LECTURE

7

CY11001
Spring 2018

- Entropy and Spontaneity
- Carnot Engine

Department of Chemistry
Indian Institute of Technology
Kharagpur

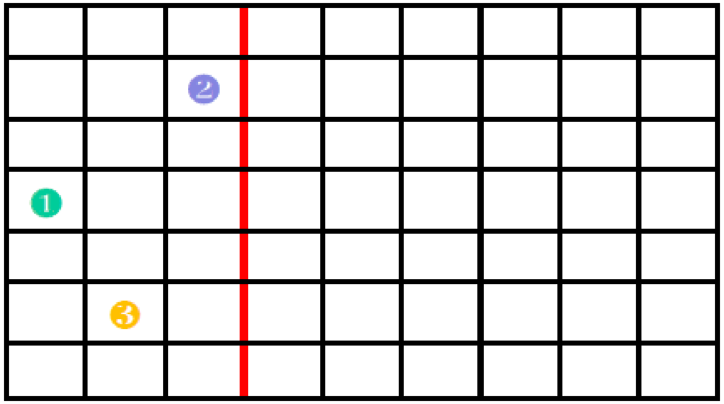
Statistical View of Entropy

The equilibrium thermodynamic state of an isolated system is the most probable state.

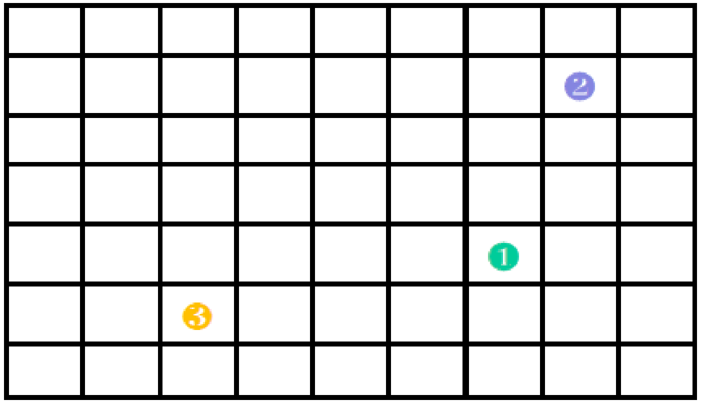
$$\boxed{S = k_B \ln W}$$

k_B is Boltzmann's constant
W is number of different ways in which the energy of the system can be arranged (number of microstates)

As $T \rightarrow 0$, $W \rightarrow 1$ and $S \rightarrow 0$
(Nernst Heat Theorem/Third Law of TD)



$W = 21 \times 20 \times 19 = 7{,}980$



$W = 63 \times 62 \times 61 = 2{,}38{,}266$

The Clausius Inequality:

$$dS = dq_{rev} \,/\, T$$
$$dS_{surr} = -\, dq \,/\, T_{surr}$$

$$\Delta S = \int_1^2 \frac{dq_{rev}}{T}$$

$$\Delta S_{surr} = \frac{-q}{T_{surr}}$$

For expansion/compression work,

$dw - dw_{\mathrm{rev}} \geq 0$

Since $dU = dq + dw = dq_{\mathrm{rev}} + dw_{\mathrm{rev}}$

$dq_{\mathrm{rev}} \geq dq$

$dq_{\mathrm{rev}}/T \geq dq/T$

For a closed system,

$dq = dU - dw$

$TdS \geq dU - dw$

$\boldsymbol{dU - TdS - dw \leq 0}$

$\boldsymbol{dS \geq dq/T}$

$\boldsymbol{TdS - dq \geq 0}$

The Clausius Inequality

Entropy can not decrease when a spontaneous change occurs in an isolated system ($dq = 0$)

Entropy and Reversibility

• Reversible process:

Reversible heat transfer between system and surrounding must occur with no finite temperature difference.

