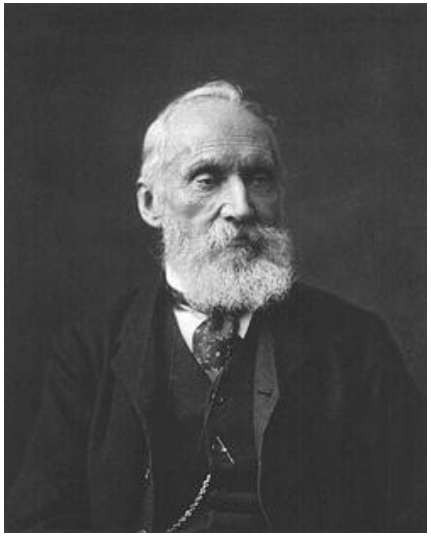
EG3029 Chemical Thermodynamics

Introduction and Principles

History of Thermodynamics

- 1650s: "Birth" of the scientific discipline
  - Boyle and Hooke found relation between pressure, temperature and volume
- 1854: Scottish physicist William Thomson
  - "*Thermo-dynamics is the subject of the relation of heat to forces acting between contiguous parts of bodies, and the relation of heat to electrical agency.*"



Source: http://en.wikipedia.org

General Remarks

- Thermodynamics <u>does</u>
  - describe a system macroscopically
  - calculate the ‘energy’ required for a physical or chemical process
  - determine a system’s equilibrium conditions
- Thermodynamics <u>doesn’t</u>
  - allow for kinetic considerations of chemical or physical processes
  - describe molecular behaviour

Dimensions and Units
General

- Do always use SI units for calculations
  - *second* s, *meter* m, *kilogram* kg, *kelvin* K, *mole* mol

  or those based on them
  - *newton* N, *joule* J, *pascal* Pa, ...

Table 1.1: Prefixes for SI Units

Multiple	Prefix	Symbol	Multiple	Prefix	Symbol
10^{-15}	femto	f	10^{2}	hecto	h
10^{-12}	pico	p	10^{3}	kilo	k
10^{-9}	nano	n	10^{6}	mega	M
10^{-6}	micro	μ	10^{9}	giga	G
10^{-3}	milli	m	10^{12}	tera	T
10^{-2}	centi	c	10^{15}	peta	P

Dimensions and Units
Summary

- Measures of amount or size
  - mass m, number of moles n, total volume V^t
  - specific volume $V=V^t/m$
- Force F, Pressure P
- Temperature T
- Work W
- Energy E (kinetic, potential)
- Heat Q

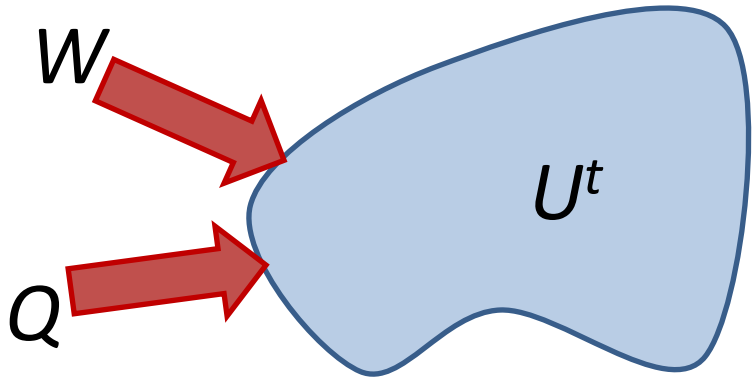
First Law of Thermodynamics
Energy Balance

- A system (e.g. a fluid) can possess energy
  - as a result of its macroscopic position (*potential*) or movement (*kinetic*)
  - or as a result of microscopic/molecular motion *internal energy*
- First Law: <u>Conservation of Energy</u>

$$\Delta E(\text{system}) + \Delta E(\text{surroundings}) = 0$$

First Law of Thermodynamics
Energy Balance

- *Closed* systems ($dm = 0$)



$$\Delta U^t = Q + W$$

$$dU^t = dQ + dW$$

- IUPAC sign convention:
  - Heat Q and work W always refer to the system
  - Energy transfer to the system: positive sign!

