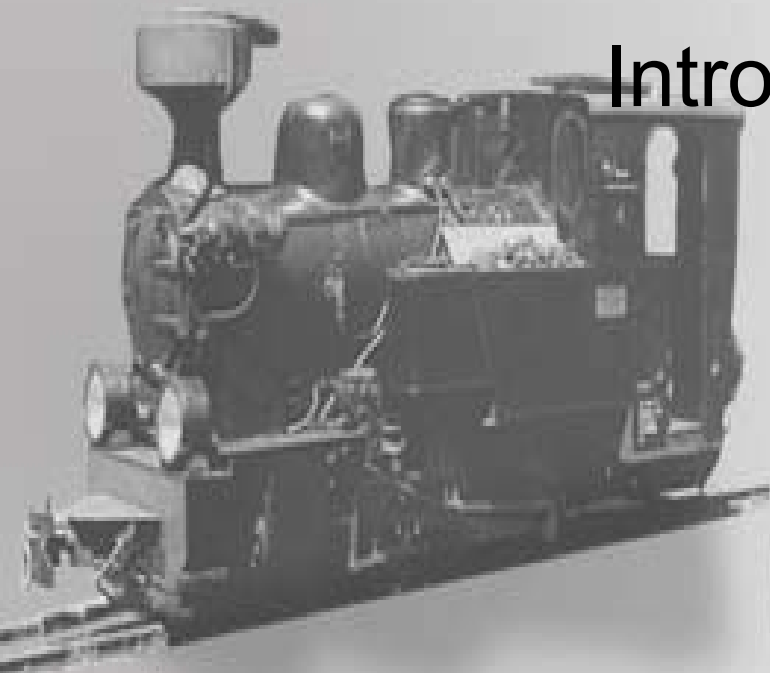
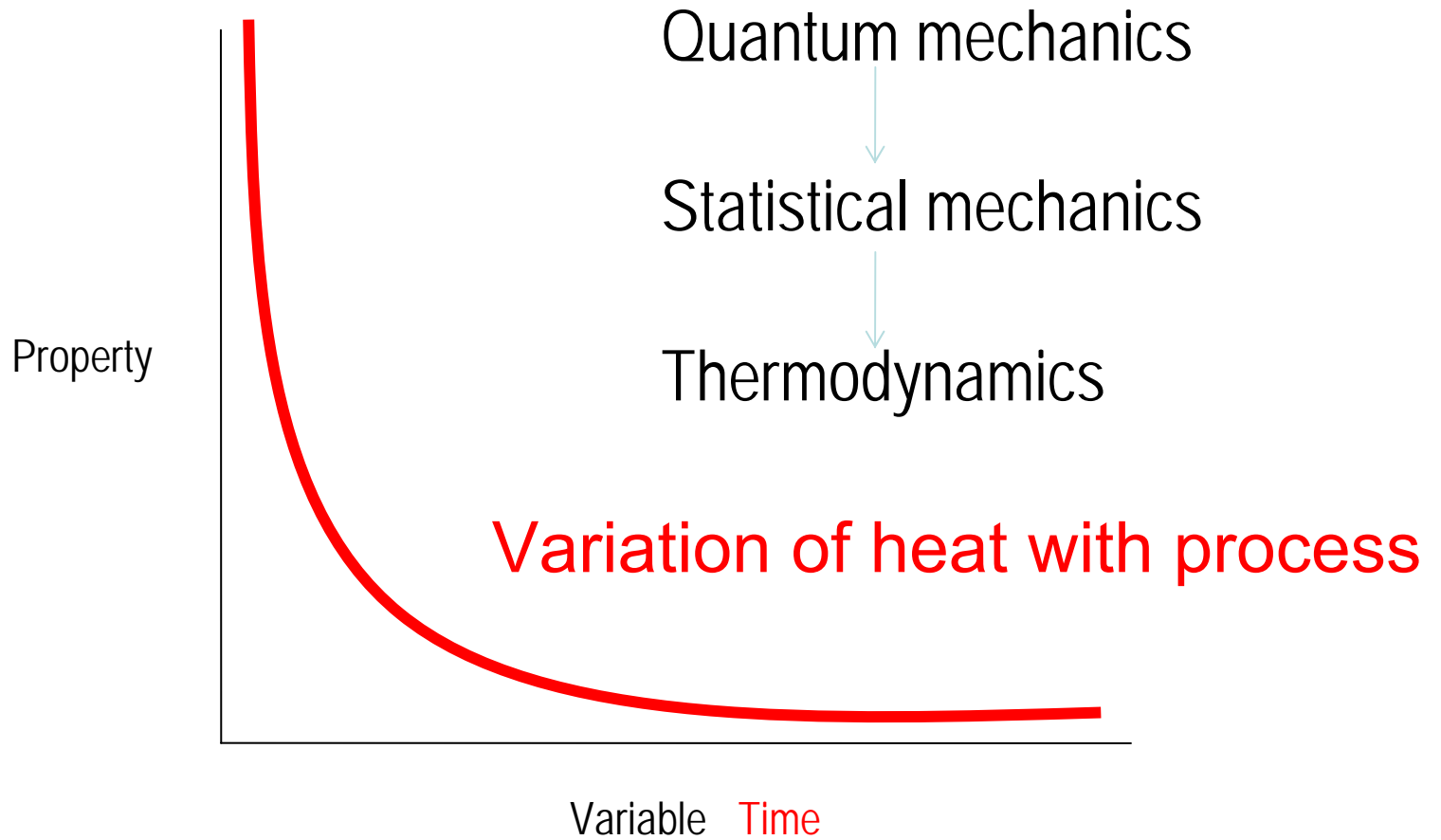