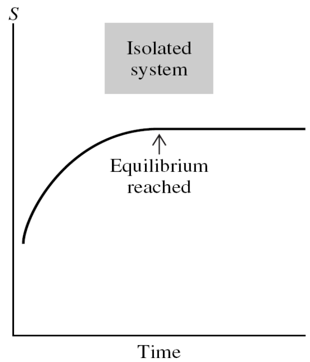
$$T_{syst} = T_{surr} \Rightarrow dS_{univ} = dS_{syst} + dS_{surr} = \frac{dq_{rev}}{T_{syst}} - \frac{dq}{T_{surr}} = 0$$

• Irreversible process (spontaneous):

The system + surrounding = universe, can be considered an isolated system. For any isolated system, $dS_{\text{univ}} = dS_{\text{syst}} + dS_{\text{surr}} > 0$

$$\boxed{\Delta S_{univ} \geq 0}$$

Entropy and Equilibrium



• For an isolated system, spontaneous changes will occur until the entropy is maximized. This leads to equilibrium.

• For a closed system (heat and work exchange with surrounding is allowed), spontaneous changes will occur until the entropy of system plus surrounding, is maximized. This leads to equilibrium.

$$dS_{total} = dS_{sys} + dS_{surr} > 0 \quad \text{Spontaneous process}$$

$$dS_{total} = dS_{sys} + dS_{surr} = 0 \quad \text{Equilibrium process}$$

$$dS_{total} = dS_{sys} + dS_{surr} < 0 \quad \text{Impossible process}$$

For any process

$$dS_{sys} + dS_{surr} \geq 0$$

"=" for reversible, equilibrium
">" spontaneous (irreversible) (real)

Conditions for Spontaneity

For a closed system $\boxed{dU - TdS - dw_{pV} - dw_{\text{non } pV} \leq 0}$ Condition for spontaneity

Const. V

$dw_{pV} = 0$

$$\boxed{dU - TdS - dw_{\text{non } pV} \leq 0}$$

for $dw_{\text{non } pV} = 0$

$$\boxed{dU - TdS \leq 0} \longrightarrow \boxed{dU_{S,\,V,\ \text{no non } pV \text{ work}} \leq 0}$$

$$\boxed{dS_{U,\,V,\ \text{no non } pV \text{ work}} \geq 0}$$

Const. T

$$\boxed{d(U-TS) \leq 0}$$

$A = U - TS$

$$\boxed{dA_{V,\,T,\ \text{no non } pV \text{ work}} \leq 0}$$

Const. T

$A = U - TS$

$$\boxed{dA - dw_{\text{tot}} \leq 0}$$

$$\boxed{dA \leq dw_{\text{tot}}}$$

$$\boxed{(-dA) \geq (-dw_{\text{tot}})}$$

$$\boxed{(-dA) = (-dw_{\text{tot}})_{\max}}$$

Helmholtz's energy /
Helmholtz's free energy /
Helmholtz's function/
Maximum Work Function

For a closed system at constant T and V, the state function $A = U\text{-}TS$ decreases during the spontaneous irreversible process

Conditions for Spontaneity

For a closed system

$$dU - TdS + pdV - dw_{\text{non }pV} \leq 0$$

Condition for spontaneity

$$dH = dU + pdV + Vdp$$

Const. p,

$$dH - TdS - dw_{\text{non }pV} \leq 0$$

for $dw_{\text{non }pV} = 0$

$$dH - TdS \leq 0$$

$$dH_{S,\,p,\ \text{no non }pV\text{ work}} \leq 0$$

$$dS_{H,\,p,\ \text{no non }pV\text{ work}} \geq 0$$

Const. T

$$d(H\text{-}TS) \leq 0$$

$G = H - TS$

$$dG_{p,\,T,\,\text{no non }pV\text{ work}} \leq 0$$

Gibbs's energy / Gibbs's free energy / Gibbs's function

$$dH - TdS - dw_{\text{non }pV} \leq 0$$

Const. T
$G = H - TS$

$$-\,dG_{p,T} \geq (-\,dw_{\text{non }pV})$$

$$-\,dG_{p,\,T} = (-\,dw_{\text{non }pV})_{\max}$$

At constant temperature and pressure, chemical reactions are spontaneous in the direction of decreasing Gibbs energy.

