II. Energy and the First Law of Thermodynamics

A. Generic Statement of the First Law for a Closed System

\[
\frac{\text{time rate of change of energy within system}}{\text{system}} = \left( \frac{\text{rate energy enters system}}{\text{system}} \right) - \left( \frac{\text{rate energy leaves system}}{\text{system}} \right)
\]

No mass enters or leaves.

Rate form of energy balance:

\[
\frac{dE_{\text{system}}}{dt} = \dot{E}_{\text{in}} - \dot{E}_{\text{out}} \tag{4-12}
\]

Integrated form of energy balance:

\[
\Delta E_{\text{system}} = E_{\text{in}} - E_{\text{out}} \tag{4-11}
\]

Note: \[
\Delta E_{\text{system}} + \Delta E_{\text{surroundings}} = 0
\]

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B. Specific Statement of First Law for a Closed System

1. Energy is conserved.
2. Energy can cross the boundary of a closed system by only two mechanisms: heat transfer and work transfer.
3. The change in energy of a closed system is equal to the net heat transferred to the system minus the net work performed by the system (4-17).

Total energy:

\[
\Delta E = Q_{\text{in,net}} - W_{\text{out,net}} \ (\text{kJ})
\]

\[E = mu + \frac{1}{2}mV^2 + mgz \ (\text{kJ})\]

The differential form of (4-17):

\[
dE = \delta Q_{\text{in,net}} - \delta W_{\text{out,net}} \ (\text{kJ})
\]

Energy per unit mass:

\[
\Delta e = q_{\text{in,net}} - w_{\text{out,net}} \ (\text{kJ/kg})
\]

\[e = u + \frac{1}{2}V^2 + gz \ (\text{kJ/kg})\]

\[w = \frac{W}{m} \quad \text{and} \quad q = \frac{Q}{m}\]

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4. (Rate form) The rate of change in energy of a closed system is equal to the rate of heat transfer to the system, minus the rate of work performed by the system plus.

\[
\frac{dE}{dt} = Q_{in,net} - W_{out,net} (\text{kW})
\]

Integration gives the previous form, (4-17):

\[
\Delta E = \int_{t_i}^{t_f} \frac{dE}{dt} dt = \int_{t_i}^{t_f} Q dt = \int_{t_i}^{t_f} W dt
\]

\[
\Delta E = Q_{in,net} - W_{out,net} (\text{kJ})
\]

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5. Example 1 (ideal gas). Two rigid, insulated chambers are connected by a valve. Chamber A is filled with air at 10 bar (gage) and 300 K and B is empty. Both chambers have a volume of 0.10 m³. The air is modeled as an ideal gas. Now open the valve and allow the system (chambers A and B) to reach equilibrium. Find the change in \( U \) and \( T \).

\[
\Delta U = c_v m (T_2 - T_1) = 0 \quad PV = mRT = \text{constant}
\]

Because \( U \) is constant and a function of only \( T \) (because the air behaves as an ideal gas) this is a constant temperature process. Joule verified this experimentally.

\[
\therefore \text{At equilibrium, } T_1 = T_2 \text{ and } P_1V_1 = P_2V_2. \text{ This is an irreversible process.}
\]

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6. Example 2 (ideal gas). A cylinder, containing $V_1 = 2.0 \text{ L}$ of air at 11 bar (gage) and 300 K, is fitted with a frictionless piston. The constant atmospheric pressure outside the cylinder is 1 bar. The air expands reversibly and isothermally to a final pressure of 0 bar (gage). Treating the air as an ideal gas, calculate $Q_{in}$, $W_{out}$, and $V_2$.

