A: Physical Chemistry

Paper III - Physical and organic Chemistry

B.Sc. Part II

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Thermodynamics

$$\text{Adiabatic index, } \gamma = \frac{f+2}{f}$$

Where, f is the number of degrees of freedom of the molecule

For monatomic gas, f=3, $\gamma = \frac{5}{3}$

For diatomic gas (O_2) and collinear molecules (CO_2) f=5,

$$\gamma = \frac{7}{5}$$

Thermodynamics

Work done

$$PV^{\gamma} = constant$$

Differentiating

$$d(PV^{\gamma}) = 0$$

Expanding the term

$$PdV^{\gamma} + V^{\gamma}dP = 0$$

$$\gamma PV^{(\gamma-1)}dV + V^{\gamma}dP = 0$$

Dividing both side by $V^{(\gamma-1)}$

$$\gamma PdV + VdP = 0$$

Adding both side with -γPdV

$$VdP = -\gamma PdV$$

Thermodynamics

It is known

$$PV = RT$$

Differentiating

$$d(PV) = d(RT)$$
$$PdV + VdP = RdT$$

Adding –PdV to both sides

$$VdP = RdT - PdV$$

Substituting $VdP = -\gamma PdV$

$$RdT - PdV = -\gamma PdV$$

Adding PdV both side of equation

$$RdT = -\gamma PdV + PdV$$

Taking PdV as common factor

$$RdT = (1-\gamma)PdV$$

Dividing the equation by factor of (1-γ)

$$PdV = \frac{RdT}{(1-\gamma)}$$

Integrating both sides

$$work\ done, w = \int_{V_1}^{V_1} PdV$$
$$= \int_{T_1}^{T_2} \frac{RdT}{(1-\gamma)}$$

Considering the constants

$$P\int_{V_1}^{V_2} dV = \frac{R}{(1-\gamma)}\int_{T_1}^{T_2} dT$$

Integrating

$$w = P(V_2 - V_1)$$
$$w = \frac{R}{(1-\gamma)}(T_2 - T_1)$$

Thermodynamics

Spontaneous and non-spontaneous process

There are two types of processes (or reactions):

spontaneous and non-spontaneous

Spontaneous process or natural processes:

proceed, when left to themselves, in the absence of any attempt to drive them in reverse.

Generally, exothermic reactions are spontaneous but some are endothermic too.

Examples of non exothermic spontaneous processes

- Mixing of gas $\Delta_{mix}H^{\ominus}$= 0 kJmol^{-1}
- NaCl (S) + H_2O →Na^+(aq) + Cl^-(aq) $\Delta_{sol}H^{\ominus}$= 4 kJmol^{-1}
- $\frac{1}{2}N_2(g) + O_2(g) \rightarrow NO_2\ (g)$ $\Delta_r H^{\Theta} = 33.2\ kJ\ mol^{-1}$
- $C(s) + 2\ S\ (l) \rightarrow CS_2(l)$ $\Delta_r H^{\Theta} = 128.5\ kJ\ mol^{-1}$

So +ΔH itself is not sufficient condition for spontaneity.

Thermodynamics

Historical Development

Caloric theory of heat

Caloric was also thought of as a weightless elf-repellent fluid that could pass in and out of pores in solids and liquids.

Count Rumford (1798)

caloric could not be a conserved "substance“

-An Experimental Enquiry Concerning the Source of the Heat which is Excited by Friction,

The first law of thermodynamics explained how heat was generated

Limitations of the first law of thermodynamics

It does not say about conversion of work into heat

It does not say anything whether the process is a spontaneous process or not.

Thermodynamics

Second law of thermodynamics

Newcomen invented piston-operated steam engine

Heat engine: A machine which can do work by using heat that flows out spontaneously from a high temperature source to a low temperature sink.

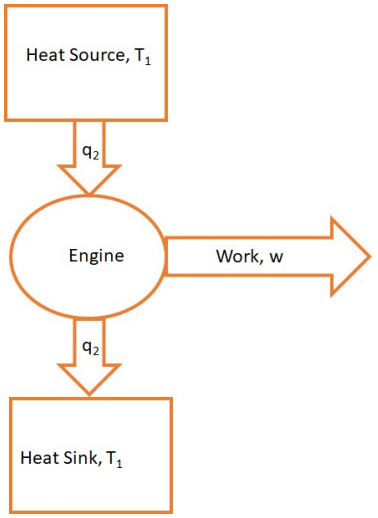


Figure 1. Schematic diagram of an engine.

