Chapter 19

1 The First Law of Thermodynamics

In a thermodynamic process, Q is positive when heat flows **into** a system, and negative when heat flows **out** of the system.

Work W is **positive** when work is done by the system against its surroundings, and hence corresponds to energy leaving the system. W is negative when work is done on the system.

1.1 Work Done During Volume Changes

- Isobaric: p is constant

$$\begin{aligned} dW &= (F)dx \\ dW &= (pA)dx, \quad \text{Pressure} = \frac{\text{Force}}{\text{Area}} \\ dW &= (p)dV \\ \int_0^W (1)dW &= p\int_{V_0}^{V_1}(1)dV \\ W &= p\left[V_1 - V_0\right] \end{aligned}$$

$$W = p\left[V_1 - V_0\right] \tag{1}$$

- Isochoric: V is constant, $\Delta U = Q - 0$

$$W = \int (p)dV = p(0) = 0$$

- Isothermal: T is constant, $0 = Q - nRT\ln\frac{V_1}{V_0}$

$$W = \int (p)dV$$
$$W = \int \left(\frac{nRT}{V}\right) dV$$
$$W = nRT\int_{V_0}^{V_1} \left(\frac{1}{V}\right) dV$$
$$W = nRT\ln\left[\frac{V_1}{V_0}\right]$$

- Adiabatic: No heat enters or exits, $Q = 0$, $\Delta U = 0 - W$

1.1.1 Question

$$dW = \int \left(\frac{nRT}{P}\right) dp$$
$$\int_0^W (1)dW = nRT\int_{p_0}^{p_1} \left(\frac{1}{P}\right) dp$$

1.1.2 19.7

(a)

$$W_{1,3} = p_1(V_2 - V_1)$$
$$W_{3,2} = 0$$
$$W_{2,4} = p_2(V_1 - V_2)$$
$$W_{4,1} = 0$$

$$W_{total} = p_1(V_2 - V_1) + p_2(V_1 - V_2)$$
$$W_{total} = p_1(V_2 - V_1) - p_2(-V_1 + V_2)$$
$$W_{total} = (p_1 - p_2)(V_2 - V_1)$$

1.1.3 19.1

$$n = 2\,\mathrm{mol}$$
$$T_0 = 27\,^\circ\mathrm{C} = 300\,\mathrm{K}$$
$$T_1 = 107\,^\circ\mathrm{C} = 380\,\mathrm{K}$$
$$W = ?$$

$$
\begin{aligned}
W &= p\int_{V_1}^{V_2}(1)dV \\
W &= p(V_2 - V_1)
\end{aligned}
$$

$$
\begin{aligned}
pV &= nRT \\
p(V_2 - V_1) &= nR(T_2 - T_1)
\end{aligned}
$$

$$
\begin{aligned}
&W = nR(T_2 - T_1) \\
&W = (2\,\mathrm{mol})(8.314\,\mathrm{J\,mol^{-1}\,K^{-1}})(380\,\mathrm{K} - 300\,\mathrm{K}) \\
&W = 1330.24\,\mathrm{J}
\end{aligned}
$$

1.1.4 19.2

$$
\begin{aligned}
n &= 6\,\mathrm{mol} \\
T_0 &= 27.0\,^{\circ}\mathrm{C} = 300\,\mathrm{K} \\
p &= \text{constant} \\
T_1 &= ? \\
W &= 2.40 \times 10^3\,\mathrm{J}
\end{aligned}
$$

$$
\begin{aligned}
W &= p\,[V_1 - V_0] \\
p\,[V_1 - V_0] &= nR\,[T_1 - T_0] \\
W &= nR\,[T_1 - T_0] \\
T_1 &= \frac{W}{nR} + T_0 \\
T_1 &= \frac{2.40 \times 10^3\,\mathrm{J}}{(6\,\mathrm{mol})(8.314\,\mathrm{J\,mol^{-1}\,K^{-1}})} + 300\,\mathrm{K} \\
T_1 &= 348.112\,\mathrm{K}
\end{aligned}
$$

