Chapter 2 Homework Solutions

2.1 Cl_2 - 3 translations + 2 rotations + 1 vibration

(a) U_m(rigid) = (3/2)RT + (2/2)RT = (5/2)RT , H_m(rigid) = (7/2)RT
$C_{p,m}$(rigid) = (7/2)R = 29.1 J/mol-K

(b) U_m(vib) = (3/2)RT + (2/2)RT + RT = (7/2)RT , H_m(vib) = (9/2)RT
$C_{p,m}$(vib) = (9/2)R = 37.4 J/mol-K

2.2 C_6H_6 (N=12) - 3 translations + 3 rotations + (3x12-6) = 30 vibrations

(a) U_m(rigid) = (3/2)RT + (3/2)RT = 3RT , H_m(rigid) = 4RT
$C_{p,m}$(rigid) = 4R = 33.2 J/mol-K

(b) U_m(vib) = (3/2)RT + (3/2)RT + 30RT = 33RT , H_m(vib) = 34RT
$C_{p,m}$(vib) = 34R = 282.5 J/mol-K

2.3 CO_2 (N=3) - 3 translations + 2 rotations + (3x3-5) = 4 vibrations

(a) U_m(rigid) = (3/2)RT + (2/2)RT = (5/2)RT , H_m(rigid) = (7/2)RT
$C_{p,m}$(rigid) = (7/2)R = 29.1 J/mol-K

(b) U_m(vib) = (3/2)RT + (2/2)RT + 4RT = (13/2)RT , H_m(vib) = (15/2)RT
$C_{p,m}$(vib) = (15/2)R = 62.3 J/mol-K

2.4 V_1 = 22.4 L , V_2 = 44.8 L , T = 273 K (constant) , n = 1.00 mol

(a) Reversible

$$\Delta U = nC_{V,m}\Delta T = 0 \qquad \Delta H = nC_{p,m}\Delta T = 0$$

$$w = -nRT\ln(V_2/V_1) = -1\,mol(8.31\,J/mol\cdot K)(273\,K)\ln(44.8/22.4) = -1570\,J$$

q = ΔU - w = +1570 J

(b) Constant p (final pressure): $p = \dfrac{nRT}{V} = \dfrac{(1\,mol)(8.31\,kPa\cdot L/mol\cdot K)(273\,K)}{44.8\,L} = 50.6\,kPa$

ΔU = ΔH = 0

$$w = -p(V_2 - V_1) = -50.6\,kPa(44.8\,L - 22.4\,L) = -1130\,kPa\cdot L = -1130\,J$$

q = ΔU - w = +1130 J

(c) $p = 0$

$\Delta U = \Delta H = 0$
$w = -p(V_2 - V_1) = 0$
$q = \Delta U - w = 0$

2.5 $p_1 = 1.00\, atm \cdot \frac{101.3\, kPa}{1\, atm} = 101.3\, kPa$ $T_1 = 300$ K $T_2 = 400$ K

$\frac{p_2}{T_2} = \frac{p_1}{T_1} \quad \rightarrow \quad p_2 = p_1 \frac{T_2}{T_1} = 101.3\, kPa \cdot \frac{400}{300} = 135.1\, kPa$

$\Delta U = nC_{V,m}\Delta T = n\left(\frac{3}{2}R\right)\Delta T = (1.0\, mol)(1.50)(8.31\, J / mol \cdot K)(400\, K - 300\, K)$

$= 1250\, J = 1.25\, kJ$

w = 0 (because V = constant)

q = ΔU-w = ΔU = 1.25 kJ

2.6 n = 1. mol , T = 100 ^oC = 373 K , $\Delta_{vap}H$ = 40.7 kJ/mol

$w = -P(V_{liq} - V_{gas}) \approx +PV_{gas} = nRT$ = (1.0 mol)(8.31 J/mol-K)(373 K) = +3100 J = +3.10 kJ

$q = \Delta H = n\Delta_{cond}H = n(-\Delta_{vap}H)$ = (1 mol)(-40.7 kJ/mol) = -40.7 kJ

