Many types of energy:
- Kinetic, Potential
- Heat
- Work

Energy inherent in molecules:

- **Internal Energy**

  - Translation
  - Rotation
  - Internal vibration

  (How much internal energy corresponds to the rate of the motions)

$\Rightarrow$ Changes because of:

- Heat addition $(\Delta T)$
- Work $(\Delta V$ in gas phase)
INTERMOLECULAR FORCES

Bond Energies Holding Molecules Together

{ TYPES OF POTENTIAL ENERGY

KINETIC + POTENTIAL ENERGY CONTRIBUTIONS TO INTERNAL ENERGY ≠ E_k, E_p

E_k ∈ MACROSCOPIC POSITION + MOTION
E_p ∈ EXTERNAL ENERGY

2.3 FIRST LAW OF THERMODYNAMICS
(AKA CONSERVATION OF ENERGY)

FROM SMITH & VAN NESS, P. 22:

"ALTHOUGH ENERGY ASSUMES MANY FORMS,
THE TOTAL QUANTITY OF ENERGY IS CONSTANT,
AND WHEN ENERGY DISAPPEARS IN ONE FORM
IT APPEARS SIMULTANEOUSLY IN OTHER FORMS.

PLURAL"
NOTES:

• WORK + HEAT CROSS THE BOUNDARY BETWEEN SYSTEM + SURROUNDINGS (AND VICE VERSA)

• ENERGY IN THE SYSTEM IS STORED AS
  \((E_k)_{\text{system}}\), \((E_p)_{\text{system}}\), \((U)_{\text{system}}\)

• ENERGY IN THE SURROUNDINGS IS STORED AS
  \((E_k)_{\text{surroundings}}\), \((E_p)_{\text{surroundings}}\), \((U)_{\text{surroundings}}\)
\[(\Delta E)_{\text{system}} + (\Delta E)_{\text{surroundings}} = 0\]

- **FINITE CHANGES**
- **BEWARE THE SIGNS**

**REMEMBER:**
- **HEAT ADDED TO THE SYSTEM** is (+)
- **WORK DONE ON THE SYSTEM** is (+)
- **HEAT ADDED TO THE SURROUNDING** is (−)
- **WORK DONE ON THE SURROUNDINGS** is (−)

**2.4 ENERGY BALANCE FOR CLOSED SYSTEMS**

"CLOSED" \(\implies\) **NO MASS TRANSPORT**

**ENERGY TRANSPORT BY HEAT + WORK ONLY.**

\[(\Delta E)_{\text{surroundings}} = -Q - W\]
\[(\Delta E)_{\text{system}} = Q + W\]
SPECIAL CASE: NO MOTION, CLOSED SYSTEM

Heat + Work ALL go TOWARDS \( U^t \) \( \uparrow \) total in system

\[ \Delta U^t = Q + W \]

No Motion, Closed System

DIFFERENTIAL CHANGES

\[ dU^t = dQ + dW \]

All units of energy (J, ft-lbf, Btu)

RECALL FROM CHE 254:

EXTENSIVE PROPERTIES (depend on amount of material)
(e.g.: \( V^t \), \( U^t \))

INTENSIVE PROPERTIES (do NOT depend on amount of material)
(e.g.: P, T)

⇒ Intensive versions of V^t + U^t:

\[ V^t = \frac{m}{\rho} \text{ or } \frac{n}{\rho} \text{ V} \]
\[ \begin{array}{c}
\text{(mass)} \left( \frac{\text{Volume}}{\text{mass}} \right) \\
\text{(mole)} \left( \frac{\text{Volume}}{\text{mole}} \right)
\end{array} \]

\[ \frac{m}{\rho} \text{ mass density} \quad \frac{m}{\rho} \text{ mole density} \]

\[ U^t = \frac{m}{\rho} U \quad \text{or} \quad U^t = \frac{n}{\rho} U \]
\[ \begin{array}{c}
\text{(mass)} \left( \frac{U}{\text{mass}} \right) \\
\text{(mole)} \left( \frac{U}{\text{mole}} \right)
\end{array} \]
\[ \text{Specific Internal Energy} \quad \text{Molar Internal Energy} \]

Effect on Energy Balance:

\[ \Delta (mU) = Q + W \]

Closed System: \( m = \text{constant} \)
\[ m \Delta U = Q + W \]

Differential Changes:

\[ d(mU) = dQ + dW \]

\[ m \, dU = dQ + dW \]

If \( m = 1 \), then

\[ \Delta U = Q + W \]

and

\[ dU = dQ + dW \]

Likewise for moles:

\[ n \Delta U = Q + W \implies \Delta U = Q + W \]

\[ d(nU) = dQ + dW \implies dU = dQ + dW \]

for \( n = 1 \).
NOTE:

THERE IS NO ABSOLUTE VALUE FOR U.

REALLY JUST A CATCH-ALL TO MAINTAIN THE FIRST LAW. (HENCE, ΔU)

EXAMPLE: (2.1)

WATER FLOWS OVER A WATERFALL 100 m IN HEIGHT. TAKE 1 kg OF THE WATER AS THE SYSTEM, AND ASSUME THAT IT DOES NOT EXCHANGE ENERGY WITH ITS SURROUNDINGS.

(a) What is its potential energy at the top of the falls w/r espect to the base of the falls?

\[
\begin{align*}
\text{Closed System} & \quad \text{AND} \quad \text{no energy exchanged} \\
\text{w/ surroundings} \\
\Rightarrow Q &= 0 \\
W &= 0 \\
(\Delta E)_{\text{sys.}} &= 0
\end{align*}
\]
\[(\Delta E)_{\text{system}} = \Delta U + E_k + E_p = 0\]

\[E_p = Mzg \quad (\text{Recall Eqn. 1.7})\]

\[M = 1\, \text{kg}\]
\[z = 100\, \text{m}\]
\[g = 9.8066\, \text{m/s}^2\]

\[E_p = \frac{1\, \text{kg} \cdot 100\, \text{m} \cdot 9.8066\, \text{m/s}^2}{1\, \text{kg} \cdot \text{m/s}^2} = 980.66\, \text{Nm} = 980.66\, \text{J}\]

(b) What is the kinetic energy of the water just before it strikes the bottom?

Has not struck bottom, so potential energy all going to kinetic energy...

\[\Delta U = 0\]

\[\Delta E_k + \Delta E_p = E_{k_2} - E_{k_1} + E_{p_2} - E_{p_1} = 0\]

Estimate: \[E_{k_1} = E_{p_2} = 0\]
\[ E_{k2} - E_{p1} = 0 \]

\[ E_{k2} = E_{p1} = 980.66 \text{ J} \]

(c) After the 1 kg of water enters the stream below the falls, what change has occurred in its state?

\[ U \rightarrow 0 \quad (E_k \rightarrow 0) \]

\[ Z = 0 \quad (E_p \rightarrow 0) \]

So where does the energy go?

\[ \Delta U = 980.66 \text{ J} \]

And, since no heat transferred to surroundings,

\[ \Delta U = mC_p \Delta T \]

\[ C_p (water) = 4.184 \quad \text{J/kg \cdot °C} \]

\[ \Delta T = \frac{\Delta U}{mC_p} \quad \text{Plug + Chug} \]
\[ \Delta T = \frac{980.66 \text{ J}}{4184 \text{ J/kg} \cdot ^\circ \text{C}} \times \frac{1}{1 \text{ kg}} \]

\[ \Delta T = 0.234 ^\circ \text{C} \]

In all cases, energy is conserved.