Criteria for spontaneity

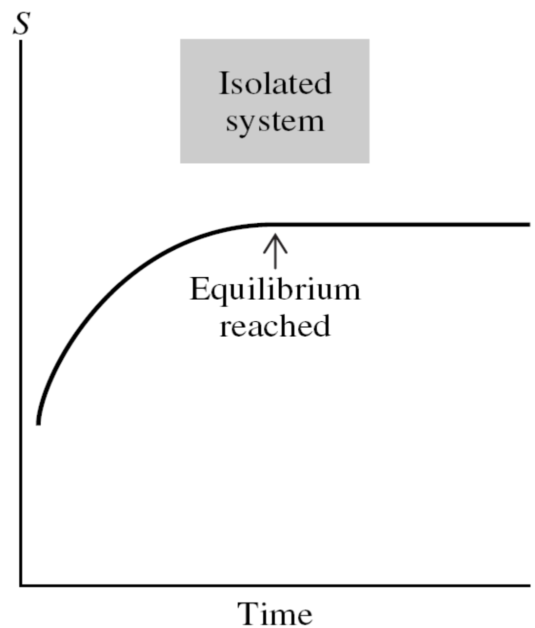
$$dS_{\text{sys}} + dS_{\text{surr}} > 0$$

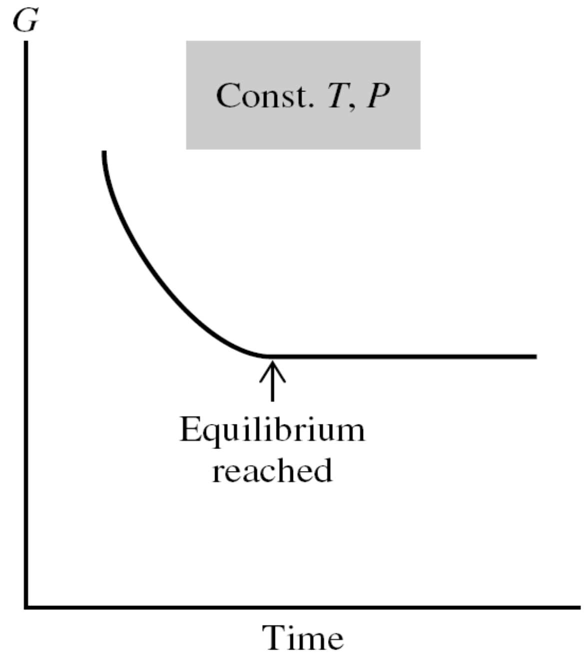
For a closed system, no non p-V (additional) work

$$dU_{S,V} \leq 0 \qquad dH_{S,p} \leq 0 \qquad dA_{V,T} \leq 0$$

$$dS_{U,V} \geq 0 \qquad dS_{H,p} \geq 0 \qquad dG_{p,T} \leq 0$$

Reversible processes carry equal sign.





Heat Engine

An engine is a device (system) that converts energy to work.

A heat engine draws heat from a hot reservoir, converts some heat to work, and releases some heat to a cold reservoir.