ΔU = q + w = -40.7 kJ + 3.10 kJ = -37.6 kJ

2.7 T = 25 ^oC = 298 K , p = 1.00 atm , **Reaction:** Mg(s) + 2 HCl(aq) → $MgCl_2$(aq) + H_2(g)

We will need n(H_2) below: $n(H_2) = 15\, g\, Mg \cdot \frac{1 mol\, Mg}{24.3\, g\, Mg} \cdot \frac{1 mol\, H_2}{1 mol\, Mg} = 0.617\, mol\, H_2$

$w = -p\{\Delta V\} = -p\{V_{prod} - V_{rct}\} = -p\{V_{H_2} + V_{MgCl_2} - V_{Mg} - V_{HCl}\} \approx -pV_{H_2}$
Simplificaion above because volumes of liquids/solids are negligible compared to volumes of gases.

$w = -p\{\Delta V\} = -pV_{H_2} = -n_{H_2}RT = -(0.617\, mol)(8.31\, J / mol \cdot K)(298\, K) = -1530\, J \approx -1.5\, kJ$

2.8 2 mol of W(s) requires 2 mol W x 6 mol CO/1 mol W = 12 mol of CO(g). T = 150 ^oC = 423 K

$w = -P\left[V_{prod} - V_{rct}\right] = +PV_{rct} = +PV_{CO}$ [Consider only gas phase reactants or products]

$w = -PV_{CO} = -n_{CO}RT = -12\, mol(8.31 J / mol \times K)(423 K) = 42,200\, J = +42.2\, kJ$

2.9 n = 1 mol , T_1 = 25 °C = 298 K , T_2 = 200 °C = 473 K
$C_{p,m}$ = a + bT , a = 20.17 J/mol-K , b = 0.37 J/mol-K^2

(a) Constant Pressure [q = ΔH]

$$q = \Delta H = \int_{T_1}^{T_2} nC_{p,m} dT = n\int_{T_1}^{T_2} \left(a + bT\right) dT = na\left[T_2 - T_1\right] + nb\left[\frac{T_2^2}{2} - \frac{T_1^2}{2}\right]$$

$$= (1mol)(20.17\,J/mol\cdot K)(473K - 298K) + (1mol(0.37\,J/mol\cdot K^2)\left[\frac{(473K)^2}{2} - \frac{(298K)^2}{2}\right]$$

$$= 3530\,J + 24960\,J = 28490\,J \approx 28.5\,kJ$$

$$w = -p\left(V_2 - V_1\right) = -pV_2 + pV_1 = -nRT_2 + nRT_1 = -nR(T_2 - T_1)$$
$$= -(1mol)(8.31\,J/mol\cdot K)(473K - 298K) = -1450\,J \approx -1.5\,kJ$$

ΔU = q + w = 28490 J +(-1450 J) =27040 J ≈ 27.0 kJ

(b) Constant Volume [q = ΔU and w = 0]

For a Perfect Gas, U and H depend only upon temperature. Therefore, the values of ΔU and ΔH are the same as in part (a):

ΔU = 27040 J ≈ 27.0 kJ
ΔH = 28490 J ≈ 28.5 kJ

Because V = constant,
w = 0
q = ΔU = 27040 J ≈ 27.0 kJ

2.10 $C_{V,m} = C_{p,m}$ - R = 37.11 - 8.31 = 28.8 J/mol-K.

$$n = 2.45\,g\cdot\frac{1mol}{44\,g} = 0.056\,mol$$

T_1 = 27 °C = 300 K , V_1 = 500 cm^3 = 0.50 L , V_2 = 3.00 L
Let's calculate T_2 for an adiabatic expansion. We'll need $R/C_{V,m}$ = 8.31/28.8 = 0.289

$$\left(\frac{T_2}{T_1}\right) = \left(\frac{V_1}{V_2}\right)^{R/C_{V,m}} \rightarrow T_2 = T_1\left(\frac{V_1}{V_2}\right)^{R/C_{V,m}} = (300\,K)\left(\frac{0.50}{3.00}\right)^{0.289} = 179\,K$$

Adiabatic Expansion: q = 0 → w = ΔU

$$w = \Delta U = nC_{V,m}\left(T_2 - T_1\right) = (0.056\,mol)(28.8\,J/mol\cdot K)(179\,K - 300\,K)$$
$$= -195\,J$$

