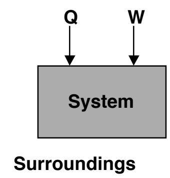
The First Law

- Chapter 1: The First Law
  - Conservation of energy
  - Terms introduced and defined (random fashion)
  - Important to understand this chapter for all future work
- The second law (covered later in chapter 2) deals with the conversion of heat to work
- Definitions
  - Some will be familiar from Phase Equilibria
- Forms of Energy
- Conservation of energy
- Energy Balances in complex systems

System



- A system is any portion of space set aside for study
  Everything else is the surroundings
- A system may be open or closed
  Open: Matter can enter, leave, or both
  Closed: No matter transfer
- Choice of open or closed depends on how a system is defined
  Does not depend on any physical constraints
- Fluid in pipe example
  Fluid flowing through a pipe
  Open system: a specific portion of the pipe
    Fluid enters and leaves,
  Closed system: a specific volume of the fluid
    No fluid transfer
    System may be compressed, but remain closed

Notation

- **Must differentiate between total system and per unit mass properties**
- **U is internal energy**
  SI unit is joule (J)

$$\underline{U} = \frac{U}{m}$$

- **$\underline{U}$ is specific internal energy**
  SI unit can be J/kg or J/mole
- **$\underline{V}$ can be specific volume (m³/kg) or molar volume (m³/mole)**
  Specific volume is reciprocal density
  Specific gravity is density/density of water
  Molar volume is molecular weight/density

$$\underline{V}\left(\frac{m^3}{kg}\right) = \frac{1}{\rho}$$

$$\text{Sp.Grav.}\left(\text{unitless}\right) = \frac{\rho}{\rho_{water}}$$

$$\underline{V}\left(\frac{m^3}{mole}\right) = \frac{\text{m.w.}}{\rho}$$

- **Formulas will use $\underline{V}$ for molar volume or specific volume**
  You must determine which is meant from context
  For chemical reactions and solution properties V is molar volume

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Intensive/Extensive Properties

- Extensive properties depend on the size or mass of the system
  Volume, U, H
- Intensive properties are independent of system size
  Pressure, temperature, specific properties, density
- Important when dealing with open systems since the mass of the system can change

Energy Transfer

- Energy is divided into two types: heat and work
  - The division will be important when we learn the second law
- Transfer implies that energy is exchanged between a system and its surroundings
- Heat is thermal energy that flows
  - Designated by Q
- Work is defined as all other forms of energy
  - Designated by W

Heat

- Heat is energy that is transferred between a system and its surroundings due to a temperature difference
- Joules (J) is the SI unit for heat
- Heat is positive when it flows from the surroundings into the system
- Systems do not posses heat, heat flows
- When heat flows into a system, it increases the system's thermal energy
- Heat flow can increase the temperature of the system or drive a reaction

Work

- **Work is any other form of energy transferred to or from the system**
  We will sub-divide work later into P-V type and others
- **Many forms of work**
  Mechanical, electrical, magnetic, gravitational
- **PV work is the easiest to understand and describe mathematically**
  Volume of system must change for it to do P-V work
  $W = -P\Delta V$
- **Work is positive when it is done on the system (scientific definition)**
  Engineers consider work done by the system to be positive

Reversible vs. Irreversible

- A process is reversible if the initial state of the system can be restored with no changes in the surroundings
- Reversible processes usually occur in infinitesimal steps so that equilibrium can be maintained during the change
- Any dissipation of energy by frictional forces, entropy transfer, or other inefficiencies makes a process irreversible
- Example of two gas cylinders initially at the same state
    - One expanded in infinitesimal steps
        - External P only infinitesimally different than internal
    - Second expanded rapidly
        - Adiabatic decompression, finite P difference
- Book uses example of gas expanding into a vacuum rapidly
    - Expansion produces no work, but compression requires work

Energy of a System

- **Three types**
  - **Kinetic Energy**
  - **Potential Energy**
  - **Internal Energy**
- **Kinetic Energy**
  - **Energy due to the motion of a system as a whole**
  - **Due to the velocity of the entire system, not molecular motion**
  - **Macroscopic flow for a gas or liquid, not motion of molecules**
  - **Translational kinetic energy = $1/2\ mv^2$**
  - **Depends on environment of system (relative motion)**

Potential Energy

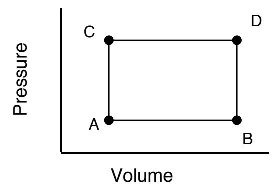
- Composed of parts due to external forces
  - Gravitational, magnetic, electrical, centrifugal
  - Depends on environment of system
- Gravitational
  - Can be converted to kinetic by dropping object
  - Object is accelerated as potential converts to kinetic
- Amount is equal to mass times height times g
  - g is acceleration due to gravity
  - 10 m times 1 kg times 9.8 m/s^2 = 98 $kg \cdot m^2/s^2$ = 98 $N \cdot m$ = 98 J
- Potential and kinetic energy are often ignored in thermodynamic analysis