First Law: $\Delta U = Q_{in} - W_{out} = 0 \Rightarrow Q_{in} = W_{out}$

Reversible expansion: $W_{out} = \int_{V_1}^{V_2} PdV$

Calculate work:

$$W_{out} = \int_{V_1}^{V_2} PdV = mRT \int_{1}^{2} \frac{dV}{V} = mRT \ln \frac{V_2}{V_1} = P_1V_1\ln \frac{P_1}{P_2}$$

$W_{out} = Q_{in} = P_1V_1\ln \frac{P_1}{P_2} = (1200 \text{ kPa})(0.002 \text{ m}^3)\ln \frac{12}{1} = 5.964 \text{ kJ}$

Calculate final volume:

$$V_2 = V_1\frac{P_1}{P_2} = 0.002\frac{12}{1} = 0.024 \text{ m}^3$$

Note: in using the ideal gas law, always use absolute pressure rather than gage.
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7. Example 3 (ideal gas). A cylinder containing 2.0 L of air at 11 bar (gage) and 300 K is fitted with a frictionless piston. The constant atmospheric pressure outside the cylinder is 1 bar. The air is expanded reversibly and adiabatically to a final pressure of 0 bar (gage). Treating the air as an ideal gas, calculate $Q_{in}$, $W_{out}$, $V_2$ and $T_2$.

First Law: $\Delta U = Q_{in} - W_{out}$

Reversible expansion:

$W_{out} = \int_{1}^{2} P \, dV$ or $\delta W = P \, dV (kJ)$ or $\delta w = P \, dv (kJ/kg)$

Recall that

$u = \frac{5}{2} RT$ or $du = \frac{5}{2} RdT$ or $du = c_v \, dT$

Ideal gas: $Pv = RT$ or $P = \frac{RT}{v}$

Integrate 1st law: $c_v \int_{1}^{2} \frac{dT}{T} = -R \int_{1}^{2} \frac{dv}{v}$ or $c_v \ln \frac{T_2}{T_1} = -R \ln \frac{v_2}{v_1}$

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Rearrange: \( c_v \ln \frac{T_2}{T_1} = -R \ln \frac{V_2}{V_1} \) to give \( \frac{T_2}{T_1} = \left( \frac{V_1}{V_2} \right)^{\frac{R}{c_v}} \)

By convention, this is written

\[
\frac{T_2}{T_1} = \left( \frac{V_1}{V_2} \right)^{k-1} \quad \text{or} \quad TV^{k-1} = \text{constant}
\]

where \( k = \frac{R}{c_v} + 1 \)

For air at room temperature, \( k = \frac{7}{5} = 1.4 \).

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Use the ideal gas law to rearrange previous equation: \( \frac{T_2}{T_1} = \frac{v_2P_2}{v_1P_1} \)

\[
\frac{P_2}{P_1} = \left( \frac{v_1}{v_2} \right)^k \quad \text{or} \quad PV^k = \text{constant}
\]

\[
\frac{T_2}{T_1} = \left( \frac{P_2}{P_1} \right)^{\frac{k-1}{k}} \quad \text{or} \quad TP^{\frac{1-k}{k}} = \text{constant}
\]

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We are finally ready to calculate $Q_{in}$, $W_{out}$, $V_2$ and $T_2$.

$Q_{in} = 0$ because the process is adiabatic.

\[
W_{out} = -\Delta U = m c_v \left( T_1 - T_2 \right)
\]
\[
= m c_v T_1 \left( 1 - \frac{T_2}{T_1} \right) = m c_v T_1 \left[ 1 - \left( \frac{P_2}{P_1} \right)^{\frac{k-1}{k}} \right]
\]
\[
= \frac{5}{2} PV_1 \left[ 1 - \left( \frac{P_2}{P_1} \right)^{\frac{2}{7}} \right] = \frac{5}{2} (1200 \text{ kPa})(0.002 \text{ m}^3) \left[ 1 - \left( \frac{1}{12} \right)^{\frac{2}{7}} \right] = 3.050 \text{ kJ}
\]

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Calculate $T_2$ and $V_2$.

\[
T_2 = T_1 \left( \frac{P_2}{P_1} \right)^{\frac{k-1}{k}} = 300 \text{ K} \left( \frac{1}{12} \right)^{\frac{2}{7}} = 147.5 \text{ K}
\]

\[
\frac{T_2}{T_1} = \left( \frac{V_1}{V_2} \right)^{\frac{R}{c_v}} \text{ or } \frac{V_1}{V_2} = \left( \frac{T_2}{T_1} \right)^{\frac{c_v}{R}}
\]

\[
V_2 = \frac{V_1}{\left( \frac{T_2}{T_1} \right)^{\frac{c_v}{R}}} = \frac{0.002 \text{ m}^3}{\left( \frac{147.5}{300} \right)^{\frac{5}{7}}} = 0.01180 \text{ m}^3
\]

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8. Example 4. Work done against the atmosphere and net work available in Examples 2, 3.

