FORMS OF ENERGY AND ENERGY TRANSFER (Sections 7.1 and 7.2)

Exercise. Brainstorm examples of "systems" that you've encountered recently that use energy. As an engineer, why is energy an important consideration?

FIRST LAW OF THERMODYNAMICS (another "tattoo" equation)

Energy can neither be _____.

Total Energy of System has 3 components: Kinetic Energy, Potential Energy, Internal Energy.

These components are always defined **relative** to something.   Height is analogous: it is usually measured relative to the floor. Consider this example of basketball players from the 1974 NCAA Championship NC State basketball team (and the mascot):

| Tommy Burleson | Monte Towe | Wolf |
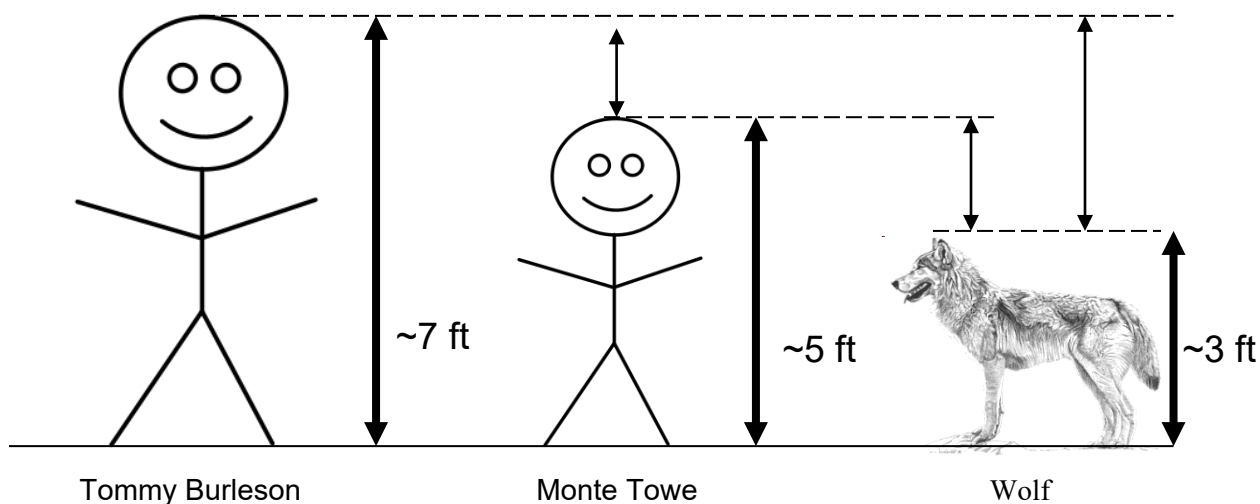
Once you define a consistent reference (in this case, the ground), you can calculate the relative changes in some metric (such as height). For example:

How much taller is Monte Towe than the Wolf?

Approach 1: Use the ground as a reference. _____

Approach 2: Use the wolf as a reference. _____

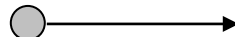Approach 3: Use Tommy Burleson as a reference. _____

In dealing with energy, we choose references that simplify calculations, but you must be consistent in your selection.

- **Note Questions 1–6 in the introduction to Chapter 7.** Answering them requires *energy balances* on the processes described.
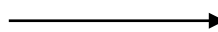
Notes with Gaps to accompany Felder, Rousseau, & Bullard, Elementary Principles of Chemical Processes.
Copyright ©John Wiley & Sons, Inc.

Three forms of energy:

1. **Kinetic energy,** E_k (J) or $\dot{E}_k$ (J / s) : energy due to motion of an object or flowing stream relative to the surface of the earth.

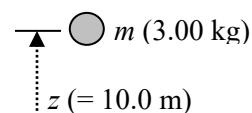body of mass m (3.00 kg) moving with velocity u (5.00 m/s)

$$E_k = \frac{1}{2}mu^2 = \frac{0.500 \mid 3.00\,\text{kg} \mid (5.00)^2\,\text{m}^2 \mid 1\,\text{N}}{s^2 \mid 1\,\text{kg} \times \text{m} / \text{s}^2} = 37.5\,\text{N} \times \text{m} = 37.5\,\text{J}$$