Thermodynamics

James Watt

Increased the efficiency and practicality of steam engines

Efficiency of an Engine: Ratio of work obtained in a cyclic process to the heat taken from source

Lazare Carnot (*French mathematician, 1803*)

In any machine the accelerations and shocks of the moving parts represent losses of moment of activity; in any natural process there exists an inherent tendency towards the dissipation of useful energy.

- *Fundamental Principles of Equilibrium and Movement*

Thermodynamics

Nicolas Léonard Sadi Carnot (1824)

What can be the maximum efficiency of the engine?

The motive power of heat (maximum efficiency of the engine) is fixed by the temperatures of the bodies between which the transfer of caloric (the reversible transfer of heat at a given temperature) is affected.

-Reflections on the Motive Power of Fire

Thermodynamics

Carnot theorem

The efficiency of a Carnot engine depends solely on the temperatures of the hot and cold reservoirs.

Carnot cycle

The cycle is consequently composed of adiabatic processes (q= 0) flows and isothermal processes (ΔT = 0) where heat is transferred but no temperature difference exists.

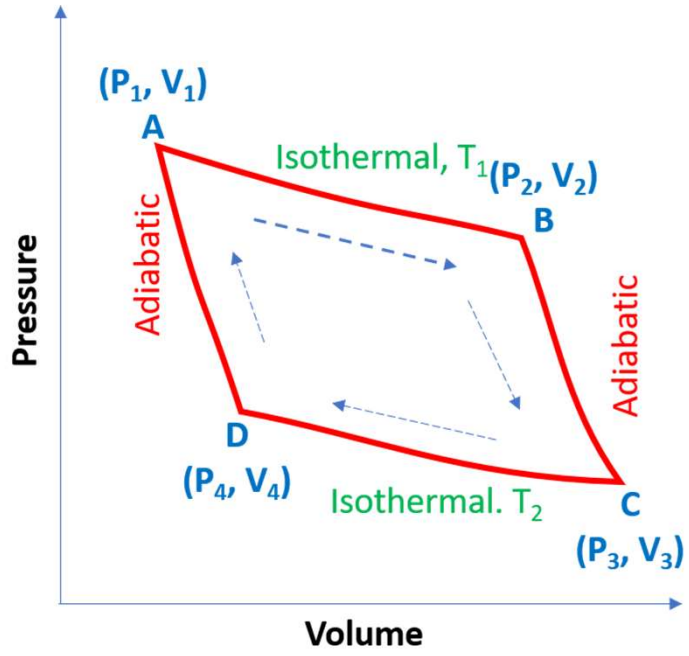


Figure 2. Indicator diagram for the Carnot cycle.

Thermodynamics

Assumptions

ideal reversible engine

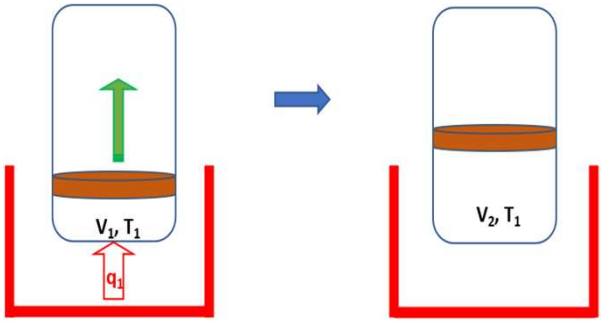
One mole of ideal gas in a frictionless piston

Four stages

1. Isothermal reversible expansion
2. Adiabatic reversible expansion
3. Isothermal reversible compression
4. Adiabatic reversible compression

Thermodynamics

Stage 1: Isothermal reversible expansion



Energy is gained from the source.

Work is done by the engine.

Change in volume is from V_1 to V_2.

From 1st law of thermodynamics

$$\Delta E = q - w$$

For isothermal change ΔE=0, q=q_1, w=w_1

$$w_1 = q_1 = RT_1 ln \frac{V_2}{V_1}$$

Thermodynamics

Stage 2: Adiabatic reversible expansion

Temperature changes from T_1 to T_2.