1.1.5 19.3

$$
\begin{aligned}
n &= 2\,\mathrm{mol} \\
T &= 65.0\,^{\circ}\mathrm{C} = 338\,\mathrm{K} \\
p_1 &= 3p_0
\end{aligned}
$$

$$
\begin{aligned}
W &= \int (p)dV \\
W &= nRT \ln \left[\frac{p_0}{p_1}\right] \\
W &= nRT \ln \left[\frac{p_0}{3p_0}\right] \\
W &= (2\,\mathrm{mol})(8.314\,\mathrm{J\,mol^{-1}\,K^{-1}})(338\,\mathrm{K}) \ln \left[\frac{1}{3}\right] \\
W &= -6174.49\,\mathrm{J}
\end{aligned}
$$

1.1.6 19.5

$$
\begin{aligned}
n &= 0.305\,\mathrm{mol} \\
T &= 22.0\,^{\circ}\mathrm{C} = 295\,\mathrm{K} \\
W &= -392\,\mathrm{J} \\
p_1 &= 1.76\,\mathrm{atm} \\
p_0 &=?
\end{aligned}
$$

$$
\begin{aligned}
W &= nRT \ln \left[\frac{p_0}{p_1}\right] \\
e^W &= e^{nRT} \cdot \frac{p_0}{p_1} \\
p_0 &= \frac{e^W}{e^{nRT}} p_1 \\
p_0 &= e^{\frac{-392\,\mathrm{J}}{(0.305\,\mathrm{mol})(8.314\,\mathrm{J\,mol^{-1}\,K^{-1}})(295\,\mathrm{K})}} (1.76\,\mathrm{atm}) \\
p_0 &= 1.04\,\mathrm{atm}
\end{aligned}
$$

1.1.7 19.6

$$
\begin{aligned}
V &= 0.200\,\mathrm{m^3} \\
p_0 &= 2.00 \times 10^5\,\mathrm{Pa} \\
p_1 &= 5.00 \times 10^5\,\mathrm{Pa}
\end{aligned}
$$

$$
\begin{aligned}
V_0 &= 0.200\,\mathrm{m^3} \\
V_1 &= 0.120\,\mathrm{m^3} \\
p &= 5.00 \times 10^5\,\mathrm{Pa}
\end{aligned}
$$

$$
\begin{aligned}
W &= 0 + p\,[V_1 - V_0] \\
W &= (5.00 \times 10^5\,\mathrm{Pa})(0.120\,\mathrm{m^3} - 0.200\,\mathrm{m^3}) \\
W &= -40\,000\,\mathrm{J}
\end{aligned}
$$

2 First Law of Thermodynamics

First Law of Thermodynamics

$$\Delta U = Q - W \tag{2}$$

2.0.1 19.9

$$\begin{aligned}
V_0 &= 0.110\,\mathrm{m}^3 \\
V_1 &= 0.320\,\mathrm{m}^3 \\
p &= 1.65 \times 10^5\,\mathrm{Pa} \\
Q &= 1.15 \times 10^5\,\mathrm{J}
\end{aligned}$$

(a)

$$\begin{aligned}
W &= p\Delta V \\
W &= (1.65 \times 10^5\,\mathrm{Pa})\left[0.320\,\mathrm{m}^3 - 0.110\,\mathrm{m}^3\right] \\
W &= 34\,650\,\mathrm{J}
\end{aligned}$$

(b)

$$\begin{aligned}
\Delta U &= Q - W \\
\Delta U &= 1.15 \times 10^5\,\mathrm{J} - 34\,650\,\mathrm{J} \\
\Delta U &= 80\,350\,\mathrm{J}
\end{aligned}$$

2.0.2 19.10

$$\begin{aligned}
n &= 5\,\mathrm{mol} \\
T_0 &= 127\,^\circ\mathrm{C} = 400\,\mathrm{K} \\
Q &= 1500\,\mathrm{J} \\
W &= 2100\,\mathrm{J} \\
T_1 &=?
\end{aligned}$$

$$\begin{aligned}
Q &= nC_V(T_1 - T_0) \\
T_1 &= \frac{Q}{nC_V} + T_0 \\
T_1 &= \frac{1500\,\mathrm{J}}{(5\,\mathrm{mol})\left(\frac{3}{2}(8.314\,\mathrm{J\,mol^{-1}\,K^{-1}})\right)} + 400\,\mathrm{K} \\
T_1 &= 424.056\,\mathrm{K}
\end{aligned}$$