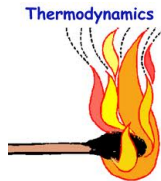


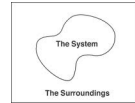
Chapter 15 - Thermodynamics

Why heat moves



Thermodynamics is only concerned with large scale observations

- Only "state" variables matter to describe the system (P, V, T)
- System is the gas
- Surroundings is everything else



**Zeroth Law** - Two systems in thermal equilibrium with a third are in equilibrium with each other

- Heat will flow between two systems at different temperatures until in equilibrium
- Heat always flows from HIGH T to LOW T

**1st Law of Thermodynamics**

What is the equation for internal energy?

$$U = \frac{3}{2}kT$$

How can you make the internal energy change?

$$\Delta T \quad +\Delta Q + W$$

**$\Delta U = \Delta Q + W$**       Book:  $\Delta U = \Delta Q - W$

+ $\Delta Q$  = system GAINS heat (does NOT have to increase T)  
 - $\Delta Q$  = system LOSES heat (does NOT have to decrease T)

+ W = work done ON system (BY surroundings)  
 - W = work done BY system (ON surroundings)

4 types of changes that can occur as gas moves from one state to another

**1) Isobaric**

**NO CHANGE IN PRESSURE**

**changing volume**

What does slope represent?  
 What does area represent?

$-P\Delta V = W$   
 $-P\Delta V = nR\Delta T = W$

$P\Delta V = Nm = J = \text{Work} = \text{area under P-V graph}$   
 But Work is opposite volume change so...

**$W = -P\Delta V$**

\*\*\*Note book uses OLD definition of work on SURROUNDINGS...this is work on SYSTEM\*\*\*

So for isobaric changes:

$W = -P\Delta V$   
 since  $PV = nRT$

**$W = -nR\Delta T$**

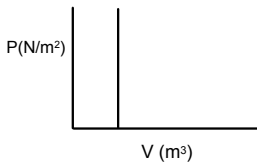
\*\*\*only if gas is at CONTANT PRESSURE

Also....  $\Delta U = W + \Delta Q$  so  $\Delta Q = \Delta U - W$   
 so...  $\Delta Q = 3/2nR\Delta T - (-nR\Delta T)$

**$\Delta Q = 5/2nR\Delta T$**        $= 5/2 N k \Delta T$        $k = \frac{R}{N_A}$

**2) Isochoric**

= constant volume = **NO WORK**

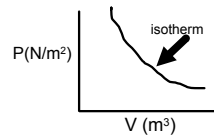


$W = 0 \dots$   
 since  $\Delta U = W + \Delta Q$   
 $\Delta U = \Delta Q$   
 $\Delta Q = 3/2nR\Delta T$

**3) Isothermal**

constant temperature

no change in INTERNAL ENERGY



Area under curve = integrate =

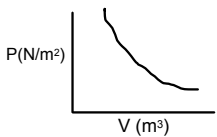
$W = -nRT(\ln(V_f/V_i))$

$\Delta U = 0 = W + \Delta Q \dots \text{so } \Delta Q = -W$

**4) Adiabatic**

constant heat

no change in HEAT



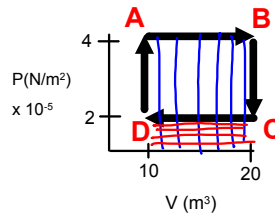
$P_1 V_1^\gamma = P_2 V_2^\gamma$

$\gamma = 5/3$   
for ideal gas

$\Delta Q = 0$

$\Delta U = \Delta Q + W \dots \text{so } \Delta U = W$   
 and  $W = 3/2nR\Delta T$

**Check Question: What is the Work done on the SYSTEM that goes through the following four changes?**



- A  $\rightarrow$  B = isobaric  
 $(4 \times 10^5)(10) = W = 4 \times 10^4 \text{ Nm}$
- B  $\rightarrow$  C = isochoric  
 $W = 0$
- C  $\rightarrow$  D = isobaric  
 $(2 \times 10^5)(10) = W = 2 \times 10^4 \text{ Nm}$
- D  $\rightarrow$  A = isochoric  
 $W = 0$