stream with mass flow rate $\dot{m}$ (3.00 kg/s) moving with velocity u (5.00 m/s) $[= \dot{V}(\text{m}^3 / \text{s}) / A_{\text{pipe}}(\text{m}^2)]$

$$\dot{E}_k = \frac{1}{2}\dot{m}u^2 = \frac{0.500 \mid 3.00\,\text{kg} \mid (5.00)^2\,\text{m}^2 \mid 1\,\text{N}}{s \qquad s^2 \mid 1\,\text{kg} \times \text{m} / \text{s}^2} = 37.5\,\frac{\text{N} \times \text{m}}{\text{s}} = 37.5\,\frac{\text{J}}{\text{s}} = 37.5\,\text{W}$$
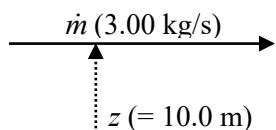
$\dot{E}_k$ is the rate at which the stream is transporting kinetic energy.

2. **Potential energy,** E_p (J) or $\dot{E}_p$ (J/s) (due to position in a gravitational or electromagnetic potential field—in CHE 205, due to height of center of mass of object above a reference height)

m (3.00 kg)

z (= 10.0 m)

Reference height: $E_P = 0$

$$E_p = mgz$$

$$= \frac{3.00\,\text{kg} \mid 9.81\,\text{m} \mid 10.0\,\text{m} \mid 1\,\text{N}}{s^2 \mid 1\,\text{kg} \times \text{m} / \text{s}^2} = 294\,\text{N} \times \text{m} = 294\,\text{J}$$

$\dot{m}$ (3.00 kg/s)

z (= 10.0 m)

Reference height: $E_P = 0$

$$\dot{E}_p = \dot{m}gz$$

$$= \frac{3.00\,\text{kg} \mid 9.81\,\text{m} \mid 10.0\,\text{m} \mid 1\,\text{N}}{s \qquad s^2 \mid 1\,\text{kg} \times \text{m} / \text{s}^2} = 294\,\frac{\text{N} \times \text{m}}{\text{s}} = 294\,\frac{\text{J}}{\text{s}} = 294\,\text{W}$$

3. **Internal energy,** U (J) or $\dot{U}$ (J / s) : sum of rotational, vibrational, and electromagnetic energies of individual molecules, atoms, and subatomic particles moving around in a body of material or a flowing stream.

Specific internal energy:

$$\hat{U}\left(\frac{\text{J}}{\text{mol}}\right) = \frac{U(\text{J})}{n(\text{mol})} \ \text{(batch)} \quad \text{or} \quad \frac{\dot{U}(\text{J} / \text{s})}{\dot{n}(\text{mol} / \text{s})} \ \text{(continuous)}$$

- **State of a species:** The temperature, pressure, and phase (solid, liquid, gas) of the species.

  State function: A property of a species that depends only on its state, and not how it got to that state. $\hat{U}$ is a state function.

- $\hat{U}$ depends strongly on the phase of a species (liquid molecules have more kinetic energy than solid molecules, and vapor molecules have *much* more kinetic energy than liquid molecules), and on temperature (molecules have more kinetic energy at higher temperatures). It depends on pressure moderately for a real gas, very slightly for a liquid or solid, and not at all for an ideal gas.

- *We can never know the value of $\hat{U}$ for a species at a given state since we can't measure energies of individual molecules, atoms, and subatomic particles & add them, but we can measure the change in $\hat{U}$ from one state to another.* For example, if we increase the temperature of a species by five degrees, we can determine the change in its specific internal energy as a result of the temperature increase. (We'll shortly find out how.)

- **Calculating E_k and E_p.** See Examples 7.2-1 and 7.2-2.

- **Exercise:** Do the Test Yourself at the end of Section 7.2

Two forms of energy transfer between a system & its surroundings

1. **Heat,** $Q(\text{kJ})$ or $\dot{Q}\,(\text{kJ}/\text{s})$: Energy transferred as a result of a temperature difference between a system and its surroundings (always from high T to low T). *Define Q as positive if heat flows to system from surroundings.* (Universal convention)