# Equilibrium and Dynamics of Chemical Systems

## Introduction to thermodynamics

<http://courses.cc.iitm.ac.in:8900>





# What is unique about Thermodynamics?

Independent of atomic and molecular theory.

In chemical systems, thermodynamics helps to keep a record of energy flow.

Equilibrium state of a chemical system can be understood from thermodynamics.

It is a logical science, three 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.

Since thermodynamics is itself a science, not dependent upon the foundations of other branches, it has an existence of its own.

A theory is the more impressive the greater the simplicity of its premises, the more different kinds of things it relates, and the more extended its area of applicability. Hence the deep impression that classical thermodynamics made upon me. It is the only physical theory of universal content concerning which I am convinced that, within the framework of the applicability of its basic concepts, it will never be overthrown.

Albert Einstein

1. Chemical thermodynamics
2. Statistical thermodynamics
3. Kinetics
4. Surface science

#### Books:

1. G. W. Castellan, Physical Chemistry, 3<sup>rd</sup> Edition, Narosa, New Delhi, 1995.
2. P. W. Atkins, Physical Chemistry, 8<sup>th</sup> Edition, Oxford University Press, Oxford, 1998.
3. Silbey, Alberty, Bawendi, Physical Chemistry, 4th Ed.

Lecture schedule

Tutorials

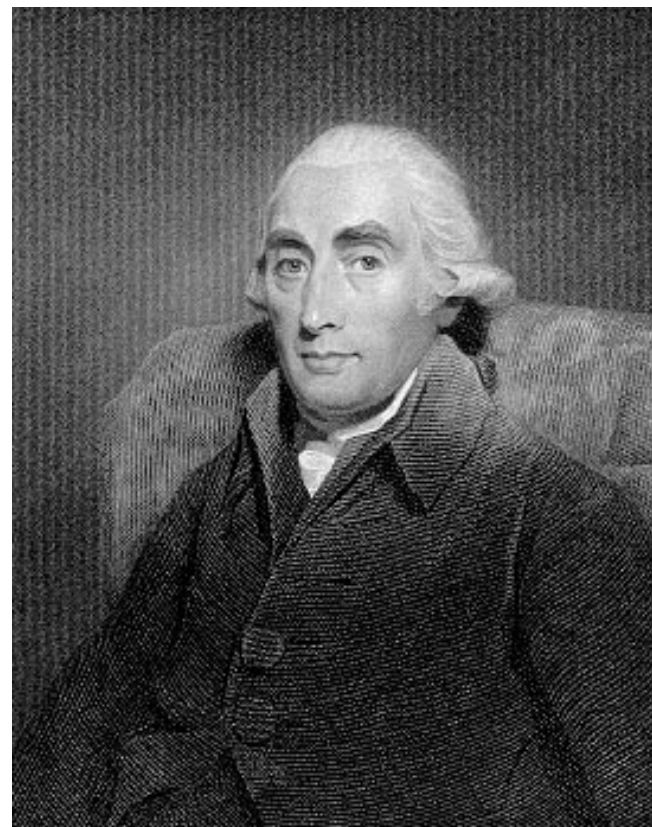
Evaluation

It is all about heat.....

