# CY101

## Microscopic and Macroscopic Structure of Chemical Systems
## Part I: Equilibrium and Dynamics of Chemical Systems

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# Equilibrium and Dynamics of Chemical Systems

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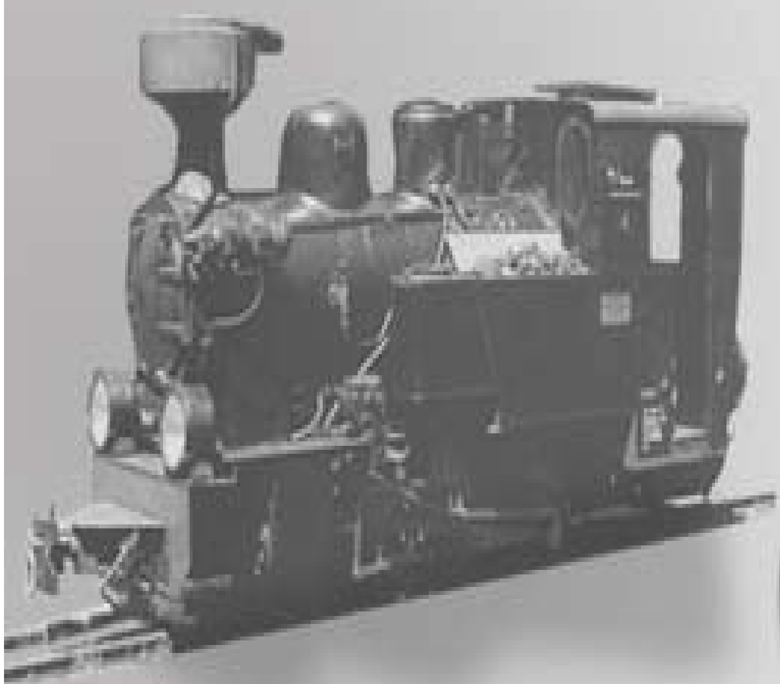

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CY 102 : Chemistry II

Department of Chemistry

Equilibrium thermodynamics: Basic concepts – The second law of thermodynamics; entropy; Calusius inequality; calculation of entropy changes in reversible and irreversible processes; third law of thermodynamics and absolute entropy; definition of free energy and spontaneity; Maxwell relations; free energy and chemical equilibria; Gibbs-Helmohltz and van't Hoff equations; thermodynamic properties from EMF measurements; Nernst equation; phase equilibria; Clausius-Clapeyron equation; phase rule; phase diagrams; one component systems; two component systems.

Dynamics of chemical processes: Basic concepts; composite reactions; opposing, parallel and consecutive reactions; reaction mechanisms; chain reactions (stationery and non-stationery); enzyme kinetics (Michaelis-Menten equation); theories of reaction rates (collision and classical transition state theory); unimolecular reactions.

Special topics: Phase transitions in multi-component systems; elementary concept of irreversible thermodynamics; fuel cells; kinetics of fast reactions; relaxation techniques; surface characterisation techniques.


1. G. W. Castellan, Physical Chemistry, 3rd Edition, Narosa, New Delhi, 1995.
2. P. W. Atkins, Physical Chemistry, 6th Edition, Oxford University Press, Oxford, 1998. (or 7th Ed.)

Teaching schedule:

Chemical Thermodynamics:

L1 Basic concepts – The second law of thermodynamics; entropy (relate it to statistical thermodynamics)

L2 Calculation of entropy changes in reversible and irreversible processes

L3 Third law of thermodynamics and absolute entropy; indication of how $S = k\ln W$ can be arrived at

L4 Clausius inequality; definition of free energy and spontaneity; conditions of equilibrium and spontaneity

L5 Free energy and chemical equilibria; Gibbs-Helmohltz and van't Hoff equations

L6 Thermodynamic properties from EMF measurements; Nernst equation

L7 Phase equilibria; Calusius-Clapeyron equation

L8 Phase rule; phase diagrams; one component systems ($H_2O$, $CO_2$, S)

L9 Two component systems

Dynamics of chemical processes:
L10-11 Basic concepts; composite reactions; opposing; parallel and consecutive reactions
L12 Reaction mechanisms; chain reactions (stationery and non-stationery)
L13 Enzyme kinetics (Michaelis-Menten equation)
L14-15 Theories of reaction rates (collision and classical transition state theory)
L16 Unimolecular reactions