**2.5 Thermodynamic State and State Functions**

The thermodynamic state of a system is the complete set of intensive variables at a particular condition of the system.

What does this mean?

A state function can be represented by a single value at a given set of conditions. (Not path or history dependent)
Example:

![Diagram of a square with points A, B, C, D, E, F, U₁, U₂, and V.](image)

Constant specific U along U₁ + U₂.

For U₁:
- U₁(A), P_A, U_A, T_A, l_A, etc.
- U₁(B), P_B, U_B, T_B, l_B, etc.
- U₁(C), P_C, U_C, T_C, l_C, etc.

For U₂:
- U₂(D), P_D, U_D, T_D, l_D, etc.
- U₂(E), P_E, U_E, T_E, l_E, etc.
- U₂(F), P_F, U_F, T_F, l_F, etc.
Notes:
1) Complete set of intensive thermodynamic properties for the state property.
2) The state property represents a single point on the graph.

Path Functions

The depend on the path taken, and the history of the system.

Key Examples: Heat and Work

\[ \int dQ = Q \]
\[ \int dW = W \]

Single values, but these represent the area under a curve.
Example: Work

\[ W = - \int P \, dV \]

Two paths:

- B → A
  - Same end points
  - Different paths
- B → C → A
  - Which has more work?
Example 2.4 When a system is taken from state a to b in Figure 2.1 along path aeb, 100 J of heat flows into the system and the system does 40 J of work.

(a) How much heat flows into the system along path aeb if the work done by the system is 20 J?

(b) The system returns from b to a along path bda. If the work done on the system is 30 J, does the system absorb or liberate heat? How much?
No information regarding motion in system
⇒ Assume all changes in $U_t$.

**Energy Balances**:

\[ \Delta U_{ab}^t = Q_{acb} + W_{acb} = 100\text{ J} - 40\text{ J} \]

- **Heat Added to the System**
- **Work Done by the System**

⇒ $\Delta U_{ab}^t = 60\text{ J}$

(a) For path AEB:

- $W_{acb} = -20\text{ J}$ (work done by system).
- $Q_{acb} = \ ?$
- $\Delta U_{ab}^t = 60\text{ J}$

\[
60\text{ J} = Q_{acb} + (-20\text{ J})
\]

⇒ $Q_{acb} = 80\text{ J}$ (heat added to the system).
(b) For PATH i'da:

\[ W_{i'da} = 30 \text{J} \quad \text{(Work done on System)} \]

\[ Q_{i'da} = ? \]

\[ \Delta U^t_{ab} = 60 \text{J} \quad \Rightarrow \quad \Delta U^t_{ba} = -60 \text{J} \]

Plug + Chug

\[ \Delta U^t_{ba} = Q_{i'da} + W_{i'da} \]

\[ -60 \text{J} = Q_{i'da} + 30 \text{J} \]

\[ \Rightarrow \quad Q_{i'da} = -90 \text{J} \]

(-) \Rightarrow \text{Heat goes from system to Surroundings}

(Heat liberated)
2.6 EQUILIBRIUM

In thermodynamics, this means:

A) ABSENCE OF CHANGE

B) ABSENCE OF TENDENCY FOR CHANGE
   (NO DRIVING FORCES FOR CHANGE)

⇒ NO CHANGE IN STATE.

WHAT POTENTIAL DRIVING FORCES → Ø?

1) MECHANICAL (PRESSURE)

2) THERMAL (TEMPERATURE)

3) MASS TRANSFER (CHEMICAL POTENTIAL)
   (LIKE CONCENTRATION)

4) CHEMICAL (REACTIONS)

⇒ OFTEN JUST NOT CATALYZED,
   SO WE ASSUME NO REACTION.
2.7 The Phase Rule (At Equilibrium)

How many unknowns must be fixed before all other properties are set?

\[ F = 2 - P + N \]

Degrees of freedom  Number of phases  Number of chemical species

What variables are we talking about?

T, P, composition of each phase.

(All intensive properties)

Phases:

Gas phase

- Pure or mixture
- Can be only one
  Why? All gases are miscible.

Liquid phases

- Pure or mixtures
- Multiple OK. (Not mandatory)
EXAMPLE 2.5 How many degrees of freedom has each of the following systems?

(a) Liquid water in equilibrium w/ water vapor.
(b) Liquid water in equilibrium w/ a mixture of water vapor and nitrogen.
(c) A liquid solution of alcohol in water in equilibrium with its vapor.

(a) 

\[
\begin{array}{c}
\text{Pure H}_2\text{O vapor} \\
\alpha \\
\beta \\
\text{Pure H}_2\text{O liquid}
\end{array}
\]

Two phases: \( \alpha, \beta \)

One component: \( H_2O \)
\[ F = 2 - \frac{2}{N} + N = 2 - \frac{2}{1} + 1 = 1 \]

Need to fix one variable for a pure fluid (VLE).

Example: Pick \( T \) \( \Rightarrow \) Calculate vapor pressure, or
Pick \( P \) \( \Rightarrow \) Calculate boiling point.

\[ T = 2 \left( \alpha + \beta \right) \]
\[ N = 2 \left( H_2O + N_2 \right) \]
\[ F = 2 - 2 + 2 = 2 \]

Need to fix 2 variables.
(C) \[ H_2O \text{ vapor} + \text{EtOH vapor} \]

Shorthand for Ethanol \[ \text{CH}_3\text{CH}_2\text{OH} \]

\[ T! = 2 \ (\alpha + \beta) \]
\[ N = 2 \ (H_2O + \text{Ethanol}) \]
\[ F = 2 - 2 + 2 = 2 \quad \text{Need to fix 2 variables.} \]

For Vapor/Liquid Equilibrium (VLE)
\[ T_\alpha = T_\beta = T \]
\[ P_\alpha = P_\beta = P \]

Liquids: (Our \( \beta \) Phase)
\[ x_i \quad (\text{where } i = 1 \text{ to } N) \]

Vapor: (Our \( \alpha \) Phase)
\[ y_i \quad (\text{where } i = 1 \text{ to } N) \]
2.8 THE REVERSIBLE PROCESS

ANOTHER "SPECIAL" CLOSED SYSTEM

from Smith & Van Ness (p. 31)

"A process is reversible when its direction can be reversed at any point by an infinitesimal change in external conditions."

Notes:

• ITS DIRECTION
  ⇒ Can't just be one direction
  e.g.: Compression or Expansion

• REVERSED AT ANY POINT
  ⇒ Accelerations are a big problem (inertia)

• INFINITESIMAL CHANGE
  ⇒ EVEN SMALL CHANGES HAVE DESIRED EFFECT (REVERSIBILITY)
EXTERNAL CONDITIONS

⇒ Changes in the surrounding affect the system.

