OUTLINE OF CHAPTER 3

Conservation of Energy

Recall

\[ \frac{\theta(t + \Delta t) - \theta(t)}{\Delta t} = \left( \text{Rate at which } \theta \text{ enters the system} \right) \]
\[ - \left( \text{Rate at which } \theta \text{ leaves the system} \right) \]
\[ + \left( \text{Rate at which } \theta \text{ is generated} \right) \]

\[ \Theta = \text{Energy(not specific energy)} \]

\[ \theta = U + M \left( \frac{v^2}{2} + \psi \right) \]

\[ U \text{ is the total internal energy,} \]
\[ \frac{v^2}{2} \text{ is the kinetic energy per unit mass} \]
\[ \psi \text{ is the potential energy per unit mass} \]

THUS

\[ \frac{d}{dt} \left[ U + M \left( \frac{v^2}{2} + \psi \right) \right] = \left( \text{Rate at which energy enters the system} \right) \]
\[ - \left( \text{Rate at which energy leaves the system} \right) \]

(one phase, one component \( \rightarrow \) no generation)
Mechanisms for Energy to Enter/Leave

With ingoing/outgoing fluid:

\[ \sum_{k=1}^{K} \dot{M}_k \left( \dot{U} + \frac{v^2}{2} + \psi \right)_k \]

Note: Specific (per unit mass) internal energy is used.

Heat Transfer (from various sources)

\[ \dot{Q} = \sum \dot{Q}_j \]

\( \dot{Q} > 0 \) if heat is added TO the system

Work (electrical)

\[ \dot{W}_s^F = \pm EI \]

\( \dot{W}_s > 0 \) if work is added TO the system. Included in the shaft work term for convenience
**Work of Fluid against pressure (open systems only)**

As fluid moves, it does work against the fluid that is ahead of it.

![Diagram showing fluid pressure and movement](image)

\[ \text{Work} = F \, dL. \quad \text{But} \quad F = PA, \quad \text{and} \quad AdL = dV \rightarrow \]

\[ \text{Work} = P \, dV = P\hat{V} \Delta M \]

\[
\begin{align*}
\left( \text{Work done by surrounding fluid in} \right) & \left( \text{pushing fluid element of mass } (M)_1 \right) = P_1 \hat{V}_1 \Delta M_1 \\
\left( \text{Work done on surrounding fluid} \right) \left( \text{by movement of fluid element of mass } (\Delta M)_2 \text{ out of the valve (since this fluid element is pushing the surrounding fluid)} \right) & = -P_2 \hat{V}_2 \Delta M_2 \\
\left( \text{Net work done on the system due to movement of fluid} \right) & = P_1 \hat{V}_1 \Delta M_1 - P_2 \hat{V}_2 \Delta M_2
\end{align*}
\]

**THUS WE WRITE**

\[
\left( \text{Net rate at which work is done on} \right) \left( \text{the system due to pressure forces} \right) \left( \text{acting on fluids moving into and out of the system} \right) = \sum_{k=1}^{K} \dot{M}_k (P\hat{V})_k
\]
Work (Shaft)

\[ \dot{W} = F \frac{dL}{dt} \]

\( \dot{W} > 0 \) if work is added to the system.

In the case the system is behaving reversibly, then \( F = PA \), where \( P \) is the pressure of the system, which is assumed uniform over \( A \). Then

\[ \dot{W} = -P \frac{dV}{dt} \]

The negative value is added because \( \dot{W} > 0 \) if \( \frac{dV}{dt} < 0 \)

Energy Conservation (First Law of Thermodynamics)

\[ \frac{d}{dt} \left[ U + M \left( \frac{v^2}{2} + \psi \right) \right] = \sum_{k=1}^{K} \dot{M}_k \left( \hat{U} + \frac{v^2}{2} + \psi \right)_k + \dot{Q} \]

\[ + \dot{W}_s - P \frac{dV}{dt} + \sum_{k=1}^{K} \dot{M}_k (P \hat{V})_k \]

Rate of change of Total Energy (Internal + External) of the system.

Energy added/subtracted associated to mass entering /leaving the system

Heat added

Shaft work

Expansion Work

Work done by fluid entering/leaving the system
**Example: Turbine**

\[
\dot{M}_1 = \dot{M}_2 \\
\dot{U}_1 = \dot{U}_2 \\
\psi_1 = \psi_2 \\
v_1 = 0 \\
\dot{M}_2 v_2^2 \text{ negligible}
\]

**Steady state**

\[
\frac{d}{dt} \left\{ U + M \left( \frac{v^2}{2} + \psi \right) \right\} = \sum_{k=1}^{K} \dot{M}_k \left( \dot{U} + \frac{v^2}{2} + \psi \right)_k + \dot{Q} \\
+ \dot{W}_s - P \frac{dV}{dt} + \sum_{k=1}^{K} \dot{M}_k (P \dot{V})_k
\]

**Adiabatic**

Turbine walls do not move (Volume remains constant)

**Thus**

\[
(-\dot{W}_s) = \dot{M}_1 P_1 \dot{V}_1 - \dot{M}_2 P_2 \dot{V}_2 = \dot{M}_1 \dot{V}_1 (P_1 - P_2)
\]
Work of a turbine/pump (no density changes in fluid) = Volumetric flowrate × Pressure differential

**ENTHALPY**

\[ H = U + PV \]

\[
\frac{d}{dt} \left[ U + M \left( \frac{v^2}{2} + \psi \right) \right] = \sum_{k=1}^{K} \dot{M}_k \left( \dot{H} + \frac{v^2}{2} + \psi \right)_k + \dot{Q} \\
+ \dot{W}_s - P \frac{dV}{dt} + \sum_{k=1}^{K} \dot{M}_k (P \dot{V})_k
\]

where \( \dot{W} = \dot{W}_s - P (dV/dt) \).