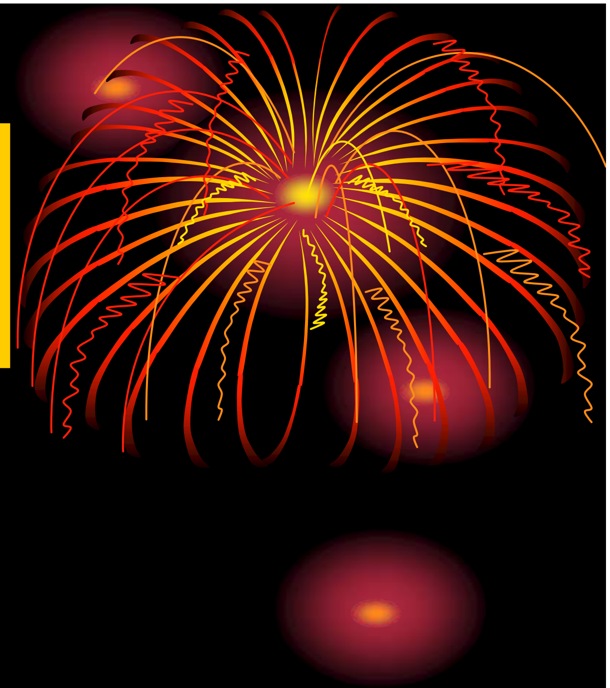
Special topics:
L17 Fast reaction kinetics
L18 Phase diagram of multi-component systems

L19: Discussion of QII somewhere in between
L20: Tutorial somewhere in between

Thermodynamics comes from Greek roots.
heat (thermo) and energy, or power (dynamics)
Thermodynamics is the study of heat and energy, and how it relates to matter in our universe.

That means, it is about everything.

# E



$P, T, n_1, n_2, \ldots.$

Fate of the system

Quantum mechanics

Thermodynamics

Statistical mechanics

## What is unique about Thermodynamics?

1. Thermodynamics is like an accountant.
In chemical systems, thermodynamics helps to keep a record of energy flow.

**2. It has predictive power.** Equilibrium state of a chemical system can be understood from thermodynamics.

3. It is a logical science, three (two) statements describe thermodynamics; deductions from these laws constitute the equations.

[Validity of thermodynamic laws depends only on the basic laws and the logical deductions which follow from them. ]

4. Since thermodynamics is itself a science, not dependent upon the foundations of other branches, it has an existence of its own. Independent of atomic and molecular theory.

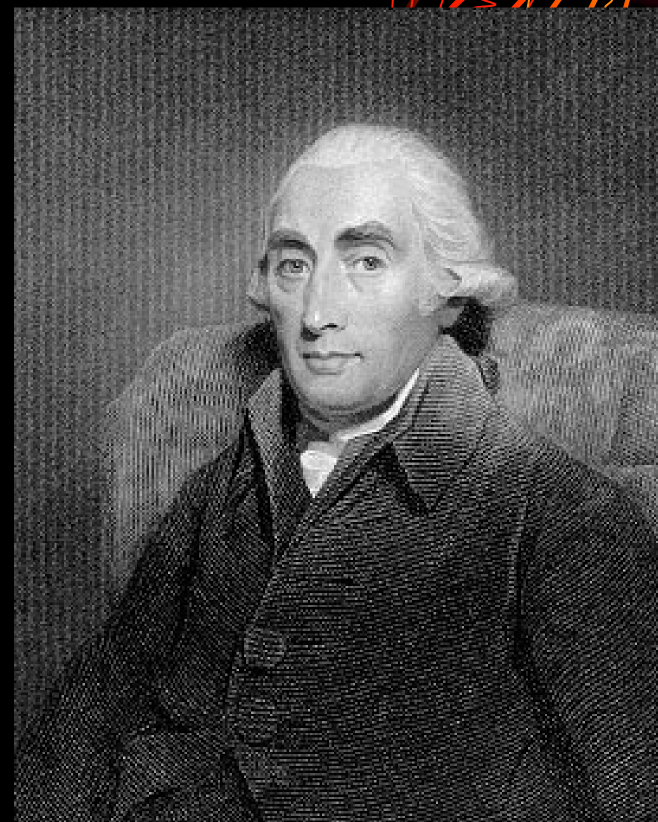
# It is all about heat….