In Examples 2 and 3, we have not considered the work done against the atmosphere. In both cases that will be

\[ W_{atm} = \int_{V_1}^{V_2} P_{atm} \, dV = P_{atm} (V_2 - V_1) \]

In Example 2, \( W_{atm} = 100 \text{kPa}(0.0240 - 0.002) \text{m}^3 = 2.20 \text{kJ} \)

The net work available in Ex. 2 is \( W_{net,out} = 5.96 - 2.20 = 3.76 \text{kJ} \).

In Example 3, \( W_{atm} = 100 \text{kPa}(0.0118 - 0.002) \text{m}^3 = 0.980 \text{kJ} \)

The net work available in Ex. 3 is \( W_{net,out} = 3.05 - 0.98 = 2.07 \text{kJ} \).

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A 2-L, plastic soda bottle is filled with air at 11 bar (gage) and 300 K. The atmospheric pressure is 1 atm. The bottle suddenly explodes. Estimate the energy released.

Key assumptions: (1) ideal gas, (2) adiabatic. This process is highly irreversible.

First Law:

\[ \Delta U = Q_{in} - W_{out} \]

Work performed:

\[ W_{out} = W_{atm} = P_{atm} (V_2 - V_1) = P_2 (V_2 - V_1) \]

Ideal gas:

\[ PV = mRT \text{ or } V_2 = \frac{mRT_2}{P_2} \]

Change in U:

\[ u = \frac{5}{2}RT \text{ or } \Delta U = mc_v (T_2 - T_1) \text{ where } c_v = \frac{5}{2}R \]
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From first law: \( \Delta U = -W_{\text{out}} \) or \( mc_v (T_2 - T_1) = P_{\text{atm}} (V_1 - V_2) \)

Solving for \( T_2 \):
\[
T_2 = T_1 \left( 1 + \frac{c_v}{R} \right) = \frac{1}{2} \left( 1 + \frac{5}{2} \right) = 221.4 \text{ K}
\]

Energy released:
\[
W_{\text{out}} = -\Delta U = mc_v (T_1 - T_2) = P_1 V_1 \frac{c_v}{R} \left( 1 - \frac{P_2 + c_v}{P_1 + \frac{c_v}{R}} \right)
\]
\[
W_{\text{out}} = \left( 1200 \text{ kPa} \right) \left( 0.002 \text{ m}^3 \right) \left[ \frac{5}{2} \left( 1 + \frac{5}{2} \right) \right] = 1.57 \text{ kJ}
\]

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10. Summary of relations used to calculate work in ideal gas, closed system (batch), compression and expansion processes.

- **Isobaric** (constant pressure): \( P = \text{constant} \)
- **Isothermal**: \( PV = \text{constant} \)
- **Adiabatic and reversible**: \( PV^k = \text{constant} \) where \( k = \frac{R}{c_v} + 1 \)
- **Polytropic**: \( PV^n = \text{constant} \), where \( 1 < n < k \) (most of the time)

\[
W_{\text{out.poly}} = \frac{P_2 V_2 - P_1 V_1}{1 - n} = \frac{mR(T_2 - T_1)}{1 - n}, \quad n \neq 1
\]
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11. Final remarks on reversible and actual processes
   a. Examples 2 and 3 involved batch reversible expansion processes. Actual processes deliver less work than reversible processes. Define an efficiency to account for this:

   \[ W_{\text{actual}} = \eta W_{\text{reversible}}, \quad 0 < \eta < 1, \text{ expansion} \]

   b. Actual compression processes require more work than reversible compression processes. Define an efficiency to account for this:

   \[ W_{\text{actual}} = \frac{W_{\text{reversible}}}{\eta}, \quad 0 < \eta < 1, \text{ compression} \]

   For batch compression and expansion processes, \( \eta \approx 0.75 \). The efficiency must be determined experimentally.

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