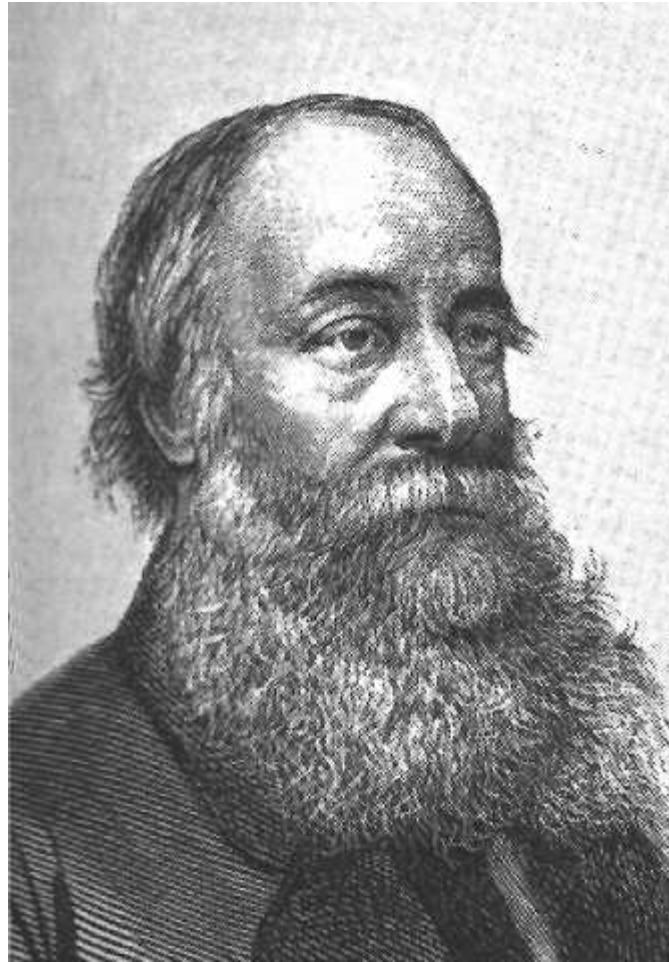


**Galileo Galilei 1564-1642**

Thermodynamics, History

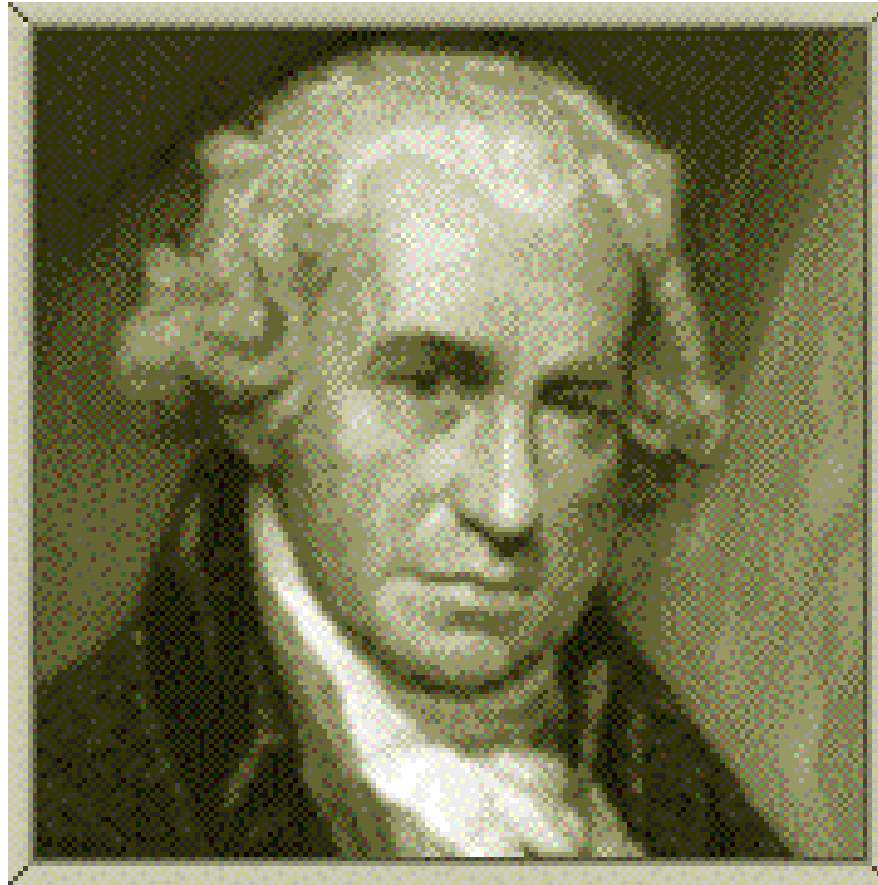