Thermodynamics, History


This sculpture recreates a 17th century experiment by Galileo, in which hand-blown glass spheres of different weights float upward or downward depending on temperature.

**Galileo Galilei 1564-1642**

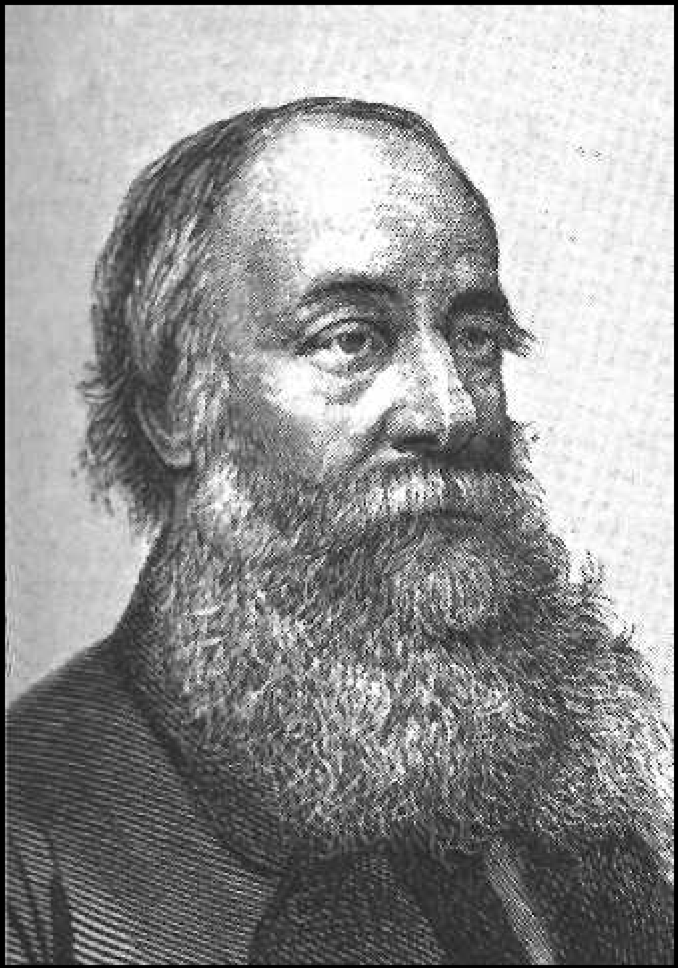
Galileo constructed the first "thermoscope" in 1592 by trapping air in a large glass bulb with a long narrow neck inverted over a container of water or wine. Any change in the temperature of the room causes the air in the bulb to expand or contract, forcing the liquid to travel up or down the tube. It was not until almost 20 years later, however, that a colleague of Galileo suggested adding a scale to the thermoscope to make the first thermometer

**Francis Bacon 1561-1626 Joseph Black, 1728 - 1799**

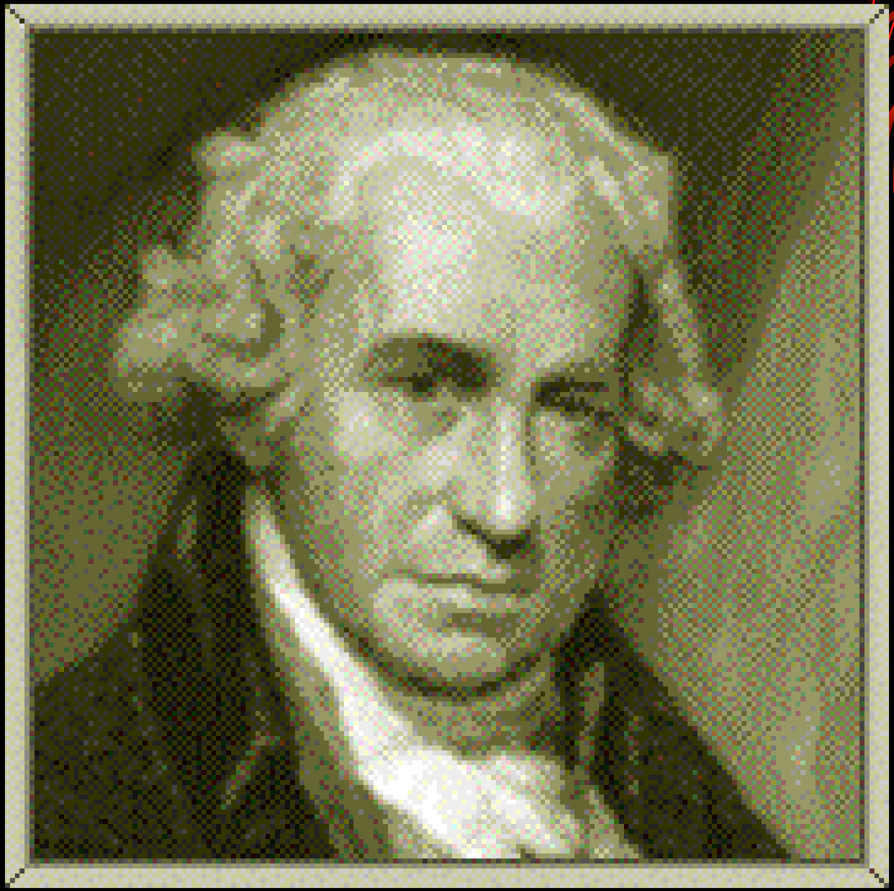
What transmitted from hot to cold?
Heat and temperature are different (1620).

