Chapter 19

1 The First Law of Thermodynamics **1**
1.1 Work Done During Volume Changes . . . 1
1.1.1 Question . . . 2
1.1.2 19.7 . . . 2
1.1.3 19.1 . . . 2
1.1.4 19.2 . . . 3
1.1.5 19.3 . . . 3
1.1.6 19.5 . . . 4
1.1.7 19.6 . . . 4

2 First Law of Thermodynamics **5**
2.0.1 19.9 . . . 5
2.0.2 19.10 . . . 5
2.0.3 19.11 . . . 6
2.0.4 19.12 . . . 6
2.0.5 19.13 . . . 7

3 Four Kinds of Thermodynamic Processes **8**
3.0.1 19.16 . . . 8
3.0.2 19.17 . . . 8
3.0.3 19.18 . . . 9

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, $0 = Q - nRT \ln \frac{V_1}{V_0}$

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

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

1.1.1 Question

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

1.1.2 19.7

(a)

$$\begin{aligned} W_{1,3} &= p_1(V_2 - V_1) \\ W_{3,2} &= 0 \\ W_{2,4} &= p_2(V_1 - V_2) \\ W_{4,1} &= 0 \end{aligned}$$

$$\begin{aligned} W_{total} &= p_1(V_2 - V_1) + p_2(V_1 - V_2) \\ W_{total} &= p_1(V_2 - V_1) - p_2(-V_1 + V_2) \\ W_{total} &= (p_1 - p_2)(V_2 - V_1) \end{aligned}$$

1.1.3 19.1

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

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

$$pV = nRT$$
$$p(V_2 - V_1) = nR(T_2 - T_1)$$

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

1.1.4 19.2

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

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

1.1.5 19.3

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

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

1.1.6 19.5

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

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

1.1.7 19.6

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

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

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

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

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

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

2.0.3 19.11

$$n = 0.0175\,\text{mol}$$

(a)

$$T_{low} = ?$$

$$\begin{aligned}
T &= \frac{pV}{nR} \\
T_a &= \frac{p_a V_a}{nR} \\
T_a &= \frac{(0.20\,\text{atm})(2.0\,\text{L})}{(0.0175\,\text{mol})(0.0821\,\text{L}\,\text{atm}\,\text{mol}^{-1}\,\text{K}^{-1})} \\
T_a &= 278.406\,\text{K} \\
T_b &= \frac{p_b V_b}{nR} \\
T_b &= \frac{(0.50\,\text{atm})(2.0\,\text{L})}{(0.0175\,\text{mol})(0.0821\,\text{L}\,\text{atm}\,\text{mol}^{-1}\,\text{K}^{-1})} \\
T_b &= 696.015\,\text{K} \\
T_c &= \frac{p_c V_c}{nR} \\
T_c &= \frac{(0.30\,\text{atm})(6.0\,\text{L})}{(0.0175\,\text{mol})(0.0821\,\text{L}\,\text{atm}\,\text{mol}^{-1}\,\text{K}^{-1})} \\
T_c &= 1252.83\,\text{K}
\end{aligned}$$

(b)

$$W_{a,b} = 0$$
$$W_{b,c} = ?$$

$$W_{b,c} = \int \frac{nR}{V} dV$$

2.0.4 19.12

$$\begin{aligned}
p &= 1.80 \times 10^5\,\text{Pa} \\
V_0 &= 1.70\,\text{m}^3 \\
V_1 &= 1.20\,\text{m}^3 \\
\Delta U &= -1.40 \times 10^5\,\text{J}
\end{aligned}$$

(a)

$$W = p\Delta V$$
$$W = (1.80 \times 10^5\,\mathrm{Pa})(1.20\,\mathrm{m}^3 - 1.70\,\mathrm{m}^3)$$
$$W = -90\,000\,\mathrm{J} = -9.0 \times 10^4\,\mathrm{J}$$

(b)

$$\Delta U = Q - W$$
$$Q = \Delta U + W$$
$$Q = -1.40 \times 10^5\,\mathrm{J} - 9.0 \times 10^4\,\mathrm{J}$$
$$Q = -3.2 \times 10^5\,\mathrm{J}$$

2.0.5 19.13

$$n = 0.450\,\mathrm{mol}$$

(a)

$$pV = nRT$$
$$T = \frac{pV}{nR}$$

$$T_a = \frac{(2.0 \times 10^5\,\mathrm{Pa})(0.010\,\mathrm{m}^3)}{(0.450\,\mathrm{mol})(8.314\,\mathrm{J\,mol^{-1}\,K^{-1}})}$$
$$T_a = 534.574\,\mathrm{K}$$
$$T_b = \frac{(5.0 \times 10^5\,\mathrm{Pa})(0.070\,\mathrm{m}^3)}{(0.450\,\mathrm{mol})(8.314\,\mathrm{J\,mol^{-1}\,K^{-1}})}$$
$$T_b = 534.574\,\mathrm{K}$$
$$T_b = 9355.04\,\mathrm{K}$$
$$T_c = \frac{(8.0 \times 10^5\,\mathrm{Pa})(0.070\,\mathrm{m}^3)}{(0.450\,\mathrm{mol})(8.314\,\mathrm{J\,mol^{-1}\,K^{-1}})}$$
$$T_c = 14\,968.1\,\mathrm{K}$$