First Law of Thermodynamics
State and Equilibrium

- *State functions* describe the <u>present</u> thermo-dynamic state of a system (however reached)
  - pressure, temperature, density (specific volume)
- Thermodynamic equilibrium means the absence of any tendency toward change on a macroscopic scale.
  - all driving forces are in balance: ‘mechanical’, ‘thermal’, ‘chemical’

First Law of Thermodynamics
State and Equilibrium

- *Phase Rule*
  - pure homogeneous fluid in equilibrium
    - state is fixed when 2 intensive thermodynamic properties are given
  - multi-phase system at equilibrium
    - Gibbs' Phase Rule for non-reacting systems

$$F = 2 - \pi + N$$

F degrees of freedom
π number of phases
N number of chem. species

First Law of Thermodynamics
Reversible Process

- A reversible process:
  - is frictionless.
  - is never more than differentially removed from equilibrium.
  - traverses a succession of equilibrium states
  - is driven by forces whose imbalance is differential in magnitude
  - can be reversed at any point by an infinitesimal change in external conditions.
  - when reversed, retraces its forward path, and restores the initial state of system and surroundings

First Law of Thermodynamics
Isochoric and Isobaric Process

- Energy balance of closed system:

$$dU^t = dQ + dW$$

$$dW = -P\, dV^t$$

$$dU^t = dQ - P\, dV^t$$

- Constant volume process:

$$-P\, dV^t = 0$$

$$dU^t = dQ$$

$$\Delta U^t = Q$$

- Constant pressure process:

$$dQ = dU^t + d(PV^t) = d(U^t + PV^t)$$

$$H = U + PV$$

First Law of Thermodynamics
Heat Capacity

- General definition:

$$C = dQ / dT$$

Problem: Q depends on the process!
Solution: Define C as function of state functions.

- Constant volume:

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

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

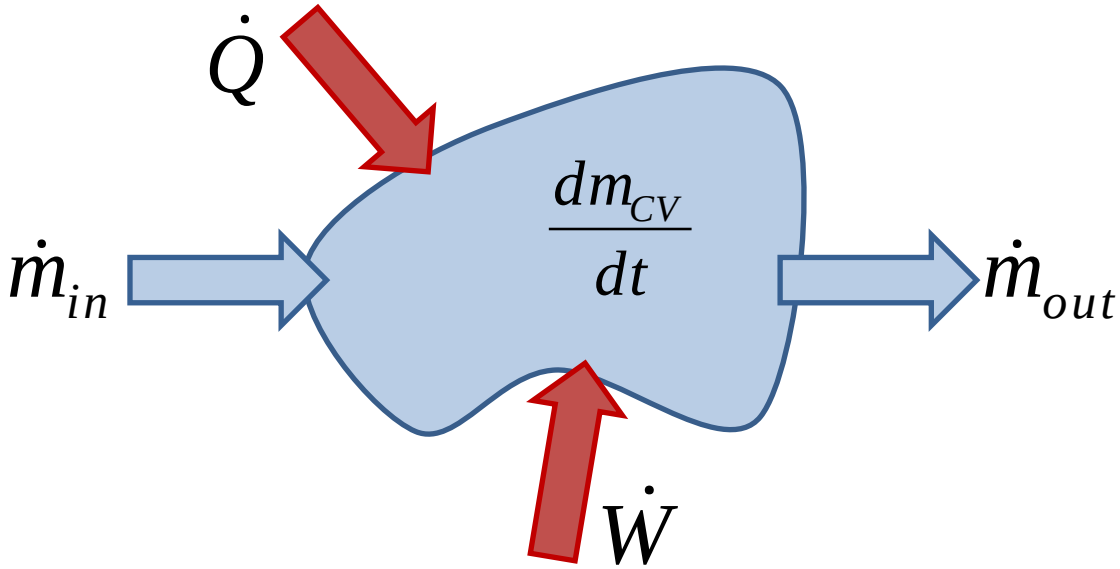
- Constant pressure:

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

$$Q = n\,\Delta H = n\int_{T_1}^{T_2} C_P\, dT$$

First Law of Thermodynamics
Open Systems

- Control volume and flow rates:



- Mass balance

$$\frac{dm_{CV}}{dt} + \left(\dot{m}_{out} - \dot{m}_{in}\right) = 0$$

First Law of Thermodynamics
Open Systems

- Energy balance

$$\frac{d(mU)_{CV}}{dt} + \Delta\left[\left(H + \tfrac{1}{2}u^2 + zg\right)\dot{m}\right] = \dot{Q} + \dot{W}$$

u velocity
z elevation above reference level
g gravity

- Steady state flow process

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

$$\Delta H + \frac{\Delta u^2}{2} + g\Delta z = Q + W$$

Ideal Gas
General

- Characteristic equations and properties

$$PV = RT$$

$$U = U(T)$$

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

$$H \equiv U + PV = U(T) + RT = H(T)$$

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

$$C_P = \frac{dH}{dT} = \frac{dU}{dT} + R = C_V + R$$

C_P and C_V are not constant, but vary only with T

Ideal Gas Processes

- Processes involve heat and work quantities

$$dQ = C_V dT + RT\frac{dV}{V}$$

$$dW = -RT\frac{dV}{V}$$

$$dQ = C_P dT - RT\frac{dP}{P}$$

$$dW = -RdT + RT\frac{dP}{P}$$

- With *PV* = *RT*

$$dW = -PdV$$

$$dQ = \frac{C_V}{R}VdP + \frac{C_P}{R}PdV$$

Ideal Gas Processes

- Isothermal process: $dT = 0$