Experiments on heat and temperature.
Caloric theory (1770)



**James Prescott Joule 1818-1889**

Against caloric theory.
Mechanical equivalence of heat (1840)



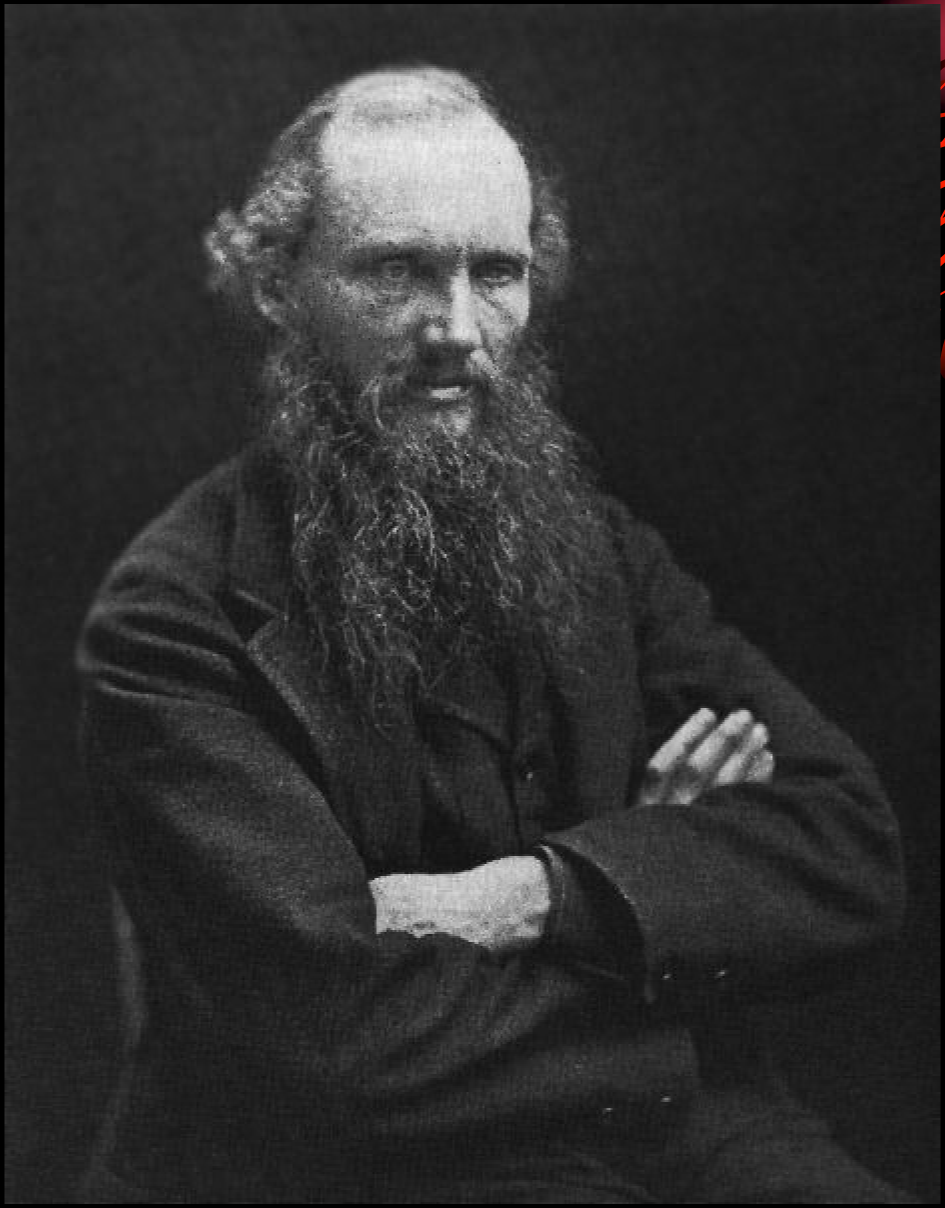