Work is done by the engine.

From 1st law of thermodynamics

$$\Delta E = q - w$$

For adiabatic change q =0, w=w_2

$$w_2 = -\Delta E$$

$$w_2 = -(C_v \Delta T)$$

Thermodynamics

Stage 3: Isothermal reversible compression

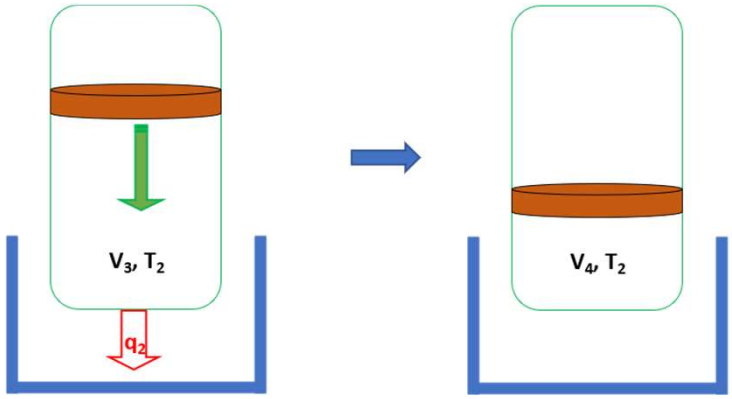
Engine is in contact with thermal sink.

Energy is given to thermal sink.

Volume changes from V_3 to V_4.

Work is done on the engine.

From 1st law of thermodynamics



$$\Delta E = -q + w$$

$\Delta E=0$, $q=-q_2$, $w=w_3$

$$w_3 = q_2 = RT_2 ln \frac{V_4}{V_3}$$

Thermodynamics

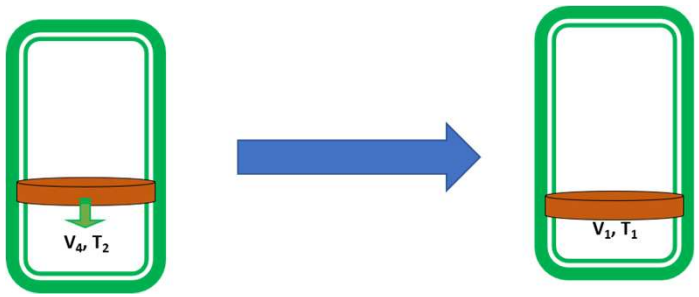
Stage 4: Adiabatic reversible compression

Temperature changes from T_2 to T_1.

Work is done on the engine with gain of internal energy.

$w=-w_4$

$$w_4 = \Delta E$$
$$w_4 = C_v \Delta T$$



Thermodynamics

Total work done

$$w = w_1 + w_2 + (-w_3) + (-w_4)$$

Substituting values from the Carnot cycle

$$w = RT_1 ln\frac{V_2}{V_1} - C_v\Delta T + \left(RT_2 ln\frac{V_4}{V_3}\right) + C_v\Delta T$$

$$w = RT_1 ln\frac{V_2}{V_1} + \left(RT_2 ln\frac{V_4}{V_3}\right)$$

Thermodynamics

For adiabatic changes, $\left(\frac{V_1}{V_2}\right)^{(\gamma-1)} = \frac{T_2}{T_1}$

For expansion from B(T_1, V_2), to C (T_2, V_3)

$\mathbf{V_1}$=V_2,

$\mathbf{V_2}$=V_3,

$\mathbf{T_1}$= T_1 and

$\mathbf{T_2}$= T_2

Substituting values

$$\left(\frac{V_2}{V_3}\right)^{(\gamma-1)} = \frac{T_2}{T_1}$$

For compression from D(T_2, V_4), to A(T_1, V_1)