EXAMPLE SYSTEM:

REVERSIBLE EXPANSION OF A GAS

STATE 1 \[\downarrow F_1\] \[\rightarrow\] STATE 2 \[\downarrow F_2\]

in both cases, surroundings @ P=0 (vacuum).

Couple of ways to go from STATE 1 to STATE 2:

(a) Sudden changes \{ IRREVERSIBLE \}

+b

Step changes

(b) Differential changes \{ REVERSIBLE \}

WHY?
(a) Sudden change
\[ F_1 \rightarrow F_2 \quad \text{(where } F_2 \ll F_1 \text{)} \]

\[ \begin{aligned} &F_1 \quad \text{STEP CHANGE IN} \quad F_1 \\ &F_2 \quad \text{Note oscillations} \end{aligned} \]

Why the oscillation?

When \( F_1 \rightarrow F_2 \), there is a force imbalance.

\( (\text{P}_1 \text{ is exerting } F_1 \text{ on piston still}) \).

Since \( F_1 \gg F_2 \), the piston accelerates up.

When the piston reaches \( z_2 \), it still has a velocity (and momentum), so the piston will overshoot \( z_2 \).

During this process, small changes in external properties cannot reverse the process.
(b) Differential Change
(very small changes)

\[ dF \Rightarrow \text{No chance to build momentum, so no oscillation.} \]

Because small changes, a small change in external properties can reverse the process.

\[ \text{REVERSIBLE CHEMICAL CHANGE:} \]

\[ \rightarrow \text{START WITH A REVERSIBLE REACTION} \]

\[ \text{EXAMPLE: } \text{CaCO}_3 \rightleftharpoons \text{CaO} + \text{CO}_2 \]

\[ \begin{array}{c}
\text{Solid} \\
\downarrow \\
\text{Solid} \\
\downarrow \\
\text{Gas}
\end{array} \]
System at equilibrium based on pressure of $\text{CO}_2$.

Again, small changes (differential) => reversible.

To be reversible:

1) No friction (heat loss)
2) Differential changes from equilibrium
3) $d$ (property) => new equilibrium, then repeat.
4) $d$ (forces)
5) Can be reversed at any point by differential change in external conditions.
6) When reversed, it retraces the path.
WHEN NOT REVERSIBLE, NEED EFFICIENCY (\( \eta \))

WHERE DOES THE REST GO?
  \( \Rightarrow \) USUALLY HEAT.

IS IT ALWAYS LOST TO SURROUNDINGS?
   NO! (FORTUNATELY)

EXAMPLE \( \rightarrow \) STEAM DRIVEN TURBINE
   FOR ENERGY RECOVERY.

\[ \text{Example 2.6} \] A horizontal piston/cylinder arrangement is placed in a constant-
temperature bath. The piston slides in the cylinder with negligible friction, and an external force holds it in place against an initial gas pressure of 14 bar. The initial gas volume is 0.03 m\(^3\). The external force on the piston is reduced gradually, and the gas expands isothermally as its volume doubles.
If the volume of the gas is related to its pressure so that the product $PV^t$ is constant, what is the work done by the gas in moving the external force?

How much work would be done if the external force were suddenly reduced to half its initial value instead of being gradually reduced?

\[
\begin{align*}
P_0 &= 14 \text{ bar} \\
V_0 &= 0.03 \text{ m}^3
\end{align*}
\]

Frictionless Piston Expanded Isothermally ($\Delta U = 0$)

\[\Rightarrow \text{ All energy is work.} \]

Also told $PV^t = \text{constant}$

How much work by gas if $V_2 = 2V_0$?
Recall,

\[ W = - \int_{V_1^t}^{V_2^t} P \, dV \]

Note: We did not take \( P \) outside of the integral because it is changing. We can substitute for \( P \) in terms of \( V^t \):

\[ PV^t = \text{constant} = k \]

\[ P = \frac{k}{V^t} \quad \text{Substitute...} \]

\[ W = - \int_{V_1^t}^{V_2^t} k \, \frac{dV^t}{V^t} = -k \int_{V_1^t}^{V_2^t} \frac{dV^t}{V^t} \]

\[ W = -k \ln \frac{V_2^t}{V_1^t} = -k \ln \left( \frac{V_2^t}{V_1^t} \right) \]

\[ k = PV^t = (14 \text{ bar})(0.03 \text{ m}^3) \left| \frac{10^5 \text{ N}}{1 \text{ bar} \cdot \text{m}^2} \right| \frac{1 \text{ J}}{1 \text{ Nm}} \]

\[ \Rightarrow k = 42000 \text{ J} \]
Plug & Chug...

\[ W = (-42,000 \text{ J}) \ln \left( \frac{0.06 \text{ m}^3}{0.03 \text{ m}^3} \right) \]

\[ W = -29,112 \text{ J} \leq \text{ REVERSIBLE} \]

**WHAT IF SUDDEN CHANGE?**

\[ P_2 = 7 \text{ bar} \]

\[ W = -P \Delta V \]

\[ = (-7 \text{ bar})(0.06-0.03) \text{ m}^3 \left| \frac{10^5 \text{ N}}{1 \text{ bar \cdot m}^2} \right| \frac{1 \text{ J}}{1 \text{ N m}} \]

\[ W = -21,000 \text{ J} \leq \text{ IRREVERSIBLE} \]

**Efficiency?**

\[ \eta = \frac{W}{W_{\text{rev}}} \times 100\% = \frac{-21,000}{-29,112} \times 100\% \Rightarrow \eta = 72.1\% \]
2.9 CONSTANT V + CONSTANT P PROCESSES

RECALL \( d(nU) = dQ + dW \)

\[ \rightarrow \text{CLOSED SYSTEM} \]

\[ \rightarrow n \text{ MOLES OF FLUID} \]

RECALL \( dW = -P \, d(nV) \)

Substitute for \( dW \)...

\[ d(nU) = dQ - P \, d(nV) \]  \text{REVERSIBLE}

Why? DIFFERENTIAL CHANGES

CASE #1: CONSTANT V

\[ \Rightarrow d(nV) = 0 \]

\[ \Rightarrow d(nU) = dQ \]

Integrate:

\[ n \Delta U = Q \] \text{CONSTANT V}

\text{NOTE: } W = 0
CASE 2: CONSTANT P

\[ d(nu) = dQ - pd(nv) \]

Solve for \( dQ \):

\[ dQ = d(nu) + pd(nv) = d(nu) + d(npv) = d(nu + npv) \]

\[ dQ = d[n(u + pv)] \]

**New Term:**

\[ \text{Enthalpy} = H = u + pv \]

**Note:** All Intensive Properties (molar or specific values)

**Substitute:**

\[ dQ = d[nH] \]

**Integrate:**

\[ Q = n\Delta H \]

\( \text{Constant P} \)
**NOtes:**

1) **this term will show up all over the place for calculating Q + W.**

2) **intensive properties, so if we set T + p, they will be fixed** (recall phase rule)

3) **we can tabulate enthalpies**

**example:** Appendix F (steam tables)

→ U, P, V all state functions

→ since \( H = f(U, P, V) \), then it is also a state function.