$+Q$ (heat added)
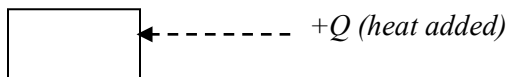
2. **Work**, $W(\text{kJ})$ or $\dot{W}\,(\text{kJ}/\text{s})$: Energy transferred any other way, such as by mechanical motion or electric current. *Define W as positive if work is done on the system by the surroundings.* (Opposite convention sometimes used)
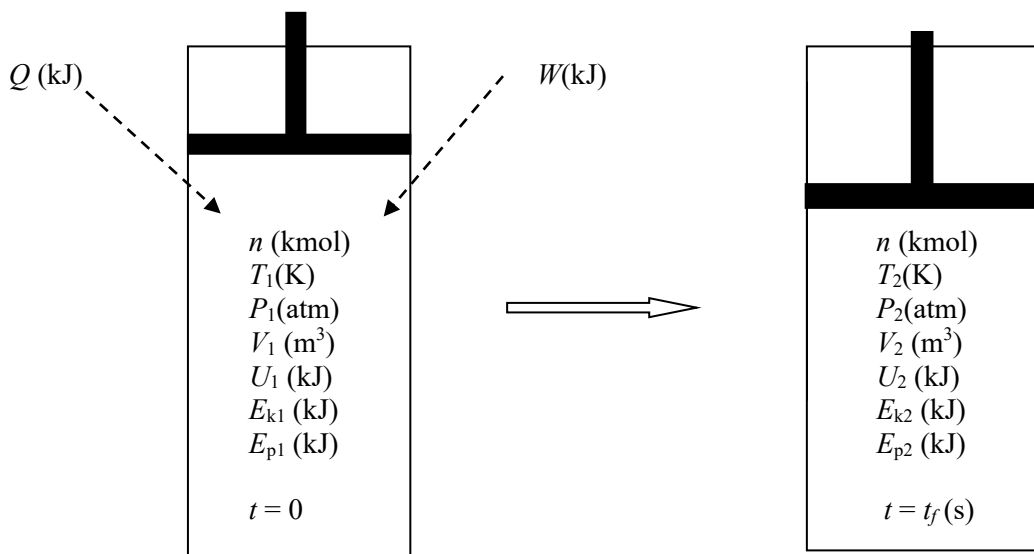

$+W$ (work done)
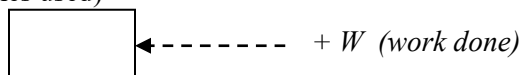
Summary:

$E_{TOT} = E_K + E_P + U$
Energy can be transferred as heat (Q) or work (W)

ENERGY BALANCES ON CLOSED SYSTEMS (Section 7.3)

- *Closed system*—no mass crosses system boundaries during process operation (batch)
  Open system—mass crosses system boundaries (continuous, semibatch)

- Consider a *nonreactive* batch process (reactive processes come in Chapter 9). Starting at one condition, add Q (kJ) heat to process and do work on the process W (kJ)

Q (kJ) W(kJ)

n (kmol)		n (kmol)
T_1(K)		T_2(K)
P_1(atm)	$\Longrightarrow$	P_2(atm)
V_1 (m^3)		V_2 (m^3)
U_1 (kJ)		U_2 (kJ)
E_{k1} (kJ)		E_{k2} (kJ)
E_{p1} (kJ)		E_{p2} (kJ)
$t = 0$		$t = t_f$ (s)

Sign convention:

- Heat (Q) added to the process is positive, heat (Q) withdrawn is negative
- Work (W) done on the process is positive, work (W) done by the process is negative

Process may involve heating or cooling (change in T), compression or decompression (change in P), and phase change, all of which lead to change in V.

Say that Δ denotes (final – initial): $\Delta T = T_2 - T_1$, $\Delta E_k = E_{k2} - E_{k1}$, $\Delta U = U_2 - U_1$, etc.

Recalling that $E_{total} = E_k + E_p + U$ for a system, and Q and W are the only ways energy can be transferred, write the law of conservation of energy (Input–Output = Accumulation) for the system between the two given times:

Net energy transferred $=$ Final system energy $-$ Initial system energy (ΔE_{total})
to the system ($Q+W$)

$$\boxed{Q + W \ = \ \Delta E_k + \Delta E_p + \Delta U}$$ **First law of thermodynamics for a closed system**

Simplifying the first law for specific systems:

- <u>System not accelerating</u> $\Rightarrow \Delta E_k = 0$

- <u>System not moving vertically</u> $\Rightarrow \Delta E_p = 0$

- No reactions or changes in phase or temperature, pressure changes < a few atm ⇒ $\Delta U \approx 0$. (For an ideal gas, $\Delta U = 0$ for pressure changes.)

