The First law of Thermodynamics

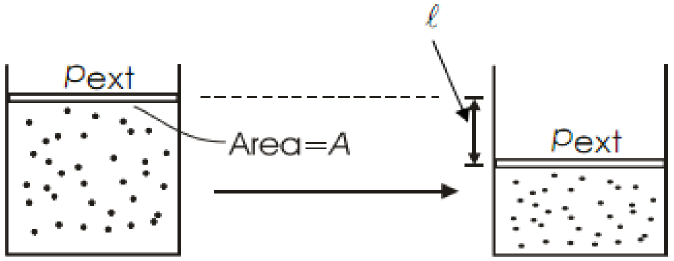
Chapter-2

Work, Heat, and the First Law

- Work: $$w = \underset{\text{applied force}}{F} \cdot \underset{\text{distance}}{\ell}$$

Expansion work

$F = p_{ext}A$



$$w = \underset{\text{convention}}{-}(p_{ext}A)\ell = -p_{ext}\Delta V$$

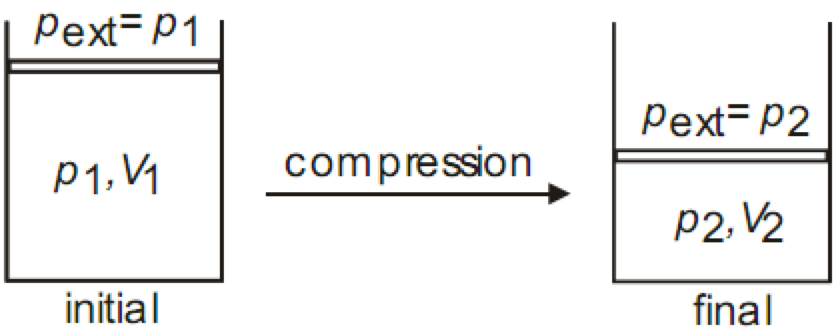
convention: Having a "-" sign here implies $w > 0$ if $\Delta V < 0$, that is, positive work means that the surroundings do work to the system. If the system does work on the surroundings $(\Delta V > 0)$ then $w < 0$.

If p_{ext} is not constant, then we have to look at infinitesimal changes

$\text{đ}w = -p_{ext}dV$ đ means this is not an exact differential

Integral $w = -\int_1^2 p_{ext}dV$ depends on the path!!!

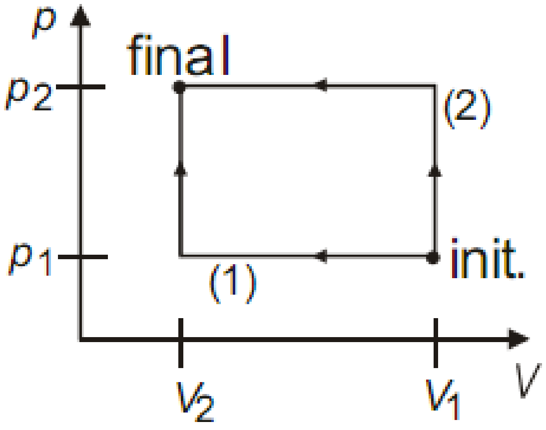
Path Dependence of Work



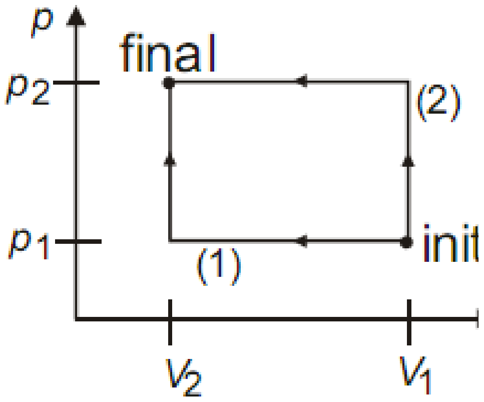
Two paths:

(1) First $V_1 \to V_2$ at $p = p_1$
then $p_1 \to p_2$ at $V = V_2$

(2) First $p_1 \to p_2$ at $V = V_1$
then $V_1 \to V_2$ at $p = p_2$



Path Dependence of Work



$$w_{(1)} = -\int_{V_1}^{V_2} p_{ext}dV - \int_{V_2}^{V_2} \cancel{p_{ext}dV}$$

$$= -\int_{V_1}^{V_2} p_1 dV = -p_1(V_2 - V_1)$$

$$\boxed{w_{(1)} = p_1(V_1 - V_2)}$$

$$w_{(2)} = -\int_{V_1}^{V_1} \cancel{p_{ext}dV} - \int_{V_1}^{V_2} p_{ext}dV$$

$$= -\int_{V_1}^{V_2} p_2 dV = -p_2(V_2 - V_1)$$

$$\boxed{w_{(2)} = p_2(V_1 - V_2)}$$

(Note $w > 0$, work done to system to compress it)

$$\boxed{w_{(1)} \neq w_{(2)}\ !!!}$$

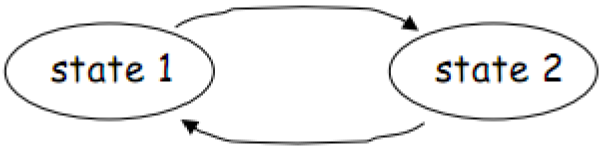
Note for the closed cycle [path (1)] - [path (2)], $\oint \bar{d}w \neq 0$

closed cycle

w is not a state function   cannot write $w = f(p,V)$

WORK

Work (w) is not a function of state.
For a cyclic process, it is possible for $\oint \bar{d}w \neq 0$



Heat

HEAT

That quantity flowing between the system and the surroundings that can be used to change the temperature of the system and/or the surroundings.

Sign convention: If heat enters the system, then it is positive.

Heat (q), like w, is a function of path. Not a state function

It is possible to have a change of state

$$(p_1,\ V_1,\ T_1)\ =\ (p_2,\ V_2,\ T_2)$$

adiabatically (without heat transferred)
or nonadiabatically.

The modern unit of heat (and work) is the Joule.

1 cal = 4.184 J

Forms of Energy

- **Macroscopic Kinetic Energy (E_K):**
- The energy associated with bulk motion of the system as a whole.
  - $E_K=\frac{1}{2}mv^2$

- **Macroscopic Potential Energy (E_P):**
- The energy associated with bulk position of the system.
  - $E_P=mgh$

- **The Internal Energy (U):**
- The energy associated with motion, position and chemical-bonding of the molecules.

Internal Energy

- Change in internal energy can result:
  1. Changes in temperature……..Sensible Heat
  2. Changes in phase…….Latent Heat
  3. Changes in chemical structure (chemical reaction)
- Two general components of internal energy:
  1. Molecular kinetic energy:
     - Translational, Rotational, Vibrational=$f(T)$
  2. Molecular potential energy
     - Attraction and Repulsion forces
- Ideal Gas: $u=f(T)$ only
- Real Gas: $u=f(T,v)$ or $f(T,P)$

Reversible and Irreversible Processes

1. **Reversible:** In a reversible process the system changes in such a way that the system and surroundings can be put back in their original states by exactly reversing the process. Changes are infinitesimally **small** in a reversible process.
    - No friction
    - Represent an idealization
    - The work obtained from a reversible process is the **maximum**

2. **Irreversible:** If the system returns to its original state, the surroundings must be alterd. This represents all real processes where the work obtained is less than reversible processes.

$$\boxed{\text{Efficiency}=\frac{w_{irrev}}{w_{rev}}}$$

First Law of Thermodynamics:

- The energy of the universe is constant. Energy can be transferred from the system to its surroundings, or vice versa, but it can't be created or destroyed.

$$\Delta E_{\text{univ}} = \Delta E_{\text{sys}} + \Delta E_{\text{surr}} = 0$$

$$[\Delta E_K + \Delta E_P + \Delta U]_{system} = \textit{Energy transferred from surroundings to system}$$

1. Closed Systems:

Most closed systems remain stationary during a process and, thus, experience no change in their kinetic and potential energies. The change in the stored energy is identical to the change in internal energy for stationary systems.

If $\Delta K_E = \Delta P_E = 0$,

$$\boxed{\Delta U = Q + W}$$

If the transfer of energy changes as the process proceeds:

$$\boxed{\frac{dU}{dt} = \dot{Q} + \dot{W}}$$

First Law of Thermodynamics:

2. Open Systems:

Energy and Work being transported by the inlet and outlet streams!!!