Finally, for \( n = 1 \) mole

\[
H = U + PV
\]

\[
\Delta H = \Delta U + \Delta (PV)
\]

**integrate:**

\[
\Delta H = \Delta U + \Delta (PV)
\]
EXAMPLE 2.8 Calculate $\Delta U$ and $\Delta H$ for 1 kg of water when it is vaporized at the constant temperature of 100°C and the constant pressure of 101.33 kPa. The specific volumes of liquid and vapor water at these conditions are 0.00104 and 1.673 m$^3$/kg. For this change, heat in the amount of 2,256.9 kJ is added to the water.

What do we know?

Constant $T$ (100°C)
Constant $P$ (101.33 kPa)
$V_{\text{liq}} = 0.00104$ m$^3$/kg
$V_{\text{vap}} = 1.673$ m$^3$/kg
$Q = 2,256.9$ kJ

Calculate $\Delta H$: Constant $P$, so $Q = \Delta H$

$\Rightarrow \Delta H = 2,256.9$ kJ

Next, solve for $\Delta U$...

$\Delta H = \Delta U + \Delta (PV)$
\[ DU = \Delta H - P \Delta V \left( \frac{1.673}{0.00104} \right) \]

Plug + Chug (+ units conversion)

\[ DU = 2,256.9 \text{ kJ} - (101.33 \text{ kPa}) (1.673 - 0.00104) \text{ m}^3 \]

\[ \left[ \frac{1 \text{ kg}}{1} \right] \left[ \frac{1 \text{ kJ}}{1 \text{ kPa} \cdot \text{m}^2} \right] \left[ \frac{1 \text{ kJ}}{1 \text{ kg} \cdot \text{m}^3} \right] = 2,087.5 \text{ kJ} = DU \]

---

2.11 **Heat Capacity**

- Related to how much heat must be transferred to a unit mass/mole of fluid to change its temperature 1 degree.

\[ C = \frac{dQ}{dT} = \text{Heat Capacity (Extensive)} \]
Note: Look for different substitutions for \( Q \) based on the process.

**Case #1: Constant Volume**

\[
C_V = \left( \frac{\partial U}{\partial T} \right)_V
\]

Heat Capacity at Constant Volume (Intensive)

Recall:

\[
dQ = d(nU)
\]

@ Constant Volume.

So, what happened to \( n \)?

\( C \) was extensive

\( C_V \) is intensive because it contains \( n \)

So, starting from:

\[
C_V = \left( \frac{\partial U}{\partial T} \right)_V
\]

\[
dU = C_V dT
\]
INTEGRATE:
\[ \Delta U = \int_{T_1}^{T_2} C_V \, dT \]

LOOKING FOR \( Q \), SO MULTIPLY BOTH SIDES BY \( n \)

\[ Q = n \Delta U = n \int_{T_1}^{T_2} C_V \, dT \]

STATE FUNCTION (Independent of Path)

\( \Rightarrow \) IN THIS CASE, \( Q \) IS INDEPENDENT OF PATH.

CASE #2: CONSTANT PRESSURE

\[ C_p = \left( \frac{\partial H}{\partial T} \right)_p \]

HEAT CAPACITY AT CONSTANT PRESSURE (INTENSIVE)

RECALL:
\[ dQ = d \left( n \, H \right) \]

@ CONSTANT PRESSURE
\[ C_p = \left( \frac{\Delta H}{\Delta T} \right)_p \]

\[ \Delta H = C_p \Delta T \]

Integrate:

\[ \Delta H = \int_{T_1}^{T_2} C_p \, dT \]

Looking for \( Q \), so multiply both sides by \( n \)

\[ Q = n \Delta H = n \int_{T_1}^{T_2} C_p \, dT \]

**EXAMPLE 2.9**

Air at 1 bar and 298.15 K (25°C) is compressed to 5 bar and 298.15 K by two different mechanically reversible processes:

(a) Cooling at constant pressure followed by heating at constant volume.

(b) Heating at constant volume followed by cooling at constant pressure.
CALCULATE HEAT AND WORK REQUIREMENTS AND $\Delta U + \Delta H$ OF THE AIR FOR EACH PATH.

**Given:**

\[ C_v = 20.78 \text{ J/mol.K} \]

\[ C_p = 29.10 \text{ J/mol.K} \]

\[ \frac{P}{RT} = \text{constant} \]

\[ V_1 = 0.02479 \text{ m}^3/\text{mol} \] (at 298.15 K, 1 bar)

\[ \Rightarrow V_2 = \frac{V_1 P_1}{P_2} = \frac{0.02479 \text{ m}^3/\text{mol}}{1 \text{ bar}} \left| \frac{1 \text{ bar}}{5 \text{ bar}} \right| = 0.004958 \text{ m}^3/\text{mol} \]

---

[Diagram of a square with labeled paths and pressures (P in bar).]
PATH: (a)

Part 1: Cooling at constant pressure

Intermediate \( T = ? \)

\[
\frac{P_1 V_1}{T_1} = \frac{P V}{T}
\]

Intermediate conditions.

\( P = P_1 \)
\( V = V_2 \) \( \therefore \) Solve for \( T \)

\[
T = \frac{V T_i}{V_1} = \frac{0.004958 \text{m}^3}{\text{mol}} \times \frac{\text{mol}}{0.02479 \text{m}^3} \times \frac{298.15 \text{K}}{1}
\]

\( \Rightarrow T = 59.63 \text{ K} \) \( \text{(Very cold!)} \)

Constant Pressure \( \Rightarrow \) \( Q = n \Delta H = n C_p \Delta T \)

\[
Q = (1 \text{ mol}) \times \frac{29.10 \text{ J}}{\text{mol} \cdot \text{K}} \times \frac{(59.63 - 298.15) \text{K}}{1}
\]
\[ Q = n \Delta H = \left[ -6,941 \text{ J} \right] \text{ path a-1} \]

\[ \Delta H = -6,941 \frac{\text{J}}{\text{mol}} \] \text{ path a-1} \\

Recall: \[ n \Delta H = n \Delta U + n \Delta (PV) \]

\[ \Rightarrow n \Delta U = n \Delta H - n \Delta (PV) \]

And \( P \) constant.

\[ \Delta U = \Delta H - P \Delta V \bigg|_{V_1} \]

\[ = \frac{-6,941 \text{ J}}{\text{mol}} - [1 \text{ bar}] \frac{(0.004958 - 0.02479) \text{ m}^3}{\text{mol}} \frac{10^5 \text{ N}}{\text{bar. m}^2} \frac{1 \text{ J}}{\text{Nm}} \]

\[ \Delta U = -4,958 \frac{\text{J}}{\text{mol}} \text{ path a-1} \]