**Molar Basis**

\[ \dot{M}_k \dot{H}_k = \dot{N}_k H_k \]

where \( H \) is the enthalpy per mole or molar enthalpy

\[ H = U - PV \]

\[
\frac{d}{dt} \left[ U + Nm \left( \frac{v^2}{2} + \psi \right) \right] = \sum_{k=1}^{K} \dot{N}_k \left[ H + m \left( \frac{v^2}{2} + \psi \right) \right)_k + \dot{Q} + \dot{W}
\]

\( m \): Mol. Weight
Commonly used forms:

\[ \frac{dU}{dt} = \sum_{k=1}^{K} (\dot{M} \hat{H})_k + \dot{Q} + \dot{W} \quad \text{(mass basis)} \]

\[ \frac{dU}{dt} = \sum_{k=1}^{K} (\dot{N} \mathcal{H})_k + \dot{Q} + \dot{W} \quad \text{(molar basis)} \]

**DIFFERENTIAL FORMS**

General equation

\[ \frac{d}{dt} \left[ U + M \left( \frac{v^2}{2} + \psi \right) \right] = \sum_{k=1}^{K} \dot{M}_k \left( \hat{H} + \frac{v^2}{2} + \psi \right)_k + \dot{Q} + \dot{W} \]  \( (a) \)

Special cases:

(i) Closed system

\[ \dot{M}_k = 0, \quad \frac{dM}{dt} = 0 \]

so

\[ \frac{dU}{dt} + M \frac{d}{dt} \left( \frac{v^2}{2} + \psi \right) = \dot{Q} + \dot{W} \]  \( (b) \)

(ii) Adiabatic process

in Eqs. a, b, and d

\[ \dot{Q} = 0 \]  \( (c) \)

(iii) Open and steady-state system

\[ \frac{dM}{dt} = 0, \quad \frac{dV}{dt} = 0, \quad \frac{d}{dt} \left[ U + M \left( \frac{v^2}{2} + \psi \right) \right] = 0 \]

so

\[ 0 = \sum_{k=1}^{K} \dot{M}_k \left( \hat{H} + \frac{v^2}{2} + \psi \right)_k + \dot{Q} + \dot{W}, \]  \( (d) \)

(iv) Uniform system

In Eqs. a and b

\[ U = M \hat{U} \]  \( (e) \)
To obtain the equations in a molar basis:

\[
\begin{align*}
\text{Replace} & \quad M \left( \frac{v^2}{2} + \psi \right) \quad \text{with} \quad Nm \left( \frac{v^2}{2} + \psi \right) \\
\dot{M}_k \left( \hat{H} + \frac{v^2}{2} + \psi \right)_k & \quad \text{missing in book} \quad \hat{N}_k \left\{ H + m \left( \frac{v^2}{2} + \psi \right) \right\}_k \\
M\hat{U} & \quad N\hat{U}
\end{align*}
\]

**KE and PE not important, no Shaft Work and only ONE Stream entering/leaving**

\[
\frac{d}{dt} \left[ U + M \left( \frac{v^2}{2} + \psi \right) \right] = \sum_{k=1}^{K} \dot{M}_k \left( \hat{H} + \frac{v^2}{2} + \psi \right)_k + \dot{Q} + \dot{W}
\]

\[
\frac{dU}{dt} = \dot{M} \hat{H} + \dot{Q} - P \frac{dV}{dt}
\]

and

\[
\frac{dM}{dt} = \dot{M}_1
\]

Missing in book
CLOSED SYSTEM

\[ \dot{M}_1 = 0 \]

\[ \frac{dU}{dt} = \dot{Q} - P \frac{dV}{dt} \]

or

\[ dU = \delta Q - PdV \]

\[ dH = \delta Q \quad \text{(for Constant P)} \]

*Very well know forms of FIRST LAW FOR CLOSED SYSTEMS*
**Equation for a Change of State 1 \rightarrow 2**

Integrate from $t_1$ to $t_2$

\[
\left\{ U + M \left( \frac{v^2}{2} + \psi \right) \right\}_{t_2} - \left\{ U + M \left( \frac{v^2}{2} + \psi \right) \right\}_{t_1} = \sum_{k=1}^{K} \int_{t_1}^{t_2} \dot{M}_k \left( \dot{H} + \frac{v^2}{2} + \psi \right)_k \, dt + Q + W
\]

where

\[
Q = \int_{t_1}^{t_2} \dot{Q} \, dt \quad W_s = \int_{t_1}^{t_2} \dot{W}_s \, dt \quad \int_{V(t_1)}^{V(t_2)} P \, dV = \int_{t_1}^{t_2} P \frac{dV}{dt} \, dt
\]

and

\[
W = W_s - \int_{V(t_1)}^{V(t_2)} P \, dV
\]