**Francis Bacon 1561-1626 Joseph Black, 1728 - 1799**



**James Prescott Joule 1818-1889**





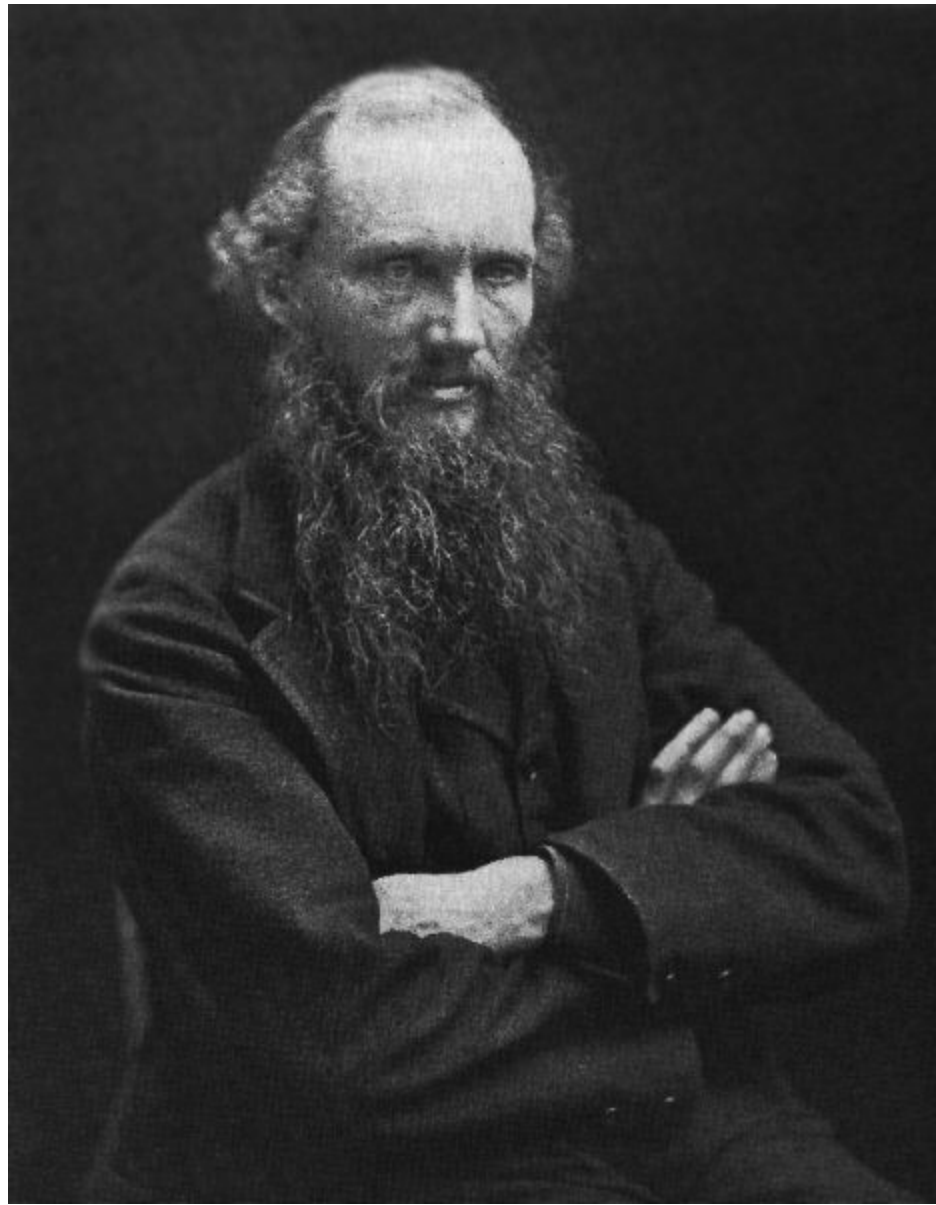
**James Watt 1736 - 1819**