**CALCULATE WORK LATER.**

Part 2: Heating at constant volume

Constant Volume \( \Rightarrow \)

\[ Q = n \Delta U = n C_V \Delta T \bigg|_{T_1}^{T_2} \]
\[ \Delta U = \frac{4,958 \text{ J}}{\text{mol}} \text{ path a-z} \]

So, overall:

\[ Q = -6,941 \text{ J} + 4,958 \text{ J} = -1,983 \text{ J} = Q \]

\[ \Delta U = -4,958 \frac{\text{J}}{\text{mol}} + 4,958 \frac{\text{J}}{\text{mol}} = 0 \frac{\text{J}}{\text{mol}} = \Delta U \]

\[ n \Delta U = Q + W = 0 \]

\[ \Rightarrow W = -Q = 1,983 \text{ J} = W \]

\[ n \Delta H = n \Delta U + n \Delta(PV) \]

But, \[ P_1V_1 = P_2V_2 \quad (T_1 = T_2) \]

\[ \Rightarrow \Delta(PV) = 0 \]
\[ \Delta H = \Delta U \]

\[ \Rightarrow \Delta H = 0 \text{ J mol}^{-1} \]

**PATH (b)**

**Part 1: Heating at constant volume.**

Intermediate \( T = ? \)

\[ \frac{P_1}{T_1} = \frac{P}{T} \]

Intermediate conditions

\[ T = \left( \frac{P}{P_1} \right) T_1 = \left( \frac{5 \text{ bar}}{1 \text{ bar}} \right) (298.15 \text{ K}) = \frac{1490.75 \text{ K}}{\text{HOT!}} \]

Constant volume, so:

\[ Q = n \Delta U = n C_v \Delta T \]

\[ = (1 \text{ mol}) \left( \frac{20.78 \text{ J}}{\text{mol} \cdot \text{K}} \right) \left( \frac{1490.75 - 298.15}{1} \right) \]

\[ \Rightarrow Q = 24,782 \text{ J} \]

path b-!
\[
\Delta U = 24,782 \frac{J}{mol} \text{ path b-1}
\]

Calculate work later.

**Part 2: Cooling at constant pressure.**

**Constant Pressure, so:**

\[
Q = n \Delta H = n C_p \Delta T
\]

\[
= \left( 1 \text{ mol} \right) \left| \frac{29.10 \frac{J}{\text{mol} \cdot \text{K}}}{\text{unit \, mole}} \right| \frac{(298.15 - 1490.75) \text{K}}{1}
\]

\[
\Rightarrow Q = -34,705 \text{ J} \quad \text{path b-2}
\]

\[
\Delta H = -34,705 \frac{J}{\text{mol}} \quad \text{path b-2}
\]

\[
n \Delta H = n \Delta U + n \Delta (PV)
\]

\[
\Delta U = \delta \Delta H - \delta \Delta (PV)
\]

and constant pressure

\[
\Delta U = \Delta H - P \Delta V \bigg|_{V_2}
\]
\[ \Delta U = -34,705 \frac{J}{m^3} - (5 \text{ bar})(0.004758 - 0.02478) \frac{m^3}{m^3} \]

\[ \begin{vmatrix} 10^5 \text{ N} & 1 \text{ J} \\ 1 \text{ bar} \cdot \text{m}^2 & 1 \text{ N} \cdot \text{m} \end{vmatrix} = -34,705 + 9,916 \]

\[ \Delta U = -24,789 \frac{J}{m^3} \] path b-z

So, overall:
\[ \Delta U = 24,782 - 24,789 = -7 \text{ J} \]
\[ \approx 0 \text{ J} \]
\[ Q = 24,782 - 34,705 = 9,923 \text{ J} = Q \]
\[ W = \Delta U - Q = -7 - (-9,923) = 9,916 \text{ J} = W \]

Within Rounding Error:
\[ \Delta U = \Delta H = 0 \]
\[ \text{\textit{S\textbf{ame R\textbf{ason}}}} \]
\[ \text{\textit{As B\textbf{efore}}} \]
NOTES:

- STATE FUNCTIONS $U + H$
- SAME ENDPOINTS $\neq$ DIFFERENT PATHS
  $\Rightarrow \Delta U + \Delta H$ SAME FOR PATHS
  \( a \) \& \( b \)
- PATH FUNCTIONS: $Q + W$

Path (a):

$Q = -1,983 \text{ J}$
$W = 1,983 \text{ J}$

Path (b):

$Q = -9,923 \text{ J}$
$W = 9,916 \text{ J}$

\( \sim \) same w/ rounding error
Example 2.10: Calculate the internal energy and enthalpy changes that occur when air is changed from an initial state of 40°F and 10 atm, where its molar volume is 36.49 ft³/lbmol, to a final state of 140°F and 1 atm. Assume for air that PV/T is constant and that \( c_v = 5 \) and \( c_p = 7 \) Btu/lbmol°F.

**First things first...** \( V_2 = ? \)

\[
\frac{P_1 V_1}{T_1} = \frac{P_2 V_2}{T_2} \implies V_2 = \frac{P_1 V_1 T_2}{T_1 P_2}
\]

\[
= \frac{10 \text{ atm}}{1 \text{ atm}} \frac{(140 + 459.67) \text{ R}}{(40 + 459.67) \text{ R}} \frac{36.49 \text{ ft}^3}{1 \text{ lbmol}} = 43.793 \text{ ft}^3/\text{lbmol}
\]
Calculating $\Delta U + \Delta H$ (state functions), so we can choose a path to simplify the calculation.

$\Rightarrow$ Two-step process

(a) Cooling at constant volume

Constant volume, so:

$$Q = n C_v \Delta T \bigg|_{T_i}^{T}$$

$\Rightarrow$ Need the intermediate temperature

$$\frac{P_i}{T_i} = \frac{P}{T}$$

Intermediate conditions

$$T = \left( \frac{P}{P_i} \right) T_i = \left( \frac{1 \text{ atm}}{10 \text{ atm}} \right) (40 + 459.67) R$$

$$T = 49.967 R \quad (\text{Expect } Q < 0)$$

Very cold! $\quad (= -409.703 \text{ °F})$
\[ Q = n \ C_v \ \Delta T \]

\[ = (1 \ \text{mol}) \left| \frac{5 \ \text{Btu}}{1 \ \text{mol} \cdot \text{°F}} \right| \left( -409.703 \ -40 \right) \text{°F} \]

\[ \text{unit: mol} \]

\[ Q = -2,248.5 \ \text{Btu} \quad \text{path (a)} \]

(b) Heating at constant pressure (expect \( Q > 0 \))

Constant pressure, so:

\[ Q = n \ \Delta H = n \ C_p \ \Delta T \bigg|_{T_2} \]

\[ = (1 \ \text{mol}) \left| \frac{1 \ \text{Btu}}{1 \ \text{mol} \cdot \text{°F}} \right| \left( 140 \text{°F} - (-409.703 \text{°F}) \right) \]

\[ \text{unit: mol} \]

\[ Q = n \ \Delta H = \boxed{3,847.9 \ \text{Btu} = Q} \quad \text{path (b)} \]

\[ \Delta H = 3,847.9 \ \text{Btu} \quad \text{path (b)} \]

\[ \Delta U = n \ \Delta H - n \ \Delta (PV) \]