- No temperature difference across system boundary (or perfect insulation) ⇒ $Q = 0$ ("*adiabatic system*")

- No moving parts, electrical currents, radiation across system boundary ⇒ $W = 0$

Exercises

(a) A can of coke is taken from a refrigerator and left standing. Write energy balance on the can from the moment it is left standing to an hour later.

(b) Example 7.3–1 (talk through it and make sure you understand it)

Measuring $\Delta \hat{U}$ for a specified change in state

- *We can never measure the true value of $\hat{U}$ at a given state – it's unknown and unknowable!* We can, however, measure Q (heat) and W (work) associated with the *change* between two states for a closed stationary system and calculate $\Delta U = Q + W \Rightarrow \Delta \hat{U} = \Delta U(\text{J}) / n(\text{mol})$. (We assume no changes in kinetic and potential energy for the system; if there are any, include them in the energy balance.)

Example:
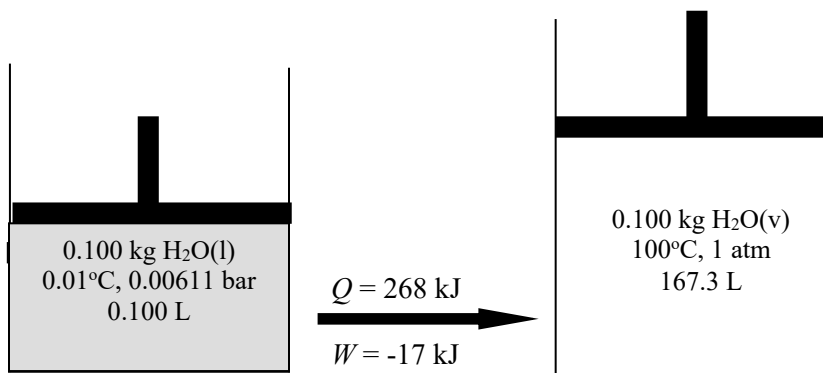
The system is the water within the cylinder. Neglecting the very slight change in potential energy due to vertical expansion of the fluid, the first law yields

$$\Delta U = Q + W = (268{-}17)\,\text{kJ} = 251\,\text{kJ}$$

$$\Rightarrow \Delta \hat{U} = \frac{251\,\text{kJ}}{0.100\,\text{kg}} = 2510\,\text{kJ} / \text{kg} \quad \text{(could convert to kJ / mol if desired)}$$

We can then say that *the specific internal energy of water vapor at 100C and 1 atm relative to liquid water at the triple point (0.01C and 0.00611bar) is 2510 kJ/kg.*

- **Internal energy table**

Notes with Gaps to accompany Felder, Rousseau, & Bullard, *Elementary Principles of Chemical Processes.*
Copyright ©John Wiley & Sons, Inc.

(a) Choose a **reference state** (phase, T, P) for a species, at which $\hat{U}$ is set equal to 0. (Example: Liquid water at the triple point, used in Tables B.5–B.7)

(b) Determine $\Delta\hat{U}$ for the change from the reference state to another. Call the result $\hat{U}$ of the species at the second state relative to the reference state. Repeat for many states, & tabulate $\hat{U}$.

(c) Thereafter, calculate $\Delta\hat{U}$ for a specified change of state (to substitute into the energy balance equation) as $\hat{U}_{final} - \hat{U}_{initial}$, substituting values from the table for both internal energies.

If you chose a different reference state, the numbers in the table would all be different but the difference between the values for any two states would always be the same. The two internal energy tables shown below for carbon dioxide at 1 atm illustrate this point.

Ref: CO_2(g, 1 atm, 0°C)

T(°C)	$\hat{U}$ (kJ/mol)
0	0.00
100	3.82
200	8.00
300	12.50

Ref: CO_2(g, 1 atm, 100°C)

T(°C)	$\hat{U}$ (kJ/mol)
0	–3.82
100	0.00
200	4.18
300	8.68

Exercise: A table of specific internal energies of nitrogen at $P = 1$ atm contains the following entries:

T(°C)	$\hat{U}$ (kJ/mol)
0	– 0.73
25	0.00
100	2.19
200	5.13

(a) What reference state was used to generate this table? _____

(b) Q: What is the physical significance of the value 2.19 kJ/mol?