$\mathbf{V_1}$=V_4,

$\mathbf{V_2}$=V_1,

$\mathbf{T_1}$= T_1

$\mathbf{T_2}$= T_1

Substituting values

$$\left(\frac{V_4}{V_1}\right)^{(\gamma-1)} = \frac{T_1}{T_2}$$

$$\left(\frac{V_1}{V_4}\right)^{(\gamma-1)} = \frac{T_2}{T_1}$$

Thermodynamics

$$\left(\frac{V_1}{V_4}\right)^{(\gamma-1)} = \frac{T_2}{T_1} = \left(\frac{V_2}{V_3}\right)^{(\gamma-1)}$$

$$\frac{V_1}{V_4} = \frac{V_2}{V_3}$$

Multiplying both side by $\frac{V_3}{V_1}$

$$\frac{V_3}{V_4} = \frac{V_2}{V_1}$$

Total work, $w = RT_1 ln\frac{V_2}{V_1} + RT_2 ln\frac{V_4}{V_3}$

Substituting $\frac{V_3}{V_4}$ with $\frac{V_2}{V_1}$

$$w = RT_1 ln\frac{V_2}{V_1} - RT_2 ln\frac{V_2}{V_1}$$

Considering common factors

$$w = R(T_1 - T_2) ln\frac{V_2}{V_1}$$

$$Thermodynamic\ efficiency, \eta = \frac{Total\ work\ done, w}{total\ heat\ absorbed, q_2}$$

$$\eta = \frac{R(T_1 - T_2) ln\frac{V_2}{V_1}}{RT_1 ln\frac{V_2}{V_1}}$$

Thermodynamics

$$Thermodynamic\ efficiency, \eta = \frac{R(T_1 - T_2) ln \frac{V_2}{V_1}}{RT_1 ln \frac{V_2}{V_1}} = \frac{T_1 - T_2}{T_1}$$

Carnot Theorem: Efficiency depended on the temperature difference of the source and the sink and independent of the working substance.

$$Thermodynamic\ efficiency, \eta = \frac{T_1 - T_2}{T_1} = 1 - \frac{T_2}{T_1}$$

Implication: efficiency of an engine will always be less than 1

Thermodynamics

Concept of entropy

In Carnot cycle

$$efficiency, \eta = \frac{total\ heat\ concverted\ to\ work}{total\ heat\ supplied}$$

$$\eta = \frac{q_1 - q_2}{q_1} = 1 - \frac{q_2}{q_1}$$

$$\eta = 1 - \frac{q_2}{q_1} = 1 - \frac{T_2}{T_1}$$

$$\frac{q_2}{q_1} = \frac{T_2}{T_1}$$

$$\frac{q_1}{T_1} = \frac{q_2}{T_2}$$

Using convention heat gain is +q and heat loss is -q

$$\frac{q_1}{T_1} = -\frac{q_2}{T_2}$$

$$\frac{q_1}{T_1} + \frac{q_2}{T_2} = 0$$

$$\sum \frac{q}{T} = 0$$

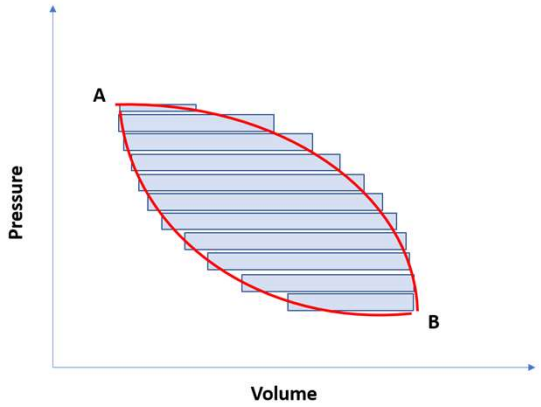
Thermodynamics

Concept of entropy

Any reversible process can be regarded as multiple carnot cycle

For infinite small cycles

$$\int \frac{dq}{T} = 0$$



$$\frac{dq_{rev}}{T} = dS$$

Thermodynamics

Spontaneous irreversible process

$$w_{irev} < w_{rev}$$

$$\eta_{irev} < \eta_{rev}$$

$$\frac{q_1 - q_2}{q_1} < \frac{T_1 - T_2}{T_1}$$

$$1 - \frac{q_2}{q_1} < 1 - \frac{T_2}{T_1}$$

$$-\frac{q_2}{q_1} < -\frac{T_2}{T_1}$$

$$-\frac{q_2}{T_2} < -\frac{q_1}{T_1}$$

$$\frac{q_1}{T_1} - \frac{q_2}{T_2} < 0$$

Physical significance

During irreversible spontaneous natural process there is increase in entropy.

Second law of thermodynamics

Entropy of universe is increasing