But, constant pressure, so...
\[ \Delta U = \Delta H - p \Delta V \]
\[ = 3,847.9 \text{ Btu/lb mol} - 1 \text{ atm} \cdot \left( \frac{437.93 - 36.49}{15 \text{ in}^2} \right) \frac{44}{15 \text{ lb mol}} \]
\[ = 3,847.9 \text{ Btu/lb mol} - 1,091.7 \text{ Btu/lb mol} \]
\[ \Delta U = 2,756.2 \text{ Btu/lb mol} \] path (b)

Overall

\[ \Delta U = n c v \Delta T = Q \]
\[ \Delta U = -2,248.5 \text{ Btu/lb mol} \] path (a)
\[ \Delta H = \Delta U + \gamma \Delta (PV) \]

But constant volume (part (a))

\[ \Delta H = \Delta U + \nu \Delta P \]

\[ \left. \right|_{1 \text{ atm}}^{10 \text{ atm}} \]

\[ = -2,248.5 \frac{\text{Btu}}{\text{lb mol}} + \frac{36.49 \text{ ft}^3}{1 \text{ lb mol}} \left( \frac{1 \text{ lb mol}}{(1-10) \text{ atm}} \right) \]

\[ \left. \right|_{0.986923 \text{ atm in}^2}^{144 \text{ in}^2} \left( \frac{1 \text{ ft}^2}{1 \text{ in}^2} \right) \left( \frac{9.47831 \times 10^{-4} \text{ Btu}}{0.737562 \text{ ft} \cdot \text{lb} \cdot \text{in}^{-1}} \right) \]

\[ = -2,248.5 \frac{\text{Btu}}{\text{lb mol}} - 893.1 \frac{\text{Btu}}{\text{lb mol}} \]

\[ \Delta H = -3,141.6 \frac{\text{Btu}}{\text{lb mol}} \quad \text{part (a)} \]

So, overall:

\[ \Delta U = -2,248.5 \frac{\text{Btu}}{\text{lb mol}} + 2,756.2 \frac{\text{Btu}}{\text{lb mol}} = 507.7 \frac{\text{Btu}}{\text{lb mol}} \]

\[ \Delta H = -3,141.6 + 3,843.9 = 706.3 \frac{\text{Btu}}{\text{lb mol}} \]
MASS AND ENERGY BALANCES FOR OPEN SYSTEMS

⇒ ADD MORE COMPLEXITY
⇒ FLOW IN + OUT OF SYSTEM
⇒ OPEN SYSTEMS

MASS + ENERGY CONSERVATION APPLY

How do we measure flow?

\( \dot{m} \) mass flow rate \( \left[ \frac{kg}{s} \right] \)

\( \dot{n} \) mole flow rate \( \left[ \frac{mol}{s} \right] \)

\( \dot{V} \) volumetric flow rate \( \left[ \frac{m^3}{s} \right] \)

\( u \) velocity \( \left[ \frac{m}{s} \right] \)
Flow terms are related

\[ m = \dot{m} \frac{\text{molecular weight}}{\dot{n}} \]

\[ \dot{m} = uA \frac{\text{cross sectional area for flow}}{\dot{g}} \]

Flow in a pipe

\[ \text{Area} = A \]

\[ \text{Avg} \ u \]

\[ m = uA \rho \]

\[ N = uA \rho \]

\[ \text{Specific density} \]

\[ \text{Molar density} \]

Example: Liquid n-terane flows at a rate of \[ \dot{m} = 0.75 \text{ kg/s} \] in a pipe w/ inside diameter \[ D = 5 \text{ cm} \]. What are \[ \dot{g}, \dot{n}, \text{ and } u? \] What would these quantities be for the same \[ \dot{m} \] if \[ D = 2 \text{ cm} \]? Assume the liquid n-terane that \[ \rho = 659 \text{ kg/m}^3 \].
\[ \dot{m} = uA \rho \quad \Rightarrow \dot{b} = \frac{\dot{m}}{\rho} \]

\[ \Rightarrow \dot{b} = \frac{0.75 \text{ kg}}{S} \left\| \frac{m^3}{659 \text{ kg}} \right\| = \frac{1.14 \times 10^{-3} m^3}{S} = \dot{b} \]

\[ \dot{n} = \frac{\dot{m}}{M} = \frac{0.75 \text{ kg}}{S} \left| \frac{\text{kmol}}{86 \text{ kg}} \right| \left| \frac{10^3 \text{ mol}}{1 \text{ kmol}} \right| = 8.72 \text{ mol} \]

Hexane: \((6 \times 12) + 14(1) = 72 + 14 = 86 \text{ g/mol}\)

\[ A = \pi (5 \text{ cm})^2 = \frac{19.63 \text{ cm}^2}{4} \]

\[ U = \frac{m}{\dot{A} \rho} = \frac{0.75 \text{ kg}}{S} \left| \frac{1}{19.63 \text{ cm}^2} \right| \left| \frac{m^3}{659 \text{ kg}} \right| \left| \frac{10^4 \text{ cm}^2}{1 \text{ m}^2} \right| \]

\[ U = 0.58 \text{ m/s} \]

For \( D = 2 \text{ cm} \):

\[ \dot{b} = 1.14 \times 10^{-3} m^3 \]

\[ \dot{n} = 8.72 \text{ mol} \]

(No change)
\[ A = \frac{\pi (2\text{cm})^2}{4} = 3.14 \text{ cm}^2 \]

\[ \Rightarrow \frac{U}{S} = \frac{19.63 \text{ cm}^2}{3.14 \text{ cm}^2} = \frac{3.63 \text{ m}}{s} = U \]

\text{MASS BALANCE FOR OPEN SYSTEMS:}

\[ \dot{m}_1 + \dot{m}_2 = \dot{m}_3 \]

\[ \frac{d}{dt} \left( \text{control volume mass} \right) \]

\[ \text{CHANGE IN} \]

\[ \text{CONTROL VOLUME MASS} \]
\[
\frac{dm_{ev}}{dt} + \Delta (\dot{m})_{fs} = 0
\]

**EXIT - ENTERING FLOW STREAMS**

But, \[\dot{m} = UA\rho\]

\[\frac{dm_{ev}}{dt} + \Delta (UA\rho)_{fs} = 0\]

**CONTINUITY EQUATION.**

If System @ Steady State:

\[\Delta (UA\rho)_{fs} = 0\]

\[\frac{dm_{ev}}{dt} = 0\] (No change in system mass w/ time)

**NOTE**: STILL FLOW IN & OUT OF SYSTEM.
\[ \Delta (uAe)_{fS} = u_2 A_2 p_2 - u_1 A_1 p_1 = 0 \]

\[ \Rightarrow m \text{ constant.} \]

\[ \Rightarrow m = \frac{U_1 A_1}{V_1} = \frac{U_2 A_2}{V_2} = \frac{U A}{V} \]

where \( V \) is specific volume \( \Leftrightarrow \frac{m^3}{kg} \)