**Sadi Carnot 1796-1832**



**Rudolf Clausius 1822 - 1888**



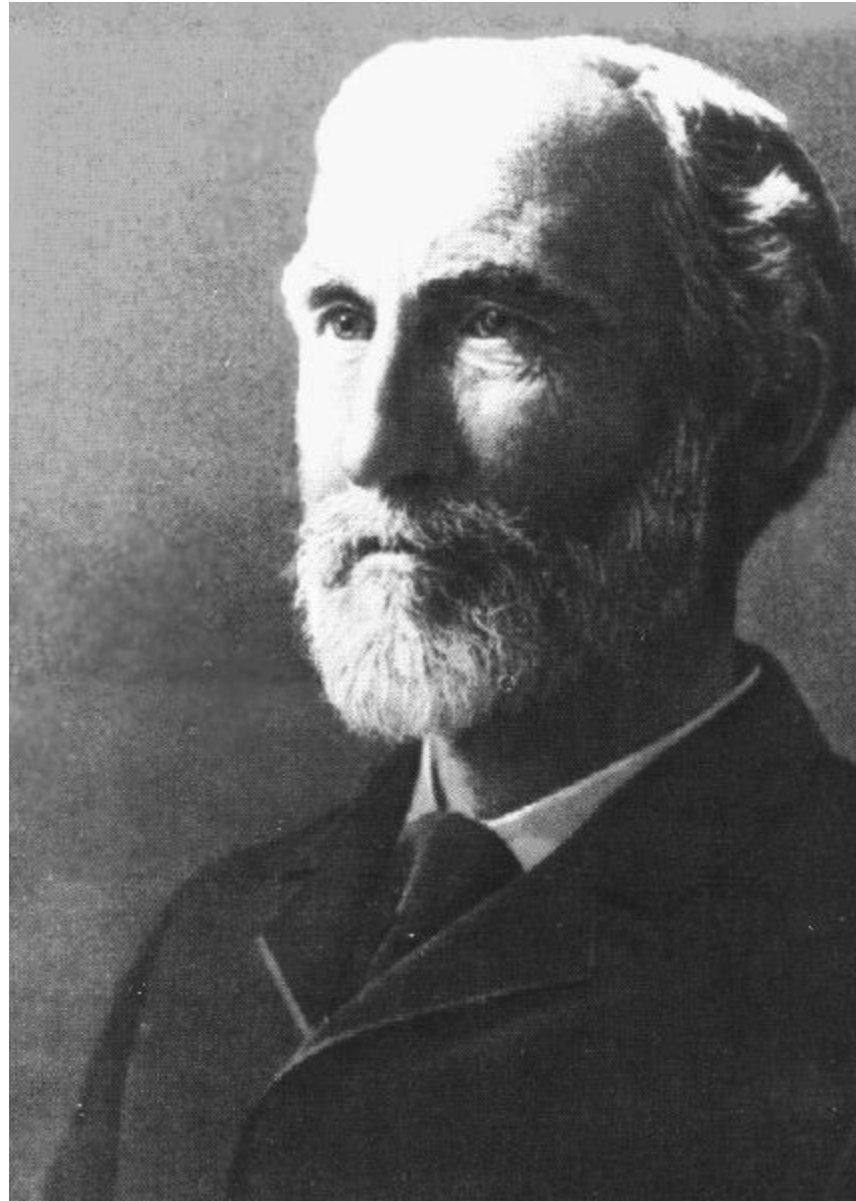
**Lord Kelvin (William Thomson) 1824-1907**