2.11 n = 3.0 mol , T_1 = 260 K , T_2 = 285 K , $C_{p,m}$ = 29.4 J/mol-K

Let's calculate $C_{V,m}$: $C_{V,m} = C_{p,m} - R = 29.4 - 8.31 \approx 21.1$ J/mol-K

Because p = constant, q = ΔH

$$q = \Delta H = nC_{p,m}\Delta T = (3.0\,mol)(29.4\,J/mol\cdot K)(285\,K - 260\,K) = 2205\,J \approx 2.2\,kJ$$

$$\Delta U = nC_{V,m}\Delta T = (3.0\,mol)(21.1\,J/mol\cdot K)(285\,K - 260\,K) = 1580\,J \approx 1.6\,kJ$$

2.12 n = 1.00 mol , $C_{V,m}$ = 20.8 J/mol-K , T_1 = 310 K , p_1 = 3.25 atm , p_2 = 2.50 atm

$$V_1 = \frac{nRT_1}{p_1} = \frac{(1.0\,mol)(0.082\,L\cdot atm/mol\cdot K)(310\,K)}{3.25\,atm} = 7.82\,L$$

$$\gamma = \frac{C_{p,m}}{C_{V,m}} = \frac{C_{V,m}+R}{C_{V,m}} = \frac{20.8+8.31}{20.8} = 1.40$$

$$p_2V_2^\gamma = p_1V_1^\gamma \;\rightarrow\; V_2^\gamma = \left(\frac{p_1}{p_2}\right)V_1^\gamma = \left(\frac{3.25}{2.50}\right)(7.82)^{1.40} = 23.06 = V_2^{1.40}$$

$$V_2 = (23.06)^{1/1.40} = 9.41\,L$$

$$T_2 = \frac{p_2V_2}{nR} = \frac{(2.50)(9.41)}{(1)(0.082)} = 287\,K$$

Adiabatic: q = 0

$$w = \Delta U = nC_{V,m}\left[T_2 - T_1\right] = (1\,mol)(20.8\,J/mol\cdot K)(287\,K - 310\,K) = -480\,J \approx -0.5\,kJ$$

2.13 n = 0.50 mol , T = 250 K $\Delta_{vap}H^o$ = 26.0 kJ/mol

p = const (phase transition). Therefore q = ΔH

$$q = \Delta H = n\cdot\Delta_{vap}H^o = (0.50\,mol)(26.0\,kJ/mol) = 13.0\,kJ$$

$$w = -p(V_{gas} - V_{liq}) \approx -pV_{gas} = -nRT = -(0.50\,mol)(8.31\,J/mol\cdot K)(250\,K)$$
$$= -1040\,J \approx -1.0\,kJ$$

ΔU = q + w = +13.0 -1.0 = 12.0 kJ

2.14 $C_6H_5C_2H_5(l) + (21/2)\ O_2(g) \rightarrow 8\ CO_2(g) + 5\ H_2O(l)$

$$\Delta_{comb}H^o = 8\Delta_f H^o(CO_2) + 5\Delta_f H^o(H_2O) - \left[1\Delta_f H^o(C_6H_5C_2H_5) + (21/2)\cdot 0\right]$$
$$= 8(-393.5) + 5(-285.8) - \left[1(-12.5)\right] = -4564.5\,kJ/mol$$

2. 15 For $N_2(g)$, a = 1.35 L^2-atm/mol^2 , b = 0.039 L/mol
n = 2 mol , T = 298 K , V_1 = 1.00 L , V_2 = 24.8 L

Internal Energy (ΔU)

$$\pi_T = \left(\frac{\partial U}{\partial V}\right)_T = \frac{n^2 a}{V^2}$$

$$\Delta U = \int_{V_1}^{V_2}\left(\frac{\partial U}{\partial V}\right)_T dV = \int_{V_1}^{V_2}\frac{n^2 a}{V^2}dV = n^2 a\left[-\frac{1}{V}\right]_{V_1}^{V_2} = n^2 a\left[\frac{1}{V_1} - \frac{1}{V_2}\right]$$

$$\Delta U = (2\,mol)^2 1.35\,L^2\cdot atm/mol^2\left[\frac{1}{1.00\,L/mol} - \frac{1}{24.8\,L/mol}\right]$$