\( \left( \frac{1}{V} = \rho \right) \)

---

**GENERAL ENERGY BALANCE:**
Figure 2.4

Energy Balance:

\[
\frac{d\left(\frac{1}{2}m v^2 + \frac{1}{2}I \omega^2 \right)}{dt} = -A \int (U + \frac{1}{2} \rho v^2) m J + Q + \text{heat work}
\]

Internal kinetic energy

\[
\text{work}
\]

\[
\text{work}
\]

\[
\text{work}
\]

Note:

\[
\Delta = \text{in} - \text{out}
\]

Units all check out.

\[
\frac{I \omega}{S \varphi} = \frac{b g}{L}
\]
**Work Rate**

Types

- **PV Work**
  - Moving fluid through entrance & exit

- **Shaft Work**
  - Pumping

- **Control volume expansion/compression**

- **Stirring**

\[
\text{Work Rate} = -\Delta \left[ (PV) m \right]_{fs} + \dot{W}
\]

Recall how we justified the sign.

\[
\frac{N}{m^2} \left| \frac{m^3}{kg} \right| \frac{kg}{s} \quad \text{All other work}
\]

So,

\[
\frac{d \left( m \overline{u} \right)_{cv}}{dt} = -\Delta \left[ (U + \frac{1}{2} u^2 + zg) m \right]_{fs} + Q - \Delta \left[ (PV)m \right]_{B} + \dot{W}
\]

Looking to get \( H \) into equation
\[
\frac{d}{dt}(mU)_{cv} = -\Delta \left( \frac{1}{2}m u^2 + m \frac{v}{g} \right)_{3} + \dot{Q} + \dot{W}
\]

or

**ENERGY BALANCE OPEN SYSTEM**

\[
\frac{d}{dt}(mU)_{cv} + \Delta \left( \frac{1}{2}m u^2 + m \frac{v}{g} \right)_{3} = \dot{Q} + \dot{W}
\]

Still no motion in the control volume.

(So our equation has limitations.)

**EXAMPLE 2.12.**

Show that Eq. 2.29 reduces to Eq. 2.23 for the case of a closed system.

\[
\frac{d}{dt}(mU)_{cv} + \Delta \left( \frac{1}{2}m u^2 + m \frac{v}{g} \right)_{3} = \dot{Q} + \dot{W}
\]

Closed System: \( \dot{m} = 0 \)

\[
\frac{d}{dt}(mU)_{cv} = \dot{Q} + \dot{W}
\]

\[
\int d(mU)_{cv} = \int_{t_1}^{t_2} \dot{Q} \, dt + \int_{t_1}^{t_2} \dot{W} \, dt
\]
\[ \Delta (mu)_{ev} = Q + W \]
\[ \Delta U = Q + W \]
\[ \text{QED.} \]

**Example 2.13**

An evacuated tank is filled w/gas from a constant pressure line. What is the relation between the enthalpy of the gas in the entrance line and the internal energy of the gas in the tank? Neglect heat transfer between the gas and the tank.

**RIGID TANK**

\[ p = 0 \]
\[ P = 0 \]
\[ T = 0 \]

\[ \Rightarrow \text{No expansion work} \]
\[ \text{No stirring} \]
\[ \text{No shaft work} \]

Energy Balance:

\[ \frac{d}{dt} \Delta (mu)_{ev} + \Delta (H+m)_{fs} = Q + W \]

neglect heat transfer

\[ w = 0 \]

\[ w = 0 \]
\[
\frac{d (m_U)_{ev}}{d\tau} + \left( H_{\text{out}} - H_{\text{in}}^{\text{tank}} \right) = 0
\]

No outlet

\[
\frac{d (m_U)_{ev}}{d\tau} - H_{\text{in}} = 0
\]

\[\text{But } m_{\text{in}} = \frac{d m_{\text{tank}}}{d\tau}\]

\[
\int \frac{d (m_U)_{ev}}{d\tau} - H_{\text{in}} \int \frac{d m_{\text{tank}}}{d\tau} = 0
\]

\[
m_2 U_2 - m_1 U_1 - H_{\text{in}} \left( m_2 - m_1 \right) = 0
\]

Tank evacuated @ \( t=0 \)

\[
\Rightarrow U_1 = 0
\]

\[
\frac{m_2 U_2}{m_2} - H_{\text{in}} \frac{m_2}{m_2} = 0
\]

\[
\boxed{U_2 = H_{\text{in}}}
\]

Why? No heat transfer.
An insulated, electrically heated tank for hot water contains 170 kg of liquid water at 60°C when a power outage occurs. If water is withdrawn from the tank at a steady rate of \( \dot{m} = 0.2 \text{ kg/s} \), how long will it take for the temperature of the water to drop from 60°C to 35°C? Assume cold water enters the tank at 10°C and negligible heat losses from the tank. For liquid water let \( C_v = C_p = C \), independent of \( T \) and \( P \).

Negligible heat losses, Insulated

\( \Rightarrow \dot{Q} = 0 \)

No real info on work:

\( \Rightarrow \) No stirring (even though we assume perfectly mixed)

\( \Rightarrow \) Incompressible, so no compression/expansion

\( \Rightarrow \) No pumping (\( \dot{W} = 0 \)) because power outage

\( \Rightarrow \) PV in H.

\( \Rightarrow \dot{W}=0 \)

\[
\frac{d}{dt}(mU)_c + \Delta (HM)_f = 0
\]

If \( m_{in} = m_{out} \), then \( m_{c} = \text{constant} \).
\[ m \frac{dv}{dt} + (H - H_f) \dot{m} = 0 \]

**tank** \[ \uparrow \]
**cold water** \[ \uparrow \]
**in.**

But

\[ \Delta H = C \Delta T = C (T - T_f) \]

**heat capacity** \[ \uparrow \]

And,

\[ m \cdot \frac{dU}{dt} = m c \frac{dT}{dt} \]

So

\[ m \dot{c} \frac{dT}{dt} + C (T - T_f) \dot{m} = 0 \]

**Separate Variables.**

\[ \frac{m dT}{T - T_f} = - \dot{m} dt \]

\[ \Rightarrow \int_{T_0}^{T} dt = - \frac{m}{\dot{m}} \int_{T_0}^{T} \frac{dT}{(T - T_f)} \]

**initial tank temperature**
$t = -\frac{m}{\dot{m}} \ln \left( \frac{T - T_1}{T_0 - T_1} \right)$

Now start substituting real numbers...