(b)

$$W = \frac{(5.0 \times 10^5\,\mathrm{Pa} - 2.0 \times 10^5\,\mathrm{Pa})(0.070\,\mathrm{m}^3 - 0.010\,\mathrm{m}^3)}{2}$$

3 Four Kinds of Thermodynamic Processes

There are four specific kinds of thermodynamic processes that occur often in practical situations:

- **Adiabatic**: No heat is transferred into or out of the system, so $Q = 0$, $\Delta U = 0 - W$.
- **Isochoric**: The volume remains constant, so $W = 0$, $\Delta U = Q - 0$.
- **Isobaric**: The pressure remains constant, so $W = p\Delta V$.
- **Isothermal**: The temperature remains constant, so $\Delta U = 0$, $Q = W$.

$$
\begin{aligned}
dQ &= nC_P dT \\
dW &= pdV \\
dW &= nRdT \\
dU &= dQ - dW \\
dU &= nC_P dT - nRdT \\
nC_V dT &= nC_P dT - nRdT
\end{aligned}
$$

3.0.1 19.16

$$
\begin{aligned}
\Delta U &= Q - W \\
W &= Q \\
W &= 410\,\mathrm{J}
\end{aligned}
$$

3.0.2 19.17

$$
\begin{aligned}
n &= 0.250\,\mathrm{mol} \\
T_0 &= 27.0\,^\circ\mathrm{C} = 300\,\mathrm{K} \\
p &= 1.00\,\mathrm{atm} \\
T_1 &= 127.0\,^\circ\mathrm{C} = 400\,\mathrm{K}
\end{aligned}
$$

(a)

(b)

$$
\begin{aligned}
W &= p\Delta V = nR\Delta T \\
W &= (0.250\,\mathrm{mol})(8.314\,\mathrm{J\,mol^{-1}\,K^{-1}})(400\,\mathrm{K} - 300\,\mathrm{K}) \\
W &= 207.85\,\mathrm{J}
\end{aligned}
$$

(c)

(d)

$$
\begin{aligned}
\Delta U &= nC_V \Delta T \\
\Delta U &= (0.250\,\mathrm{mol})(28.46\,\mathrm{J\,mol^{-1}\,K^{-1}})(400\,\mathrm{K} - 300\,\mathrm{K}) \\
\Delta U &= 711.5\,\mathrm{J}
\end{aligned}
$$

(e)

$$
\begin{aligned}
\Delta U &= Q - W \\
Q &= \Delta U + W \\
Q &= 711.5\,\mathrm{J} + 207.85\,\mathrm{J} \\
Q &= 919.35\,\mathrm{J}
\end{aligned}
$$

(f)

$$
\begin{aligned}
W &= p\Delta V = nR\Delta T \\
W &= (0.250\,\mathrm{mol})(8.314\,\mathrm{J\,mol^{-1}\,K^{-1}})(400\,\mathrm{K} - 300\,\mathrm{K}) \\
W &= 207.85\,\mathrm{J}
\end{aligned}
$$

3.0.3 19.18

$$
\begin{aligned}
n &= 0.0100\,\mathrm{mol} \\
T_0 &= 27.0\,^\circ\mathrm{C} = 300\,\mathrm{K}
\end{aligned}
$$

(a)

$$
\begin{aligned}
T_1 &= 67.0\,^\circ\mathrm{C} = 340\,\mathrm{K} \\
\Delta V &= V
\end{aligned}
$$

$$
\begin{aligned}
Q &= nC_V \Delta T \\
Q &= (0.0100\,\mathrm{mol})(12.47\,\mathrm{J\,mol^{-1}\,K^{-1}})(340\,\mathrm{K} - 300\,\mathrm{K}) \\
Q &= 4.988\,\mathrm{J}
\end{aligned}
$$

(b)

$$
\begin{aligned}
Q &= nC_P \Delta T \\
Q &= n(C_V + R)\Delta T \\
Q &= (0.0100\,\mathrm{mol})(12.47\,\mathrm{J\,mol^{-1}\,K^{-1}} + 8.314\,\mathrm{J\,mol^{-1}\,K^{-1}})(340\,\mathrm{K} - 300\,\mathrm{K}) \\
Q &= 8.314\,\mathrm{J}
\end{aligned}
$$

(c)

(d)

$$\Delta U = nC_V \Delta T$$
$$\Delta U = (0.0100\,\mathrm{mol})(12.47\,\mathrm{J\,mol^{-1}\,K^{-1}})(40\,\mathrm{K})$$
$$\Delta U = 4.988\,\mathrm{J}$$