Flow Work:

$$\left.\begin{aligned} (\dot{W}_{flow})_{in} &= -P_{in}A_{in}\frac{dx}{dt} = P_{in}A_{in}\vec{V}_{in} \\ \dot{n} &= \frac{A\vec{V}}{v} \end{aligned}\right\} \longrightarrow \boxed{(\dot{W}_{flow})_{in} = P_{in}\dot{n}_{in}v_{in}}$$

Flow Energy:

$$\boxed{(Energy_{flow})_{in} = \sum_{in}\dot{n}_{in}(u + e_K + e_P)_{in}}$$

First Law of Thermodynamics:

$$\underbrace{0}_{\text{Steady-State}} = \underbrace{\sum_{in} \dot{n}_{in}(u+e_K+e_P)_{in}}_{\text{Energy flowing into system with inlet}} - \underbrace{\sum_{out} \dot{n}_{out}(u+e_K+e_P)_{out}}_{\text{Energy flowing out of the system with outlet}} + \dot{Q} + \left[\dot{W}_s + \underbrace{\sum_{in} \dot{n}_{in}(Pv)_{in}}_{\text{Flow work from the inlet streams}} + \underbrace{\sum_{out} \dot{n}_{out}(-Pv)_{out}}_{\text{Flow work from the outlet streams}}\right]$$

The inlet and outlet streams always include both internal energy and flow work. Therefore, we define a new **property enthalpy**, *h* (*J/mol*):

$$h = u + Pv$$

The first law becomes:

$$\boxed{\left(\frac{dU}{dt}\right)_{sys} = \sum_{in} \dot{n}_{in} h_{in} - \sum_{out} \dot{n}_{out} h_{out} + \dot{Q} + \dot{W}_s}$$

❖ Ideal Gas: $Pv=RT \longrightarrow h_{\text{ideal gas}} = u+Pv = u+RT = f\,(T \text{ only})$

Read Example 2.4

Read Example 2.5

Heat Capacity

The heat capacity of a system - the amount of energy transfer due to heating required to produce a unit temperature rise in that system

$$\boxed{C \equiv \frac{\delta Q}{\Delta T}}$$

C *is NOT a state function* (since ***Q*** is not a state function) – it depends on the path between two states of a system $\Rightarrow$

(isothermic – ***C*** $= \infty$, adiabatic – ***C*** $= 0$)

The specific heat capacity $c \equiv \dfrac{C}{m}$

C_p and C_v

$$C = \frac{\delta Q}{dT} = \frac{dU + PdV}{dT}$$

V = const

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

the heat capacity at constant volume

P = const

$$C_P = \left(\frac{\partial H}{\partial T}\right)_P$$

the heat capacity at constant pressure

For an ideal gas:

$$C_V = \frac{3}{2}R \quad C_P = \frac{5}{2}R$$

$$C_v = a + BT + CT^2 + DT^{-2}$$

$$C_p = A + BT + CT^2 + DT^{-2} + ET^3$$

The parameters are listed in Appendix A.2 for ideal gases

C_p and C_v…A few more notes

Liquids and Solids: $C_p \approx C_v$

Closed systems at constant *P*: $q = \Delta h$

- Mean Heat Capacity for Gases, $\overline{C}_p$: the average between two temperatures, often 298 K and *T*,

$$\boxed{\overline{C}_p = \frac{\int_{298}^{T} C_p dT}{T - 298}}$$

- ***Read Example 2.6***:

Read Example 2.9:

First Law for Phase Changing Systems-Latent Heat and Sensible Heat

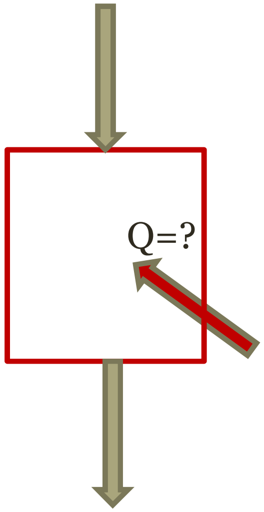
When a solid melts or a liquid boils, energy must be added but the temperature remains constant! It takes energy to break the bonds holding the material together. The amount of energy it takes to melt or boil a certain amount of material is called a **latent heat** which is the change of **enthalpy** during a phase transition at constant **pressure**:

$$\boxed{\Delta h_{vap} = f(T)}$$

Latent heats are normally known at the boiling point, i.e. at **1 bar**. What if we need to calculate the latent heat at another pressure???

Then we need to construct an appropriate thermodynamic pathway using **Sensible Heat,** which is the energy exchanged by a thermodynamic system that changes the temperature..... $Q=mC_p\Delta T$

Read Example 2.10:



Liquid
10 mol/s
T=25 ^{o}C

Q=?