Internal Energy

- More difficult concept than kinetic and potential energy
- Depends on inherent properties of system and its environment
- Inherent properties
  - Composition (chemical make up)
  - Physical form (solid, liquid, or gas)
- Environmental effects
  - Temperature, pressure, electric/magnetic field, etc.
- A compressed spring has a higher internal energy than one at rest
- Container of $H_2 + O_2$ vs. same P/T of H_2O

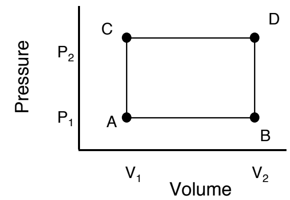
State Functions

- Many thermodynamic calculations depend on this concept
- Internal energy is a state function (along with H, F, and G)
- The internal energy difference between two states is only dependent upon the parameters that specify the states, not the path taken to get from one state to the other
- Consider a simple P-V system
  $\Delta U = U_2 - U_1$
  $\Delta U = U_D - U_A$
- ΔU does not depend on path, only the initial and final P-V values
- The path can go thru C or B of neither



Work

- **Work is path dependent**
  It is not a state function
- **Consider the simple P-V system**
  We will change its state reversibly
  by simply changing the temperature



- **Path 1**
  Isobaric (constant P) expansion from A to B, then
  isochoric (constant V) pressure increase from B to D
- **Path 2**
  Isochoric pressure increase from A to C, then
  isobaric expansion from C to D
- **Work done on the system**
  Path 1: $W = -P_1(V_2 - V_1)$
  Path 1: $W = -P_2(V_2 - V_1)$
  Work is different for two paths

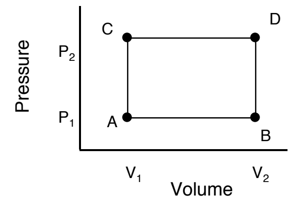
Cyclic Processes

- **This system can be cycled through P and V following the path A-B-D-C**
- **The work done during the cycle is:**

$$W = \oint P\,dV$$

$$W = -P_1\left(V_2 - V_1\right) - P_2\left(V_1 - V_2\right)$$

$$W = \left(P_2 - P_1\right)\left(V_1 - V_2\right)$$



- **Work is positive for path A-B-D-C**
- **Would be negative for reverse path**
- **Since U is a state function, any difference in internal energy due to work after the cycle must be compensated by heat flow (can be reversible or not) (example calculation)**

Closed Systems

- In a closed system
  - No matter enters or leaves system
  - Boundaries may expand or contract due to work
  - Thermal energy may flow in and out
- Neglecting kinetic and potential energy, the first law is:

$$\delta Q + \delta W = dU$$

- U is internal energy
  - Differential quantity because it is a state function
  - Not a function of path, can take a true derivative
- Q and W (heat and work)
  - Are path dependent, not state functions
- If kinetic and potential energy terms are considered:

$$\delta Q + \delta W = dU + d(PE) + d(KE)$$

Open Systems

- Matter can flow into and out of a system
- The first law must be modified to account for:
  The internal energy of the material entering and leaving
  The work done as material is pushed in and out of the system
- U change due to mass change (m_i for mass into, m_o for mass out)

$$dU_{flow} = U_i \delta m_i - U_o \delta m_o$$

- Work due to flow into system

$$\delta(\text{flow work}_i) = P\underline{V}_i \delta m_i$$

- The first law can then be rewritten grouping flow and system terms

$$\sum_{m_i} \left(U_i + P_i V_i\right) \delta m_i - \sum_{m_o} \left(U_o + P_o V_o\right) \delta m_o + \delta Q + \delta W = dU$$

Enthalpy

- **In many calculations, the terms U + PV appear together**
  For any constant pressure process Q = U + PV
  In materials, most reactions happen at 1 atm (const. P)
- **The grouping U + PV is given a special designation**
  It is a state function since it contains only state functions

$$H \equiv U + PV$$

Steady State

- **A system that does not change with time is at steady state**
  - **Time invariant**
  - **Matter may enter and leave**
  - **Useful to analyze any continuous process**
    - **pumps, turbines, chemical reactors, furnaces**
- **First law can be re-written for dU = 0**

$$Q + W = \sum_{m_o} \underline{H}_o m_o + \sum_{m_i} \underline{H}_i m_i$$

$$\delta Q + \delta W = \sum_{m_o} \underline{H}_o \delta m_o + \sum_{m_i} \underline{H}_i \delta m_i$$