James Watt    1736 - 1819

**Sadi Carnot 1796-1832**

Theoretical heat engine. 1824 “On the Motive Power of Fire”

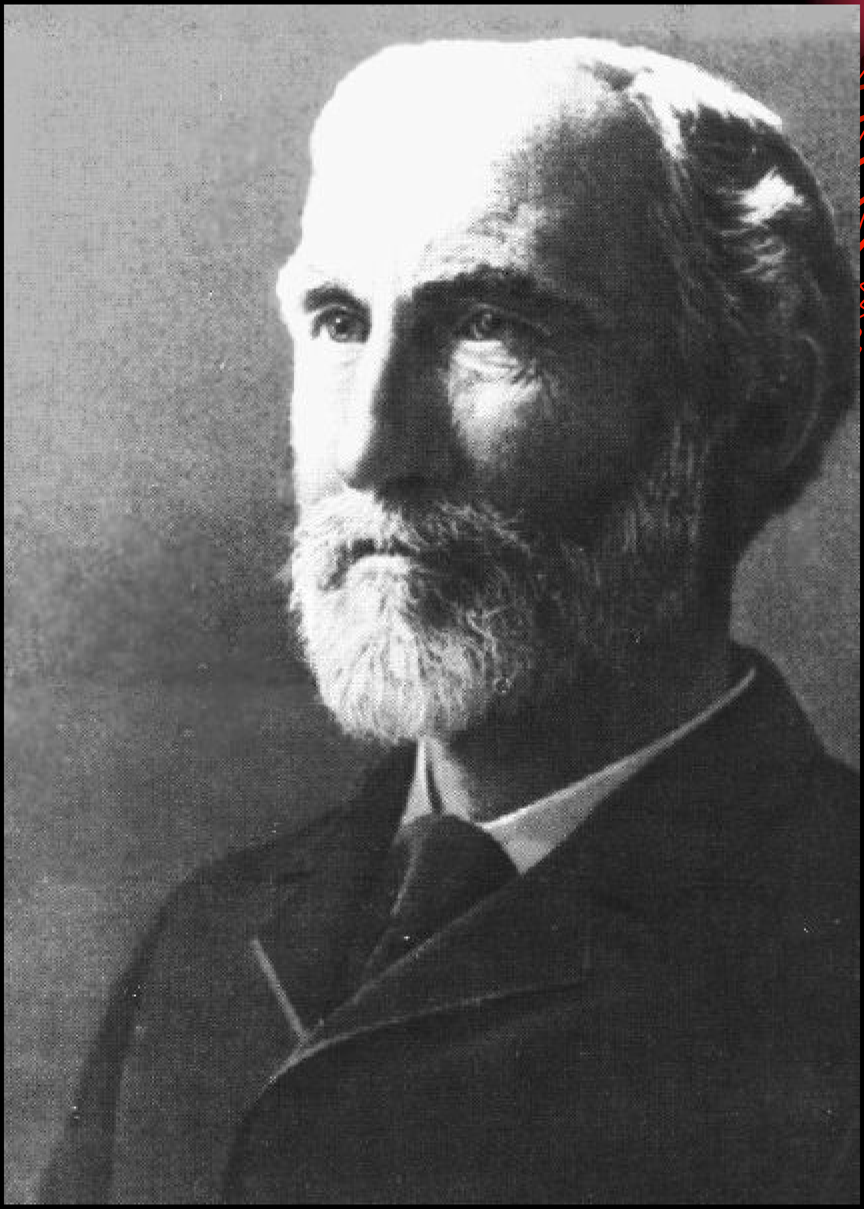
## Rudolf Clausius 1822 - 1888

Stated 1st and 2nd law (1850)