Vapor
T=100 ^{o}C

First Law for Systems with Chemical Reactions
Enthalpy of Reactions

- Chemical reaction: process in which new molecular species (*products*) are formed from the initial species (*reactants*).
- General Reaction: $aA + bB \longrightarrow cC + dD$
- A…D are species: solid(s), liquid(L), or gas(g)
- a…d are balancing numbers, or stoichiometric coefficients; chosen to balance elements on both sides of reaction.
- A large amount of energy is stored in the chemical bonds within the molecules. Due to the chemical reaction, the energy might change. The change in the amount of energy can be shown in the enthalpy of reaction!

Enthalpy of Reaction

$$\Delta h^{o}{}_{rxn} = \sum_{\Pr oducts} \nu_i h_i^{o} - \sum_{\mathrm{Re}\,ac\tan ts} \upsilon_i h_i^{o}$$

$\nu_{\mathbf{i}}$ = Stoichiometric number

h_i=enthalpy of formation at 25°C and 1 atm (appendix A.3)

This equals to <u>0</u> for pure substances, such as H_2, O_2 etc

$\Delta H^o < 0 \rightarrow$ reaction is *exothermic* (heat released)

$\Delta H^o > 0 \rightarrow$ reaction is endothermic (heat absorbed)

What if the reaction is not happening at 25 °C?

$$\Delta h_{rxn,T} = \sum \nu_i (\Delta h^{o}{}_{f,298})_i + \int_{298}^{T} \left(R \sum_i \nu_i \left(A_i + B_i T + C_i T^2 + \frac{D_i}{T^2} + EiT3 \right) \right) dT$$

Read Example 2.12

Read Example 2.13!

Reversible Processes in Closed Systems
A Few useful Cases

- **Reversible, Isothermal Expansion (Compression), Ideal gas**

$$\boxed{W = nRT \ln \frac{P_2}{P_1}} \qquad \boxed{\Delta U = 0} \qquad \boxed{Q = -nRT \ln \frac{P_2}{P_1}}$$

- **Reversible, Adiabatic Expansion (Compression), Ideal gas**

$$\boxed{\Delta U = W = \frac{nR}{K-1}\left[T_2 - T_1\right]} \qquad \boxed{K = \frac{C_p}{C_v}}$$

Closed Thermodynamic Cycles

Closed cycles will form the basis of our heat engine discussion.

A closed cycle is one in which the system returns to the initial state (same *p*, *V*, and *T*) and are used to produce power or refrigeration since we can repeat them continuously.

- U is a state function. Therefore: $\Delta U = 0$
- The net work is the enclosed area: $\int p dV \neq 0$
- Energy is conserved (1^{st} Law): $W = Q \neq 0$

This is the reason that neither W nor Q is a state function. It makes no sense to talk about a state having a certain amount of W.

Introduction to Heat Engines

One of the primary applications of thermodynamics is to Turn heat into work. The standard heat engine works on a cyclic process:

1) extract heat from a hot reservoir,
2) perform work, using some of the extracted heat,
3) dump unused heat into a cold reservoir (often the environment).
4) repeat over and over.

Energy is conserved: $Q_h = Q_c + W$

Heat Engine Efficiency

We pay for the heat input, Q_H, so:

Define the efficiency

$$\varepsilon \equiv \frac{\text{work done by the engine}}{\text{heat extracted from reservoir}} = \frac{\text{results}}{\text{cost}}$$

$$\boxed{\varepsilon \equiv \frac{W}{Q_h} = \frac{Q_h - Q_c}{Q_h} = 1 - \frac{Q_c}{Q_h}}$$

Valid for all heat engines.
(Conservation of energy)

What's the best we can do?

Carnot Cycle for an Ideal gas

The Carnot cycle is an ideal heat engine cycle that offers insights into other heat engines, including the atmosphere. It is a reversible cycle, performed by an ideal gas, that consists of two isothermal processes linked by two adiabatic processes, as illustrated below:

$$-W_{net} = |W_{12}| + |W_{23}| - |W_{34}| - |W_{41}|$$

$$\Delta U_{cycle} = 0 = W_{net} + Q_{net}$$

$$-W_{net} = Q_{net} = \underset{Q_H}{\underset{\searrow}{Q_{12}}} + \underset{0}{\underset{\searrow}{Q_{23}}} + \underset{Q_C}{\underset{\searrow}{Q_{34}}} + \underset{0}{\underset{\searrow}{Q_{41}}} = |Q_H| - |Q_C|$$

Efficiency of the cycle:

$$\eta \equiv \frac{net\ work}{heat\ absorbed\ \ from\ the\ hot\ reservoir} = \frac{W_{net}}{Q_H} = \frac{Q_H - Q_C}{Q_H}$$

Carnot cycle is the most efficient one! No engine can produce more efficiency than the Carnot cycle!