Heat Capacity

- The amount of thermal energy that must be transferred into a system to change its temperature is its heat capacity
- No underscore is used even though heat capacity has mass (kg or moles) in its units, J/mole•K or J/kg•K
- The simplest form of heat capacity is for a constant volume system that does no mechanical work
- C_V is a function of temperature and the specific volume of the system

$$\delta Q + \delta W = dU$$

$$\delta W = 0$$

$$\delta Q = dU$$

$$\delta Q = dU = mC_V dT$$

$$C_V dT = \frac{dU}{m} = d\underline{U}$$

$$C_V \equiv \left(\frac{\partial \underline{U}}{dT}\right)_V$$

$$dU = mC_V dT$$

Heat Capacity

- **Unless constrained, most materials expand when heated**
  - **Thermal energy increases U**
  - **PV work is done by the system as it expands**
- **If we consider only mechanical work (PV)**
- **At constant pressure, dP = 0, so PdV = d(PV)**
- **Tables list C_P since that is how most experiments are performed**
- **Tables give a, b, and c coefficients**

$$C_P = a + bT + cT^{-2}$$

- **Heat capacity is a function of T and P**

$$\delta Q + \delta W = dU$$
$$\delta Q - PdV = dU$$
$$\delta Q = dU + PdV$$
$$\delta Q = d(U + PV) = dH$$
$$dH = mC_P dT$$
$$d\underline{H} = C_P dT$$
$$C_P \equiv \left(\frac{\partial H}{\partial T}\right)_P$$

Heat Capacity

- **Example problems**

Adiabatic Flow

- **Adiabatic means no heat is added or removed from the system**
  - **Rapid processes are often adiabatic**
  - **Well insulated systems are often adiabatic**
- **Steady state flow through a valve is adiabatic ($\delta Q = 0$)**
- **First law** $\underline{H}_i m_i - \underline{H}_o m_o + \delta Q + \delta W = dU$

  Steady state $dU = 0$

  Adiabatic $\delta Q = 0$

  No work, system is valve $\delta W = 0$

  No mass accumulation in system $m_i = m_o$
- **Flow through a valve is isenthalpic** $H_i = H_o$
- **Joule-Thomson coefficient**

  Change in temperature with pressure at constant H

  Zero for an ideal gas

$$\mu_{JT} = \left(\frac{\partial T}{\partial P}\right)_H$$

Ideal Gas

- For an ideal gas, the equation of state is $P\underline{V} = RT$
- We previously stated that for an ideal gas: $\left(\frac{\partial \underline{U}}{\partial \underline{V}}\right)_T = 0$
  This will be proven in Chapter 3
- Find the relationship between $\underline{H}$ and P
- Show the value of the Joule-Thomson coefficient

Heat Capacity of an ideal gas

- Derive the C_P-C_V relationship
- Typical values for ideal gases

	C_P	C_v
Monatomic ideal gas (He, Ar)	3/2R	5/2R
Diatomic gas (O_2, H_2)	5/2R	7/2R

- Compare to value calculated using coefficients

Non-Ideal Gases

- Show Figures 1.8 and 1.9 as phase diagram examples
- Critical temperature
  below gas can be compressed to liquid at constant T
  above, cannot form a liquid
  far above, all have ideal behavior
- Use compressibility (Z) or reduced pressure/temperature to describe non-ideal behavior
-

Adiabatic Compression/Expansion

- Adiabatic means no heat flow in or out of the system
- A change in pressure changes the temperature
  Nature example air cools as it rises and pressure drops
- Derivation of adiabatic relations
- Example of helium in insulated tank

Enthalpy of Formation

- Enthalpy is a state function
- Neither U nor H can be calculated in absolute terms
  There is no zero point for energy
  Use reference state
- Reference condition: stable state of elements at 298 K, 1 atm.
  Stable state is gaseous O_2 for oxygen
- CO_2 example

Enthalpy Change, Chemical Rxns

- Can be calculated from tabulated heats of formation of species in rxn
- Methane example at 298 K
- Generic example at 298 K
- At temperature other than 298 K
  Add heat capacity term

Adiabatic temperature change

- **Adiabatic flame temperature (AFT)**
  Highest possible temperature produced by combustion
- **Actual temperature can be reduced for many reasons**
  Reactions don't always go to completion
  Heat loss
  others
- **Tables to track moles in and out for fuel, air, and exhaust components**
- **Other examples**
  Polymerization reaction
  Combustion reaction

Application of ATF to ceramics

- Drying and firing ceramics
- Heat ware and air (including water in air)
- Recover heat from combustion
- Heat for chemical reactions
- Heat loss

Dryer Example

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