**Lord Kelvin (William Thomson) 1824-1907**

Ludwig Boltzmann 1844-1906



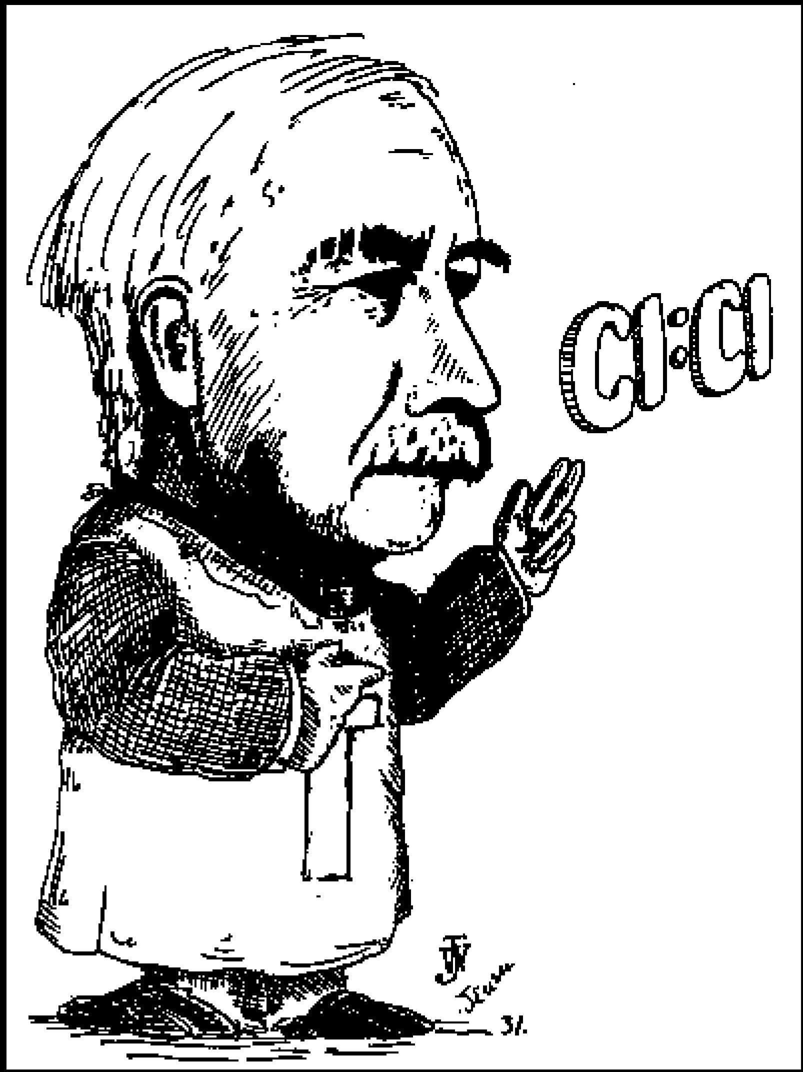
1873-1878,
Chemical Equilibrium

**Josiah Willard Gibbs 1839-1903**

Jacobus Henricus van 't Hoff 1852-1911

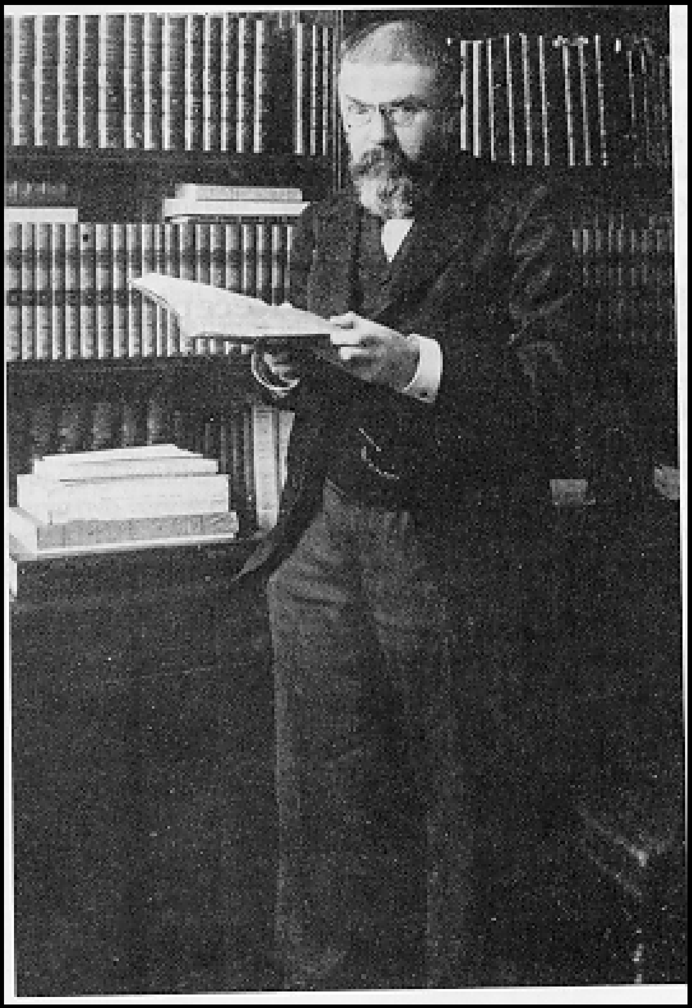

**Walther Hermann Nernst 1864 - 1941**

Third Law, 1918




**Gilbert Newton Lewis 1875-1946**

1923: Activity



**Henri Poincare 1854 - 1912**

# Antoine-Laurent Lavoisier (1743–1794)

“Analysis and Synthesis of Air--Composition of Oxides and Acids--Composition of Water--Theory of Combustion--Respiration and Animal Heat--Permanence of Weight of Matter and Simple Substances- -Imponderable Nature of Heat and Its Role in Chemistry. “