Lectures of T. Pradeep



**Ludwig Boltzmann 1844-1906**

Lectures of T. Pradeep



**Josiah Willard Gibbs 1839-1903**  
Lectures of T. Pradeep



**Jacobus Henricus van 't Hoff 1852-1911**

Lectures of T. Pradeep



**Walther Hermann Nernst 1864 - 1941**





## Gilbert Newton Lewis 1875-1946

# 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

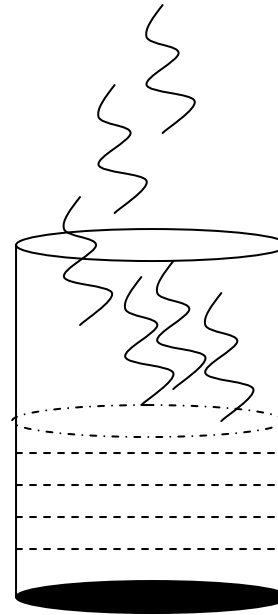
### Process, Path

State function, Path function

Exact and inexact differentials

Work, heat  
Exothermic, endothermic

# First Law



$$dU = dq - dw$$

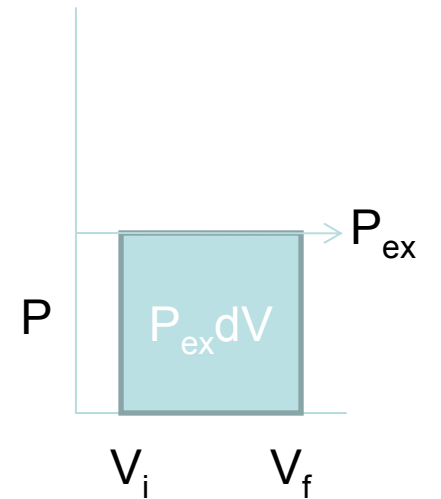
Internal energy of an isolated system is constant

$$\text{Work} = -P_{\text{ex}} dV$$

$$\text{Free expansion} = 0$$

$$\text{Isothermal work} = \int -(nRT/V) dV = -nRT \ln V_f/V_i$$

(reversible)



Indicator diagram  
James Watt

**Enthalpy,  $H = U + PV$**   
**Calorimetry**  
**Isotherm and adiabat**

**Thermochemistry**  
**Heat of formation,  $\Delta_f H^\circ$**

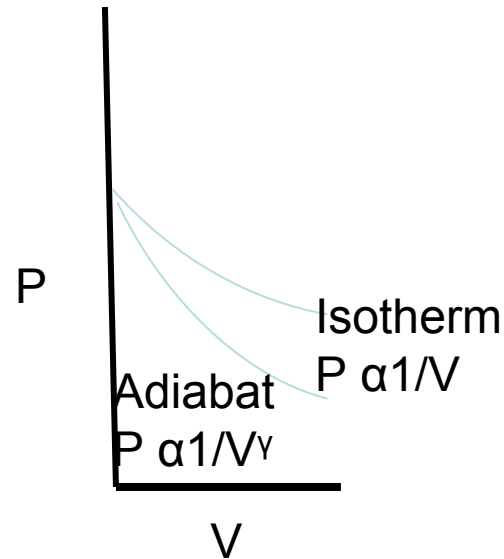
**Hess's Law**

**Born-Haber Cycle**

**Kirchhoff's equation**

$$\Delta_r H^\circ (T_2) = \Delta_r H^\circ (T_1) + \int \Delta_r C_p^\circ dT$$

**Equipartition principle**



Joule experiment  $\Pi_T = (\partial U / \partial V)_T$

Joule-Thomson Experiment

$$\mu = (\partial T / \partial P)_H$$