\quad w = -\int_{V_i}^{V_f} p\,dV$

Virial equation of state: $pV_m = RT\left(1 + \frac{B}{V_m}\right)$ or $pV = nRT\left(1 + \frac{nB}{V}\right)$

(Because $V_\mathrm{m} = V/n$). So, p can be expressed as $p = \frac{nRT}{V} + \frac{n^2RTB}{V^2}$. Then,

$$w = -\int_{V_i}^{V_f} p\,dV = -nRT\ln\frac{V_f}{V_i} - n^2RTB\left(\frac{1}{V_i} - \frac{1}{V_f}\right)$$

The first term corresponds to the perfect gas.

(a) $w = -1573.3\ \mathrm{J} - \{1^2\ \mathrm{mol}^2 \times 8.31451\ \mathrm{J\ K^{-1}\ mol^{-1}} \times 273\ \mathrm{K} \times (-21.7\ \mathrm{cm^3\ mol^{-1}}) \times (1/500\ \mathrm{cm^3} - 1/1000\ \mathrm{cm^3}) = -1573.3\ \mathrm{J} + 49.3\ \mathrm{J} = \mathbf{-1524\ J}$

(b) $w = -1.00\ \text{mol} \times 8.31451\ \text{J K}^{-1}\ \text{mol}^{-1} \times 273\ \text{K} \times \ln(1000\ \text{cm}^3/500\ \text{cm}^3) =$ **-1573.3 J**