The engine itself is a system that undergoes a cyclical process

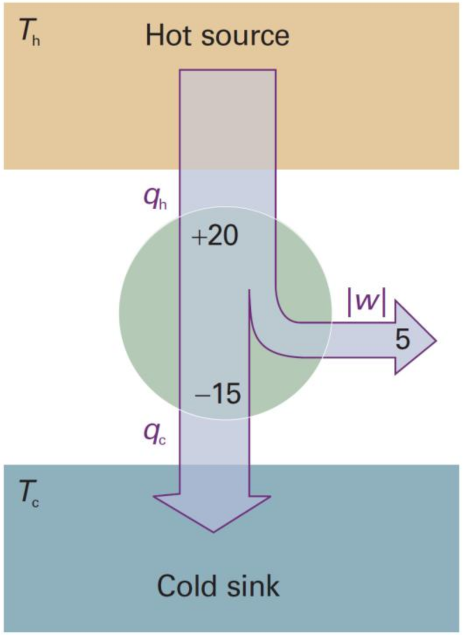


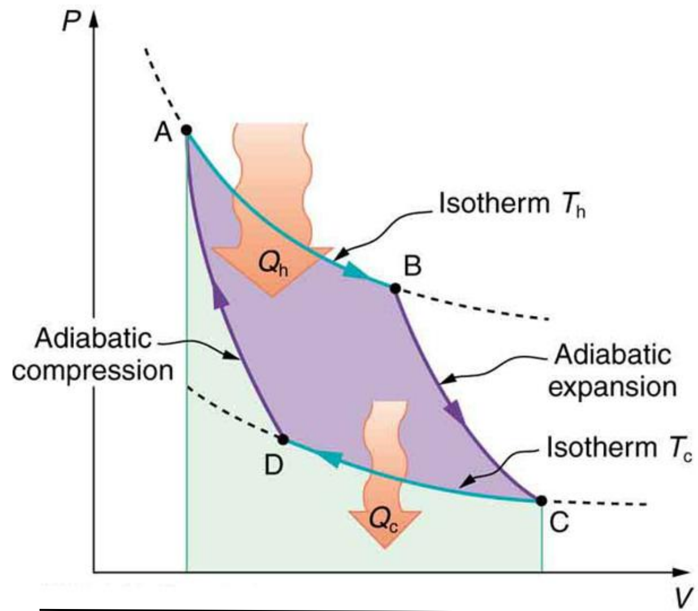
Fig. 3.7 Suppose an energy q_h (for example, 20 kJ) is supplied to the engine and q_c is lost from the engine (for example, $q_c = -15$ kJ) and discarded into the cold reservoir. The work done by the engine is equal to $q_h + q_c$ (for example, 20 kJ + (−15 kJ) = 5 kJ). The efficiency is the work done divided by the energy supplied as heat from the hot source.

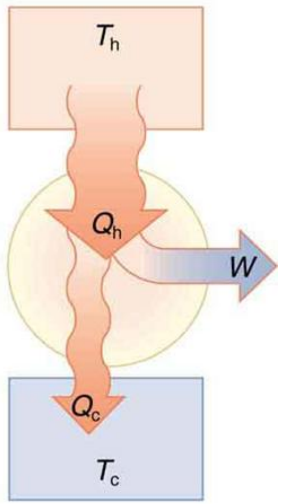
Experiments suggested:

(Clausius) An engine does not exist whose sole effect is to transfer heat from a **cold body to a hot body.**
(Kelvin) An engine does not exist that operates in a cycle and performs work by exchanging heat with only one reservoir!

Carnot Engine (1825, Sadi Carnot)

Ideal gas is used and all steps are reversible





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

$$T_h V_B^{\gamma-1} = T_C V_C^{\gamma-1}$$

$$T_h V_A^{\gamma-1} = T_C V_D^{\gamma-1}$$

$$\left(\frac{V_B}{V_A}\right)^{\gamma-1} = \left(\frac{V_C}{V_D}\right)^{\gamma-1} \quad \left(\frac{V_B}{V_A}\right) = \left(\frac{V_C}{V_D}\right)$$

$$\ln(V_D/V_C) = -\ln(V_\mathbf{B}/V_A)$$

	1 (A to B)	2 (B to C)	3 (C to D)	4 (D to A)	Total (A to A)
w	$-nRT_h \ln(V_B/V_A)$	$C_V(T_c-T_h)$	$-nRT_c \ln(V_D/V_C)$	$C_V(T_h-T_c)$	$-nR(T_h-T_c)\ln(V_B/V_A)$
q	$nRT_h \ln(V_B/V_A)$	0	$nRT_c \ln(V_D/V_C)$	0	$nR(T_h-T_c)\ln(V_B/V_A)$
ΔU	0	$C_V(T_c-T_h)$	0	$C_V(T_h-T_c)$	0
(q_{rev}/ T)	$nR\ln(V_B/V_A)$	0	$nR\ln(V_D/V_C)$	0	0

Efficiency of Carnot cycle

$$\eta = \frac{\text{work performed}}{\text{heat absorbed from source}}$$

$$\eta = \frac{-w_{\text{tot}}}{\text{q}} = \frac{nR(T_h - T_c)\ln(V_B/V_A)}{nRT_h \ln(V_B/V_A)}$$

$$= \frac{T_h - T_c}{T_h} = 1 - \frac{T_c}{T_h} < 1$$

$$\eta = 1 - \frac{T_c}{T_h} = 1 + \frac{q_c}{q_h}$$

All reversible engines have same efficiency regardless of their construction

The total change in q_{rev}/T during a Carnot cycle:

$$\boxed{\frac{q_{rev}}{T} = \frac{q_h}{T_h} + \frac{q_c}{T_c} = 0}$$

Change in q_{rev}/T around any closed path is **0**.
It is a state function.