$$= 5.18\,L\cdot atm\cdot\frac{101\,J}{1\,L\cdot atm} = 523.\,J$$

Work (w)

$$\left(p + \frac{n^2 a}{V^2}\right)(V - nb) = nRT \quad\rightarrow\quad p = \frac{nRT}{V - nb} - \frac{n^2 a}{V^2}$$

$$w = -\int_{V_1}^{V_2} p\,dV = -\int_{V_1}^{V_2}\left[\frac{nRT}{V - nb} - \frac{n^2 a}{V^2}\right]dV = -nRT\int_{V_1}^{V_2}\frac{1}{V - nb}dV + n^2 a\int_{V_1}^{V_2}\frac{1}{V^2}dV$$

$$w = -nRT\left[\ln(V - b)\right]_{V_1}^{V_2} + n^2 a\left[-\frac{1}{V}\right]_{V_1}^{V_2} = -nRT\ln\left[\frac{V_2 - nb}{V_1 - nb}\right] + n^2 a\left[\frac{1}{V_1} - \frac{1}{V_2}\right]$$

$$w = -(2\,mol)(8.31\,J/mol\cdot K)(298\,K)\ln\left[\frac{24.8 - 2\bullet 0.039}{1.0 - 2\bullet 0.039}\right] + (2\,mol)^2\left(1.35\,L^2\cdot atm/mol^2\right)\left[\frac{1}{1.0\,L} - \frac{1}{24.8\,L}\right]$$

$$= -16,290\,J/mol + (5.40\,L\cdot atm/mol)\cdot\frac{101\,J}{1\,L\cdot atm} = -16290\,J + 545\,J$$

$$= -15,745\,J \simeq -15.7\,kJ/mol$$

Note: Observe that the work is less negative than it would be if there were no attractive forces (i.e. if a = 0). This is because some of the work energy released in the expansion must be used to pull the attractive molecules further from each other.

Heat (q)

$\Delta U = +523$ J/mol
$w = -15745$ J/mol

$q = \Delta U - w = +523 - (-15745) = +16{,}268$ J/mol $\approx +16.3$ kJ/mol

2.16
$$T_1 = \frac{P_1V_1}{nR} = \frac{(1.0\,atm)(22.4\,L)}{(1\,mol)(0.082\,L\cdot atm/mol\cdot K)} = 273\,K$$
$$T_2 = \frac{P_2V_2}{nR} = \frac{(1.0\,atm)(44.8\,L)}{(1\,mol)(0.082\,L\cdot atm/mol\cdot K)} = 546\,K$$
$$T_3 = \frac{P_3V_3}{nR} = \frac{(0.50\,atm)(44.8\,L)}{(1\,mol)(0.082\,L\cdot atm/mol\cdot K)} = 273\,K$$
$$C_{V,m} = (3/2)R = 1.5(8.31\,J/mol\cdot K) = 12.5\,J/mol\cdot K$$
$$C_{p,m} = C_{V,m} + R = 12.5 + 8.3 = 20.8\,J/mol\cdot K$$

Step 1 → 2 (Constant Pressure)

$$w = -p(V_2 - V_1) = (-1.0\,atm)(44.8\,L - 22.4\,L) = -22.4\,L\cdot atm \cdot \frac{101\,J}{1\,L\cdot atm} = -2260\,J$$
$$\Delta U = nC_{V,m}\left(T_2 - T_1\right) = (1\,mol)(12.5\,J/mol\cdot K)(546\,K - 273\,K) = +3410\,J$$
$$q = \Delta H = nC_{p,m}\left(T_2 - T_1\right) = (1\,mol)(20.8\,J/mol\cdot K)(546\,K - 273\,K) = +5680\,J$$

Step 2 → 3 (Constant Volume)

$w = 0$
$$q = \Delta U = nC_{V,m}\left(T_3 - T_2\right) = (1\,mol)(12.5\,J/mol\cdot K)(273\,K - 546\,K) = -3410\,J$$
$$\Delta H = nC_{p,m}\left(T_3 - T_2\right) = (1\,mol)(20.8\,J/mol\cdot K)(273\,K - 546\,K) = -5680\,J$$

Step 3 → 1 (Isothermal)