When fluid entering does not change in time

\[
\sum_{k=1}^{K} \int_{t_1}^{t_2} \dot{M}_k \left( \dot{H} + \frac{v^2}{2} + \psi \right)_k \, dt = \sum_{k=1}^{K} \left( \dot{H} + \frac{v^2}{2} + \psi \right)_k \int_{t_1}^{t_2} \dot{M}_k \, dt
\]

\[
= \sum_{k=1}^{K} \Delta M_k \left( \dot{H} + \frac{v^2}{2} + \psi \right)_k
\]
DIFFERENCE FORMS

General equation
\[
\left[ U + M \left( \frac{v^2}{2} + \psi \right) \right]_{t_2} - \left[ U + M \left( \frac{v^2}{2} + \psi \right) \right]_{t_1} = \sum_{k=1}^{K} \int_{t_1}^{t_2} \dot{M}_k \left( \hat{H} + \frac{v^2}{2} + \psi \right)_k \, dt + Q + W \tag{a}
\]

Special cases:
(i) Closed system
\[
\left[ U + M \left( \frac{v^2}{2} + \psi \right) \right]_{t_2} - \left[ U + M \left( \frac{v^2}{2} + \psi \right) \right]_{t_1} = Q + W \tag{b}
\]
and
\[
M(t_1) = M(t_2)
\]

(ii) Adiabatic process
In Eqs. a and b
\[
Q = 0 \tag{c}
\]

(iii) Open system, flow of fluids of constant thermodynamic properties
\[
\sum_{k=1}^{K} \int_{t_1}^{t_2} \dot{M}_k \left( \hat{H} + \frac{v^2}{2} + \psi \right)_k \, dt = \sum_{i=1}^{K} \Delta M_i \left( \hat{H} + \frac{v^2}{2} + \psi \right)_k \tag{d}
\]
in Eq. a

(iv) Uniform system
\[
\left[ U + M \left( \frac{v^2}{2} + \psi \right) \right] = M \left( \hat{U} + \frac{v^2}{2} + \psi \right) \tag{c}
\]
in Eqs. a and b

**To obtain the equations in a molar basis:**

Replace
\[
M \left( \frac{v^2}{2} + \psi \right) \quad \text{with} \quad Nm \left( \frac{v^2}{2} + \psi \right)
\]

\[
\dot{M}_k \left( \hat{H} + \frac{v^2}{2} + \psi \right)_k \quad \text{with} \quad \dot{N}_k \left[ H + m \left( \frac{v^2}{2} + \psi \right) \right]_k
\]

\[
M \dot{U} \quad \text{with} \quad N \dot{U}
\]
Real fluids need pressure or molar volume.

But $U$ and $H$ are monotone with temperature (the higher the temperature, the higher is $U$ or $H$). So add a known amount of heat and measure the change in temperature. For constant volume

$$Q = NC_V\{T(t_2) - T(t_1)\}$$

Therefore

$$C_V = \frac{Q}{N\{T(t_2) - T(t_1)\}}$$
BUT \[ dU = Q - PdV = Q \]

(V is constant; Note that pressure will change)

or

\[ U(t_2) - U(t_1) = Q \]

Thus, one can correlate the change in temperature of a known amount of gas at constant volume to its change of internal energy (a zero needs to be picked) by making these measurements. Also, one obtains \( C_V \)

\[ C_V(T, V) = \lim_{T(t_2) - T(t_1) \to 0} \frac{U(t_2) - U(t_1)}{T(t_2) - T(t_1)} = \left( \frac{\partial U}{\partial T} \right)_V = \left( \frac{\partial U(T, V)}{\partial T} \right)_V \]
A similar experiment, now at constant pressure

\[ Q = U(t_2) - U(t_1) + P\{V(t_2) - V(t_1)\} \]
\[ = H(t_2) - H(t_1) = NC_P\{T(t_2) - T(t_1)\} \]

Then

\[ C_P(T, P) = \left( \frac{\partial H}{\partial T} \right)_P = \left( \frac{\partial H(T, P)}{\partial T} \right)_P \]

Ideal Gases

* denotes functions of \( T \) only

\[ C_P^*(T) = \frac{dH}{dT} \quad \text{and} \quad C_V^*(T) = \frac{dU}{dT} \]

But \( PV = RT \). Then \( H = U + RT \). Then

\[ C_P^*(T) = \frac{dH}{dT} = \frac{d(U + RT)}{dT} = C_V^*(T) + R \]
We will use (in general)

\[ C_p^*(T) = a + bT + cT^2 + dT^3 + \cdots \]

Solids and Liquids \( PV \ll U \).

Then

\[ H \approx U \]

Lever RULE.