A: It is $\Delta\hat{U}$ for the process N_2(__, _____ atm, _____°C) → N_2(__, _____ atm, _____°C)

(c) What is $\Delta\hat{U}$ for the process N_2(g, 1 atm, 200°C) → N_2(g, 1 atm, 100°C)? _____

(d) Calculate the heat required to cool 2.00 mol N_2 from 200°C to 100°C.

ENERGY BALANCES ON OPEN SYSTEMS AT STEADY-STATE (Section 7.4)
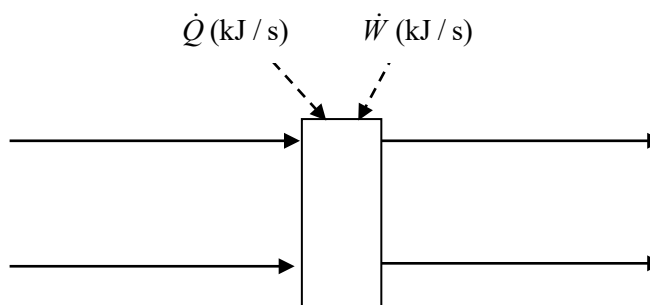
$\dot{Q}$ (kJ / s) = rate of heat transfer to the system

$\dot{W}_s$ (kJ / s) = rate of *shaft work* done on the system by its surroundings, which includes energy transmitted by moving parts (pistons, propellers, turbines,...) or electric currents that cross the system boundary.

$\dot{m}_j$ (kg / s or mol / s) = flow rate of a jth component within a stream

Note: There may be one or more inlet (feed) streams and one or more outlet streams, and the same species may enter in several streams at different states (velocity, elevation, pressure, volume). It can get complicated fast!

Energy Balance: An energy balance on this system states that "input = output" (why no generation, consumption, or accumulation terms?), where "input" is the total rate at which energy is transferred to the system from the surroundings (as heat and by being transported in by the input streams) and "output" is the total rate of energy transfer out:

$$\dot{Q} + \dot{W} + (\dot{E}_{total})_{in} = (\dot{E}_{total})_{out}$$

or since $\dot{E}_{total} = \dot{U} + \dot{E}_k + \dot{E}_p$:

$$\dot{Q} + \dot{W} = \Delta \dot{U} + \Delta \dot{E}_k + \Delta \dot{E}_p \qquad \text{(Each term has units of kJ / s)}$$

where

$$\Delta\dot{U} = \left[\sum_{\substack{\text{outlet} \\ \text{streams}}} \dot{m}_j \hat{U}_j - \sum_{\substack{\text{inlet} \\ \text{streams}}} \dot{m}_j \hat{U}_j \right]$$

$$\Delta\dot{E}_k = \left[\sum_{\substack{\text{outlet} \\ \text{streams}}} \tfrac{1}{2} \dot{m}_j u_j^2 - \sum_{\substack{\text{inlet} \\ \text{streams}}} \tfrac{1}{2} \dot{m}_j u_j^2 \right], \quad \Delta\dot{E}_p = \left[\sum_{\substack{\text{outlet} \\ \text{streams}}} \dot{m}_j g z_j - \sum_{\substack{\text{inlet} \\ \text{streams}}} \dot{m}_j g z_j \right]$$

We could use this form of the equation for all energy balance calculations; however, in an open system there are two forms of work— *flow work* and *shaft work* — which it is convenient to separate.

$\dot{W}_f$ = *flow work* (also known as "PV work"), work done to push entering fluid streams into system minus work done by exiting fluid streams pushing back the surroundings

$\dot{W}_s$ = *shaft work*, all other work transmitted across system boundary by moving parts (pistons, turbines, rotors, propellors,...), electrical currents, radiation

- This notation is can be inserted into the energy balance. (see end of notes for full derivation)

$$\dot{Q} + \dot{W} = \Delta\dot{U} + \Delta\dot{E}_p + \Delta\dot{E}_k$$

$$\dot{Q} + \left(\dot{W}_s + \dot{W}_f \right) = \Delta\dot{U} + \Delta\dot{E}_p + \Delta\dot{E}_k$$

$$\dot{Q} + \left(\dot{W}_s - \Delta\left(P\dot{V} \right) \right) = \Delta\dot{U} + \Delta\dot{E}_p + \Delta\dot{E}_k$$

$$\dot{Q} + \dot{W}_s = \boxed{\Delta\dot{U} + \Delta\left(P\dot{V} \right)} + \Delta\dot{E}_p + \Delta\dot{E}_k$$