What is this the same as? Total Work =  $-2 \times 10^4 \text{ Nm}$

Area of enclosed cycle = work done ON SYSTEM

**Heat and ideal gases**

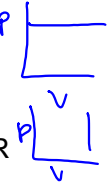
$\Delta Q = nC_p\Delta T$  (gas at CONSTANT P)

$\Delta Q = nC_v\Delta T$  (gas at CONSTANT V)

$C_p = 5/2R$      $C_v = 3/2R$      $C_p - C_v = R$

$\gamma = \frac{C_p}{C_v} = \frac{5/2R}{3/2R} = 5/3 = \gamma$

$\gamma$



**2nd Law of Thermodynamics**

- Heat will only flow spontaneously from high temperature to low temperature
- Total entropy of the universe ALWAYS increases during heat exchange

\*\*\*This is why you cannot have a perpetual motion machine...some energy is always lost to non-useful energy = entropy\*\*\*

Entropy = amount of disorder = S

According to 2nd Law

$\Delta S = \Delta Q/T$  (note T must be K!!!)

units = J/K



Check Question

Water freezes in your freezer causing a DECREASE in entropy. How does this not break the 2nd Law of Thermodynamics?

$$\Delta S_{ice} = \frac{\Delta G}{T}$$

$$= \frac{-TmL_f}{273}$$

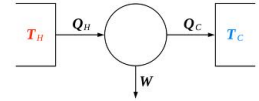
$$\Delta S_{sur} = \frac{+Q}{T}$$

$$= \frac{+T\Delta x}{T}$$

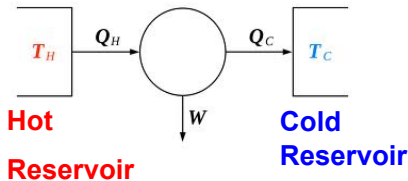
$$\text{Spontaneous} = \Delta S_{ice} + \Delta S_{sur} > 0$$

**2nd Law and Heat Engines**

\*Uses the fact that heat flows from high to low temperature



\*Creates work from heat the flows  
\* Some heat lost to entropy ( $Q_C$ )



efficiency = how well engine converts  $Q_H$  into  $W$

All real heat engines lose some heat to the environment  
 Efficiency =  $\frac{W}{Q_H} = \frac{Q_H - Q_C}{Q_H}$   
 Maximum for the Carnot cycle  
 Extracting heat  $Q_H$  and using it all to do work  $W$  would constitute a perfect heat engine, forbidden by the second law.

**Carnot Engine = maximum efficiency possible**

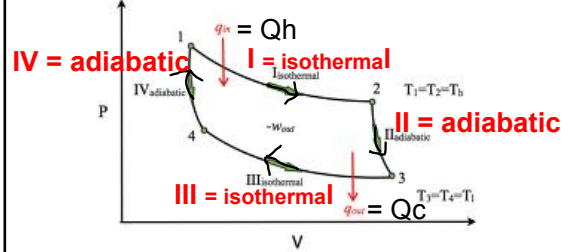
$$\frac{Q_c}{Q_h} = \frac{T_c}{T_h}$$

$$Q_h = Q_c + W$$

Since  $e = \frac{Q_h - Q_c}{Q_h} = 1 - Q_c/Q_h$

For Carnot  $e = 1 - T_c/T_h$  in K!!!

Carnot Cycle



Dippy Bird and the Carnot Cycle

$T_1 = T_c = \text{cooler due to evaporation}$

$T_2 = T_h = \text{warmer (no evaporation)}$

Step AB: isothermal expansion  
Step BC: adiabatic expansion  
Step CD: isothermal compression  
Step DA: adiabatic compression

Work cycle =  $(T_2 - T_1) \ln(V_1/V_2)$   
 $T_1 = 293 \text{ K}$   
 $T_2 = 295 \text{ K}$

Harold Williams, *Slack Eye Physical Chemistry from Thermodynamics*

How Dippy Really works:

- 1) System is at equilibrium ( $T_h = T_c$ )
- 2) Evaporation caused vapor inside to condense (lose energy), reducing  $PV/RT$  (less gas inside = less  $n$ )
- 3)  $P$  at bottom is bigger so it increases pushing fluid up
- 4) Fluid causes change in CM above PP so bird dips
- 5) There is a tube at the bottom exposed to vapor so bubble rises when dips, causing fluid to move back down