$$Q = -W = RT \cdot \ln \frac{V_2}{V_1} = -RT \cdot \ln \frac{P_2}{P_1}$$

- Isobaric process: $dP = 0$

$$Q = \Delta H = \int_{T_1}^{T_2} C_P dT$$

- Isochoric process: $dV = 0$

$$Q = \Delta U = \int_{T_1}^{T_2} C_V dT$$

Ideal Gas Processes

- Adiabatic process: $dQ = 0$

$$\frac{T_2}{T_1} = \left(\frac{V_1}{V_2}\right)^{R/C_V}$$

$$\frac{T_2}{T_1} = \left(\frac{P_2}{P_1}\right)^{R/C_P}$$

$$\frac{P_2}{P_1} = \left(\frac{V_1}{V_2}\right)^{C_P/C_V}$$

$$\gamma \equiv \frac{C_P}{C_V}$$

$$TV^{\gamma-1} = const.$$

$$TP^{(1-\gamma)/\gamma} = const.$$

$$PV^{\gamma} = const.$$

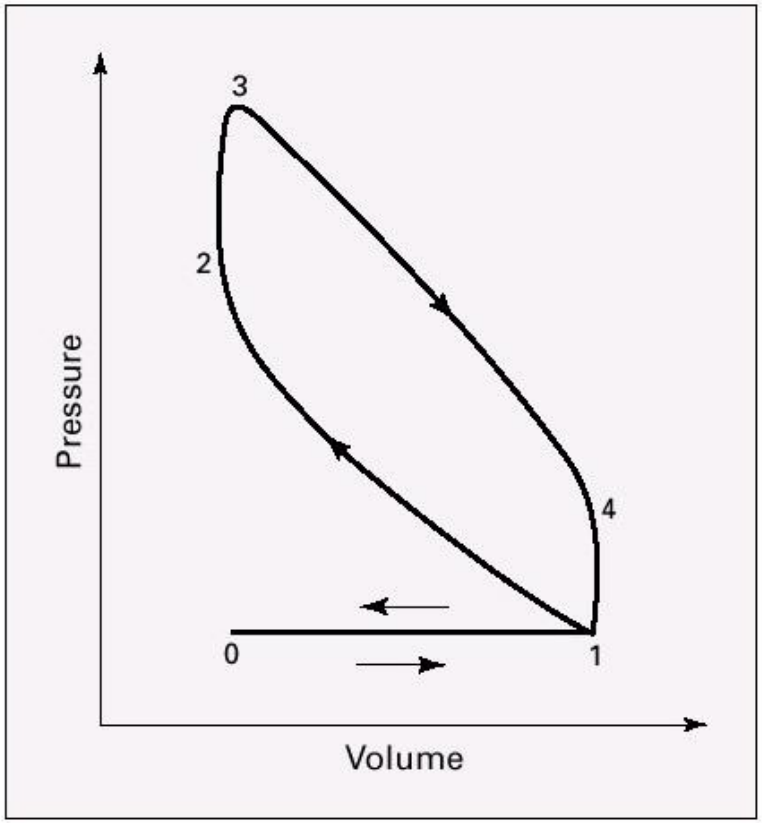
- Polytropic process

$$TV^{\delta-1} = const.$$

$$TP^{(1-\delta)/\delta} = const.$$

$$PV^{\delta} = const.$$

Ideal Gas
Cycle processes: Otto Engine



Real process

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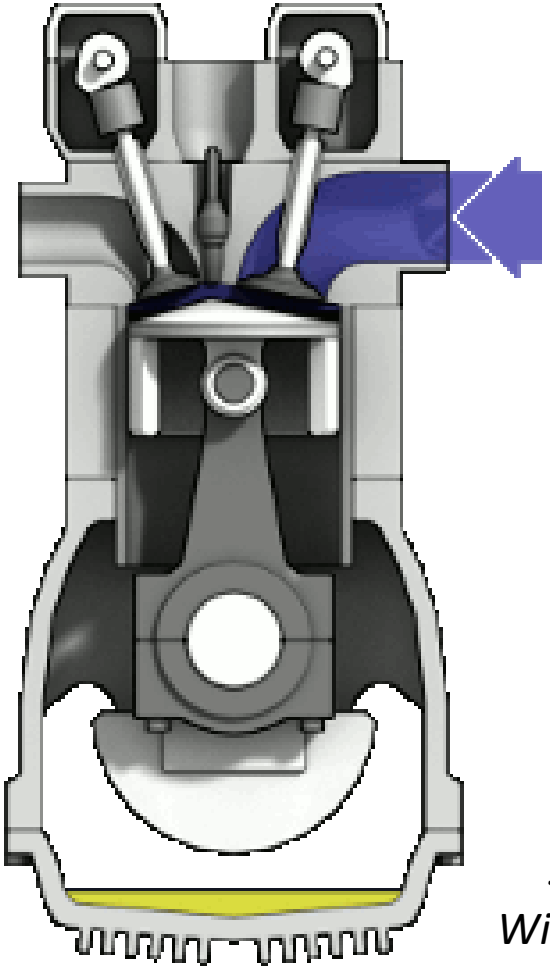
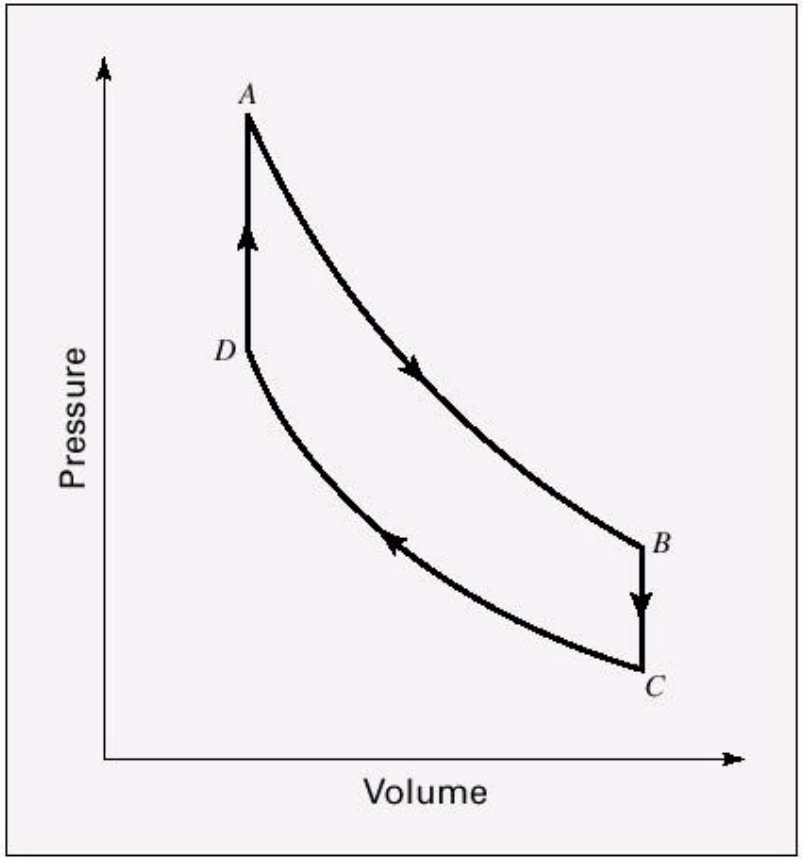


Source: Wikipedia

Ideal Gas
Cycle processes: Otto Engine

- Four-stroke engine
- Single-phase process
- Combustion at *V* = const.
- Spark ignition
- Compression of fuel/air mixture
- Compression ratio

$$r = \frac{V_C}{V_D}$$



Standard process