$m = 190 \text{ kg}$  
$m = 0.2 \text{ kg/s}$

$T_1 = 10^\circ \text{ C}$  
$T_0 = 60^\circ \text{ C}$  
$T = 35^\circ \text{ C}$

Plug in:

$t = -\frac{190 \text{ kg} \cdot \text{s}}{0.2 \text{ kg}} \ln \left( \frac{35 - 10}{60 - 10} \right)$

$= -950 \text{ s} \left( -0.6931 \right) \Rightarrow t = 658 \text{ s}$

$\approx 11 \text{ min}$

Next, steady flow processes...
Energy Balances for Steady-State Flow Processes

\[ \frac{d(mU)}{dt} = 0 \]

\[ \Rightarrow \text{No expansion/compression work} \]

So,

\[ \Delta \left[ (H + \frac{1}{2} u^2 + zg) m \right] = \dot{Q} + \dot{W}_s \]

If one entrance + one exit...

\[ \Delta (H + \frac{1}{2} u^2 + zg) = \frac{\dot{Q}}{m} + \frac{\dot{W}_s}{m} = \dot{Q} + \dot{W}_s \]

First Law for Steady State, Steady Flow Process

\[ \Delta H + \frac{1}{2} \Delta (u^2) + g \Delta z = \dot{Q} + \dot{W}_s \]

\[ \text{First Law for Steady State, Steady Flow Process} \]

\[ \text{with one entrance + one exit.} \]
Check units:

\[ \frac{\Delta H}{J} \quad \frac{\Delta (u^2)}{m^2/s^2} \quad \frac{j}{m^2} \quad \frac{Q}{J} \quad \frac{W_s}{J} \]

\[ \text{for unit mass} \quad \text{for unit mass} \]

\[ \frac{(kg \cdot m)}{s^2} \quad \frac{m}{kg} \quad \frac{kg}{s} \]

Often, kinetic and potential energies are negligible. Therefore:

\[ \Delta H = Q + W_s \quad \text{First Law for steady state, steady flow} \]

\[ \Delta U = Q + W \quad \text{First Law for non-flow process,} \]

Simulate
A Flow Calorimeter for Enthalpy Measurements

- Very low velocity $\Rightarrow \frac{1}{2}u^2 \approx 0$
- No elevation change $\Rightarrow \Delta z \approx 0$
- No shaft work

$\Rightarrow \Delta H = Q = h_2 - h_1$

$Q$ is determined from resistance heater, so $Q$ is known.

Figure 2.7
\( H_1 \) set arbitrarily = 0 @ \( T=0^\circ C \) (Water)

\( \Rightarrow H_2 = H_1 + Q = Q \)

We can add specific quantity \( Q \), and therefore we know \( H_2 \) @ \( P_2 + T_2 \),

\[ \text{Measured}. \]

\( \Rightarrow \) Tabular Data. (See Appendix F.)

Once \( H \) is set, calculate \( U \) from

\[ U = H - PV. \]

---

**Example 2.15**

Flow rate: \( 4.15 \text{ g/s} \)

\( T_1 = 0^\circ C \)

\( T_2 = 300^\circ C \)

\( P_2 = 3 \text{ bar} \)

\( Q = 12,740 \text{ W} \)

Water completely vaporized.

\( H_2 ? \) if \( H_1 = 0 @ 0^\circ C \).
\[ H_2 = \frac{Q}{M} = \frac{12,740 \text{ J}}{S} = \frac{3,070 \text{ J}}{g} \]

**Example 2.16** Air at 1 bar and 25°C enters a compressor at low velocity, discharges at 3 bar, and enters a nozzle in which it expands to a final velocity of 600 m/s at the initial conditions of pressure and temperature. If the work of compression is 240 kJ/kg, how much heat must be removed during compression?

\[ F = 2 - 1 + 1 = 2 \quad \text{(and } T+P \text{ set)} \]

![Components](plane) (gas) (air)

Also, entropy is a state property. Start and end at same point, so \( \Delta H = 0 \)

No elevation change in nozzle, so \( \Delta Z = 0 \).

\[ \frac{1}{2} \Delta (u^2) = Q + W \]

\[ \text{Work of Compression} \]
\[
\frac{1}{2} \left[ (600 \text{ m}^3 - (0 \text{ m}^3) \right] = Q + \frac{240 \text{ kJ}}{\text{kg}}
\]

\[\text{(+) because work done on system. (compression)}\]

\[\frac{180,000 \text{ m}^2}{\text{s}^2}, \frac{\text{kg}}{\text{kg}}, \frac{1 \text{ kJ}}{\text{kg}}, 10^3 \text{J} = Q \frac{240 \text{ kJ}}{\text{kg}}\]

\[\frac{180 \text{ kJ}}{\text{kg}} - 240 \text{ kJ} = Q \frac{-60 \text{ kJ}}{\text{kg}}\]

Heat Removed from System.

Example 2.17
Water at 200°F is pumped from a storage tank at the rate of 50 gpm. The motor for the pump supplies work at the rate of 2 hp. The water goes through a heat exchanger, giving up heat at the rate of 40,000 Btu/min, and is delivered to a second storage tank at an elevation of 50 ft. above the first tank. What is the temperature of the water delivered to the second tank?
Steady State, Steady Flow Process

\[ \Delta H + \frac{\Delta (u^3)}{2g} + \frac{\partial}{\partial x} \Delta z = Q + W_s \]

Storage tank

Velocities \( \approx 0 \)

\[ \dot{Q} = \frac{50 \text{ gal}}{\text{min}} \quad \dot{m} = \dot{Q} \quad (p = 60.1 \text{ lb/in}^2) \]

\[ \dot{m} = \frac{50 \text{ gal}}{\text{min}} \times \frac{60.1 \text{ lb}}{8.33 \text{ lb/gal}} \times \frac{g \text{ ft}^3}{7.48 \text{ gal}} = 402 \frac{\text{lb}}{\text{min}} \]

\[ Q = -\frac{40000 \text{ Btu}}{\text{min}} \quad \text{min} = -99.5 \frac{\text{Btu}}{\text{lb}} \]

(\(-\)) because heat transferred to the surroundings.

\[ W_s = \frac{2 \text{ hp}}{1.4 \text{ hp/s}} \times \frac{0.947831 \text{ Btu}}{1 \text{ in}} \times \frac{1 \text{ min}}{402 \text{ lb/min}} = 0.21 \frac{\text{Btu}}{\text{lb}} \]

(\(+\)) because added to system.
\[
\frac{9}{\Delta z} = \frac{32.174 \text{ ft}^2}{\frac{1}{8} \text{ in}^2} \left| \frac{\text{lbm} \cdot \text{ft}}{32.174 \text{ lbm} \cdot \text{ft}} \right| \frac{50 \text{ ft}}{1}
\]

\[
\frac{9.47831 \times 10^{-4} \text{ Btu}}{0.7375562 \text{ Btu/lbm}} = 0.064 \text{ Btu/} \text{lbm}
\]

\[\Delta H = -99.5 \text{ Btu/} \text{lbm} + 0.21 \text{ Btu/} \text{lbm} - 0.064 \text{ Btu/} \text{lbm} \]

\[\Delta H = -99.35 \text{ Btu/} \text{lbm} \]

Go to steam tables for water property at 200°F (p. 755)

\[H_{\text{Sat,liq}} = 168.09 \text{ Btu/} \text{lbm} \]

\[H_2 - 168.09 = -99.35 \Rightarrow H_2 = 68.74 \text{ Btu/} \text{lbm} \]

From steam tables, \[T_{\text{sat}} = 100.74^\circ \text{F} \] (p. 755)