**System**

**Surroundings**

**Characterization of a system**

Based on properties

(1) intensive properties and (2) extensive properties

**Types of systems**

(1) open, (2) closed, and (3) isolated systems.

(1) homogeneous or (2) heterogeneous

**Chemical system**

Phase, Component

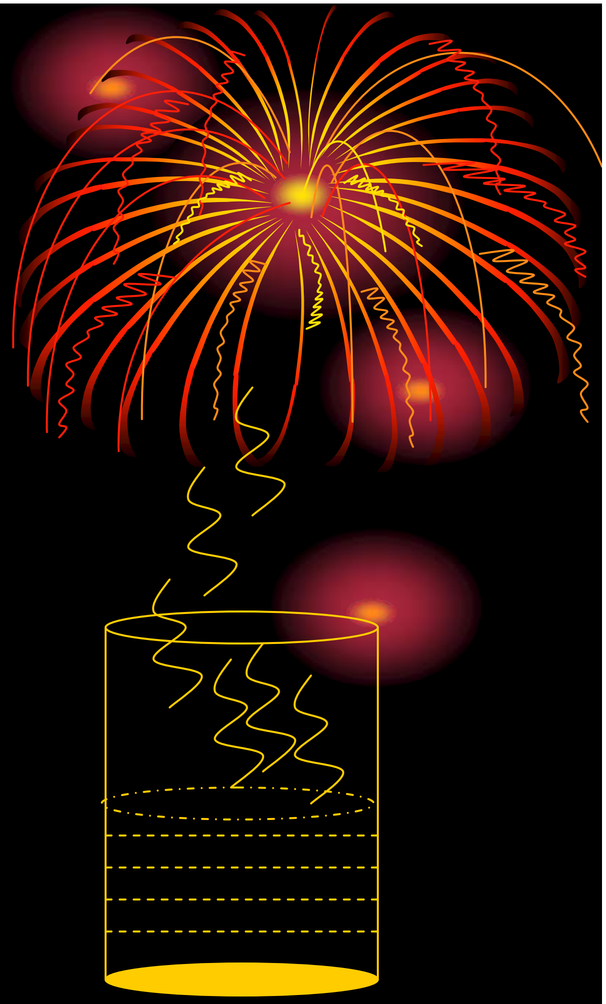
**Process, Path**

**State function, Path function**

# First Law

$$dU = dq - dw$$

$$w = \int (nRT/V)\, dV = nRT \ln V_f/V_i$$



Enthalpy, H = U + PV

State function

Thermochemistry

Hess’s Law
Lavoisier – Laplace Law
Born-Haber Cycle

Kirchhoff’s equation

Equipartition principle