- This equation can be simplified by defining a new term: **Enthalpy**

$$\hat{H} = \hat{U} + P\hat{V} \qquad (7.4\text{-}7)$$

$\hat{H}$ is the *specific enthalpy* of a species at pressure P with internal energy $\hat{U}$ and specific volume $\hat{V}$. Like $\hat{U}$, $\hat{H}$ is **(a)** a state property, **(b)** unmeasurable (since it includes $\hat{U}$), **(c)** heavily dependent on phase, moderately dependent on temperature, slightly dependent (real gases, liquids & solids) or independent (ideal gases) of pressure.

- Since the *change* in $\hat{U}$ from one state to another ($\Delta\hat{U}$) can be determined, the change in $\hat{H}$ for the same state change ($\Delta\hat{H}$) can be determined as

$$\Delta\hat{H} = \Delta\hat{U} + \Delta(P\hat{V}) = (\hat{U}_{outlet} - \hat{U}_{inlet}) + (P_{outlet}\hat{V}_{outlet} - P_{inlet}\hat{V}_{inlet})$$

We can therefore prepare a table of specific enthalpies relative to a reference state at which $\hat{U}$ or $\hat{H}$ is defined to be 0. Values of $\hat{H}$ for water determined in this manner can be found in the steam tables, B.5–B.7. (See Example 7.5-1 and Section 7.5b.)

$$\boxed{\dot{Q} + \dot{W}_s = \Delta\dot{H} + \Delta\dot{E}_k + \Delta\dot{E}_p} \quad \text{(Each term has units of kJ/s)} \qquad \textbf{7.4-15}$$

where

$$\left.\begin{array}{l} \Delta\dot{H} = \displaystyle\sum_{\substack{\text{outlet}\\\text{streams}}} \dot{m}_j \hat{H}_j - \sum_{\substack{\text{inlet}\\\text{streams}}} \dot{m}_j \hat{H}_j \quad \left[= \sum_{\substack{\text{outlet}\\\text{streams}}} \dot{m}_j(\hat{U}_j + P\hat{V}_j) - \sum_{\substack{\text{inlet}\\\text{streams}}} \dot{m}_j(\hat{U}_j + P\hat{V}_j)\right] \\[3em] \Delta\dot{E}_k = \left[\displaystyle\sum_{\substack{\text{outlet}\\\text{streams}}} \tfrac{1}{2}\dot{m}_j u_j^2 - \sum_{\substack{\text{inlet}\\\text{streams}}} \tfrac{1}{2}\dot{m}_j u_j^2\right], \quad \Delta\dot{E}_p = \left[\displaystyle\sum_{\substack{\text{outlet}\\\text{streams}}} \dot{m}_j gz_j - \sum_{\substack{\text{inlet}\\\text{streams}}} \dot{m}_j gz_j\right] \end{array}\right\} \begin{array}{l} \textbf{First law of thermodynamics for an} \\ \textbf{open system at steady state} \end{array}$$

Applying the open system balance equation (we will discuss reactive systems in Ch. 9):

- Drop unimportant terms in (7.4-15):
  - If there are no phase changes, reactions, or temperature changes and relatively small pressure changes (no more than a few atm) from inlet to outlet, drop $\Delta\dot{H}$.
  - If there are phase changes, reactions or significant temperature changes from inlet to outlet, usually $\Delta\dot{E}_k$ and $\Delta\dot{E}_p$ are negligible compared to $\Delta\dot{H}$ — drop them.
  - If there are no significant velocity changes from inlet to outlet, drop $\Delta\dot{E}_k$. If there are no significant elevation changes from inlet to outlet, drop $\Delta\dot{E}_p$.
  - If the system and the surroundings are at the same temperature or the system is very well insulated (adiabatic), drop $\dot{Q}$.
  - If the system contains no moving parts or electric currents that cross its boundary, drop $\dot{W}_s$.

- If $\Delta\dot{H}$ remains in the equation, use a table of enthalpies (e.g., B.5–B.7 for water) to look up the values of $\hat{H}_j$ to substitute into Eq. (7.4-14a), or wait until Chapter 8 to learn how to estimate those values.