$\Delta U = \Delta H = 0$
$$w = -nRT_3\ln(V_1/V_3) = -(1\,mol)(8.31\,J/mol\cdot K)(273\,K)\ln(22.4/44.8) = +1570\,J$$
$q = -w = -1570$ J

Totals:
$\Delta U_{tot} = \Delta U_{1\to 2} + \Delta U_{2\to 3} + \Delta U_{3\to 1} = +3410 - 3410 + 0 = 0$ J
$\Delta H_{tot} = \Delta H_{1\to 2} + \Delta H_{2\to 3} + \Delta H_{3\to 1} = +5680 - 5680 + 0 = 0$ J
$w_{tot} = w_{1\to 2} + w_{2\to 3} + w_{3\to 1} = -2260 + 0 + 1570 = -690$ J
$q_{tot} = q_{1\to 2} + q_{2\to 3} + q_{3\to 1} = +5680 - 3410 - 1570 = +700$ J

Note: As expected, $\Delta U_{tot} = \Delta H_{tot} = 0$ around the cycle.
U and H are State Functions

However, $q_{tot} \neq 0$ and $w_{tot} \neq 0$ around the cycle.
q and w are not State Functions

To within roundoff error, $w_{tot} + q_{tot} \approx 0$ because $q_{tot} + w_{tot} = \Delta U_{tot} = 0$

2.17 n = 1.0 mol
Note: The initial temperature and pressure (required for the calculation) was not given in the problem. We'll use $T_1 = 298$ K , $p_1 = 1.0$ atm.

$$V_1 = \frac{nRT_1}{p_1} = \frac{(1\,mol)(0.082\,L\cdot atm/mol\cdot K)(298\,K)}{1.0\,atm} = 24.4\,L$$

$C_{p,m} = (7/2)R = (7/2)(8.31) = 29.1$ J/mol-K
$C_{V,m} = C_{p,m} - R = 29.1 - 8.3 = 20.8$ J/mol-K

Step a: Constant volume heating to $p_2 = 2\,p_1 = 2$ atm

$$\frac{T_2}{T_1} = \frac{p_2}{p_1} = 2 \;\rightarrow\; T_2 = 2T_1 = 2(298) = 596\text{ K}$$

w = 0

$$q = \Delta U = nC_{V,m}\left(T_2 - T_1\right) = (1\,mol)(20.8\,J/mol\cdot K)(596\,K - 298\,K) = +6190\,J$$

$$\Delta H = nC_{p,m}\left(T_2 - T_1\right) = (1\,mol)(29.1\,J/mol\cdot K)(596\,K - 298\,K) = +8670\,J$$

Step b: Adiabatic Expansion from $T_2 = 596$ K back to $T_3 = 298$ K

q = 0

$$w = \Delta U = nC_{V,m}\left(T_3 - T_2\right) = (1\,mol)(20.8\,J/mol\cdot K)(298\,K - 546\,K) = -6190\,J$$

$$\Delta H = nC_{p,m}\left(T_3 - T_2\right) = (1\,mol)(29.1\,J/mol\cdot K)(298\,K - 546\,K) = -8670\,J$$

We'll need V_3 for last step.

$$\left(\frac{T_2}{T_3}\right) = \left(\frac{V_3}{V_2}\right)^{R/C_{V,m}} \;\rightarrow\; \frac{V_3}{V_2} = \left(\frac{T_2}{T_3}\right)^{C_{V,m}/R} = \left(\frac{596}{298}\right)^{20.8/8.31} = 5.66$$

$V_3 = 5.66\,V_2 = 5.66(24.4) = 138.3$ L

Step c: Isothermal Compression from V_3 = 138.3 L to V_1 = 22.4 L

$\Delta U = \Delta H = 0$

$w = -nRT\ln(V_1/V_3) = -(1\,mol)(8.31\,J/mol\cdot K)\ln(24.4/138.3) = +4300\,J$

q = -w = -4300 J

Totals:

ΔU_{tot} = +6190 - 6190 + 0 = 0

ΔH_{tot} = +8670 - 8670 + 0 = 0

w_{tot} = 0 - 6190 + 4300 = -1890 J $\neq$ 0

q_{tot} = +6190 + 0 -6190 = +1890 J $\neq$ 0