- Substitute all other known values into the equation, and solve for whichever value is unknown (usually $\dot{Q}$ in this text).

Example 1: Example 7.4-2

Notes with Gaps to accompany Felder, Rousseau, & Bullard, *Elementary Principles of Chemical Processes.*
Copyright ©John Wiley & Sons, Inc.

Example 2. Pump 10 kg $H_2O(l)$/s through a 5-cm ID pipe to a point 125 meters above the pipe inlet. How much shaft work must the pump deliver to the water? Assume $T_{in} = T_{out}$ and neglect any heat transferred to or from the water in the pipe between inlet & outlet. (Note: the "system" is defined as the water in the pipe).

$\dot{m}_{out}$ (kg $H_2O(l)$/s)

u_{out} (m/s)

125 m

10 kg $H_2O(l)$/s

u_{in} (m/s)

Pump
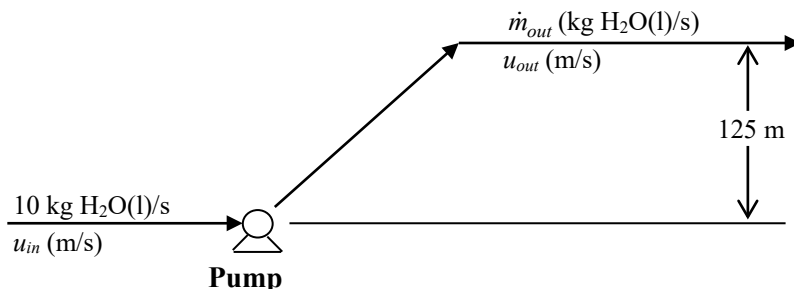
Solution: First, prove that the inlet and outlet fluid velocities (u_{in} and u_{out}) must be the same.

Next, cross out negligible terms in the balance equation:

$$\dot{Q} + \dot{W}_s = \Delta\dot{H} + \Delta\dot{E}_k + \Delta\dot{E}_p \quad \Rightarrow \quad \underline{\hspace{3cm}}$$

Finally, substitute what you know to determine all terms in the equation but $\dot{W}_s$ and solve the equation to prove that $\dot{W}_s = 12.3\,\text{kW}$ —that is, the pump must deliver 12.3 kW of power to the water.

Q: More electrical power than 12.3 kW must be delivered to run the pump. Why?

A:

Example 3. Example 7.5-3

STEAM TABLES (Sect. 7.5b)
So, where do you start to find values of $\hat{H}, \hat{U}, \hat{V},$ and other values that appear in the energy balance? If the species is water, you're in luck – the *steam tables* in Tables B.5, B.6, and B.7 have tabulated values. For other species, we'll cover that in Chapter 8.

- Table B.5: Saturated Steam Temperature Table

  Find the following properties of saturated water (water on the vapor-liquid equilibrium curve) at 32°C. Include units in your responses.

  Vapor pressure = _____

  Specific volume of liquid water _____ and water vapor _____

  Reference state used to determine internal energies and enthalpies _____

  Specific internal energy of liquid water _____ and water vapor _____

  Specific enthalpy of liquid water _____ and water vapor _____

  Heat of vaporization _____

- Table B.6 : Saturated Steam Pressure Table

  Find the following properties of saturated water at 4.2 bar

  Boiling point = _____

- Table B.7: Superheated Steam Table

  If a point falls within the "stairstep box" outlined on Table B.7, then water is a liquid. Outside the box, water is a superheated vapor. Use Table B.7 to find the following properties of water at 20 bar and 350°C.

  Phase _____

  Specific internal energy relative to liquid water at the triple point _____

  Specific enthalpy relative to liquid water at the triple point _____

  Specific volume _____

  Dew point temperature _____
  Specific internal energy of liquid water _____ and water vapor _____
      at the dew point temperature
  Specific enthalpy of liquid water _____ and water vapor _____
      at the dew point temperature
  Specific volume of liquid water _____ and water vapor _____
      at the dew point temperature

  Also note that the following APEx functions can be used to retrieve these values. This is especially handy if interpolation is required for values which are in between listed values on the steam table:

  - SteamSatT - returns values from the saturated steam temperature table (Table B.5)
  - SteamSatP - returns values from the saturated steam pressure table (Table B.6)
  - SteamSH - returns values from the superheated steam table (Table B.7)