

CY1001

BASIC CONCEPTS

Lecture 1

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Atomists and ionists

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

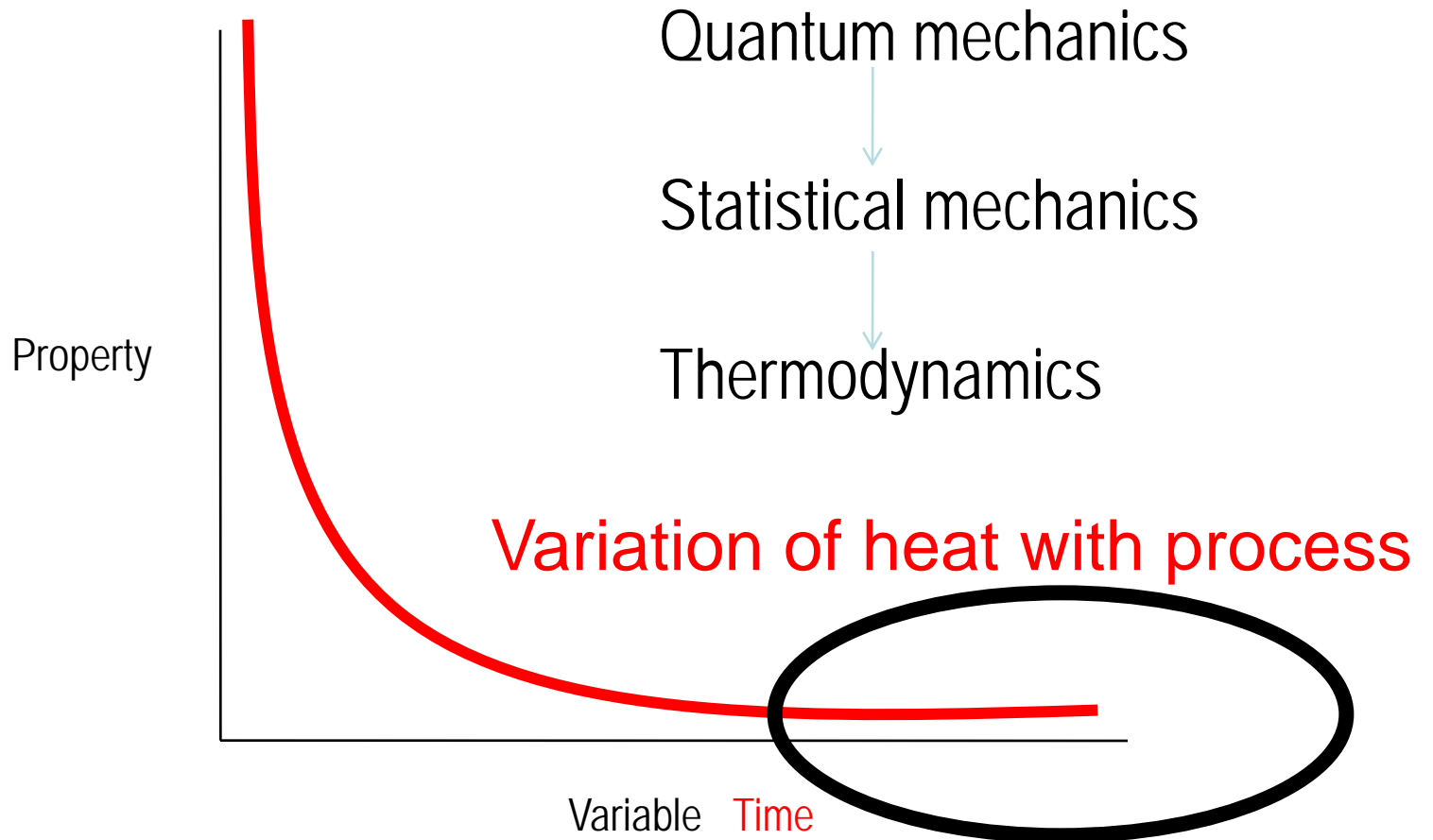
Books:

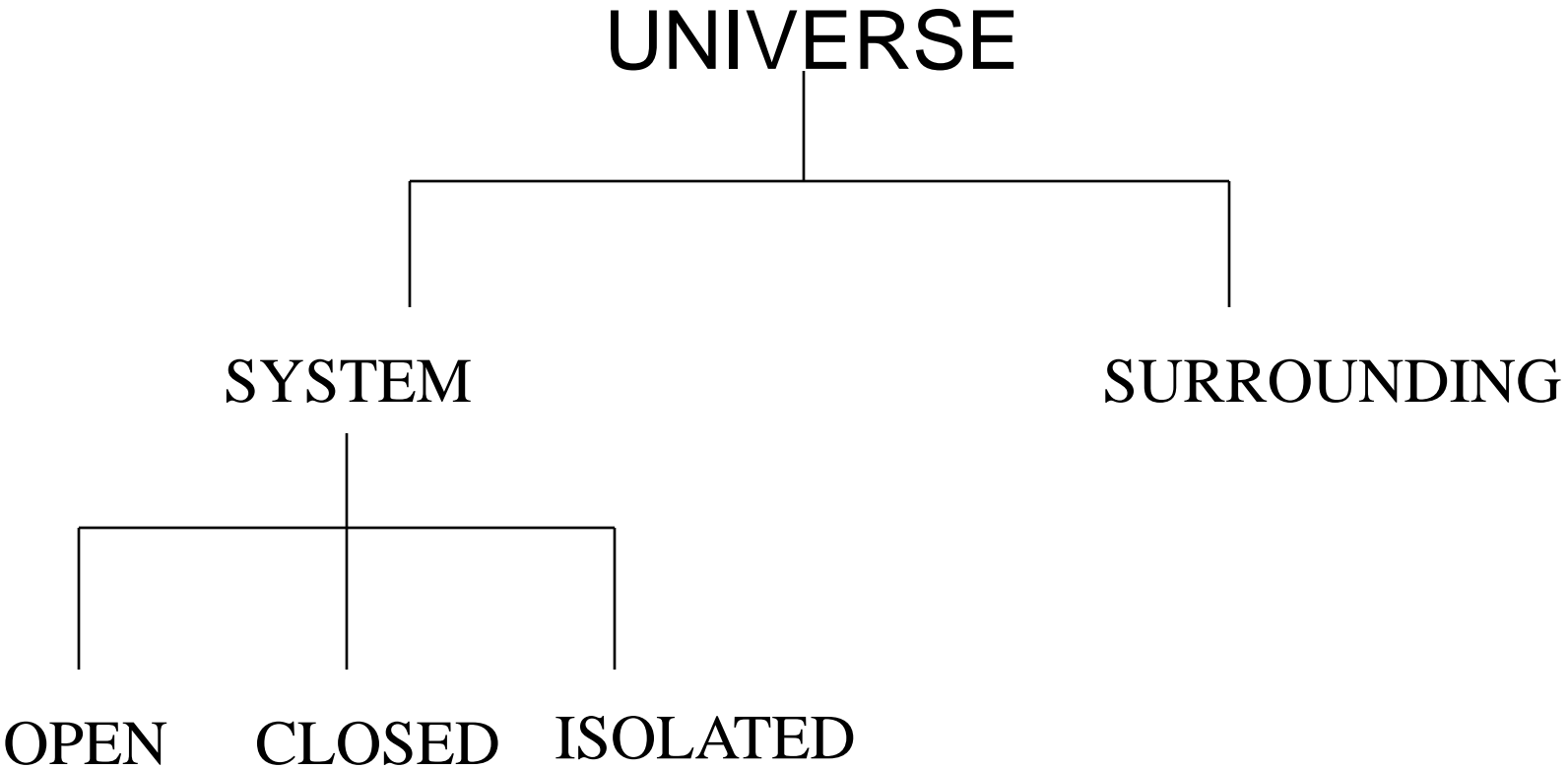
1. G. W. Castellan, Physical Chemistry, 3rd Edition, Narosa, New Delhi, 1995.
2. P. W. Atkins, Physical Chemistry, 8th Edition, Oxford University Press, Oxford, 1998.
3. Silbey, Alberty, Bawendi, Physical Chemistry, 4th Ed.

Lecture schedule

Tutorials

Evaluation





Intensive and Extensive Variables

Pressure, Volume, Temperature, Heat, Mass

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

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

Zeroth Law

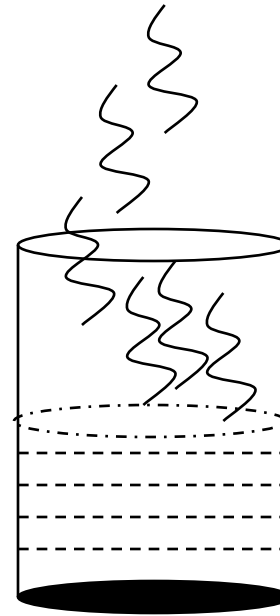
$A \longleftrightarrow B$ and $B \longleftrightarrow C$, then $A \longleftrightarrow C$ { $\longleftrightarrow =$ thermal equilibrium }

First Law

Law of conservation of energy

Work, heat
Exothermic, endothermic

First Law



$$dU = dq - dw$$

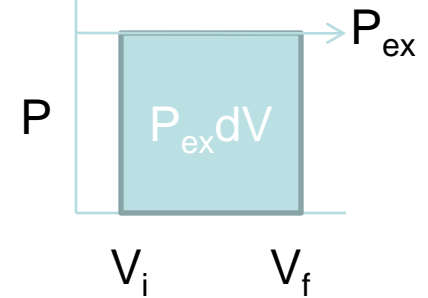
Internal energy of an isolated system is constant

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

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

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

(reversible)



Indicator diagram
James Watt

q and w are **positive**, when energy is transferred to the system

q and w are **negative**, when energy is lost from the system

Exact and Inexact differentials

$$\int_a^b dU = U_b - U_a = \Delta U \quad \text{Exact differential}$$

$$\int_a^b \partial w = w(\neq w_b - w_a) \quad \text{Inexact differential}$$

Test for exactness-Euler's theorem

if $z = f(x, y)$ then, $dz = \left(\frac{\partial z}{\partial x}\right)_y dx + \left(\frac{\partial z}{\partial y}\right)_x dy$

When $\left[\frac{\partial}{\partial y}\left(\frac{\partial z}{\partial x}\right)_y\right]_x = \left[\frac{\partial}{\partial x}\left(\frac{\partial z}{\partial y}\right)_x\right]_y$ Then z is an **exact differential**

Sum of two inexact differentials can be
an exact differential (first law)

Inexact differentials can be converted to exact differentials by
multiplying with integrating factors

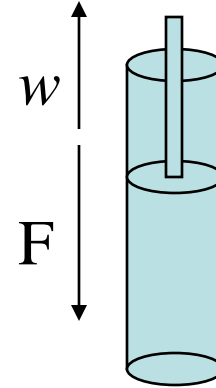
The General Expression for Work

From Physics, Work, $w = Fd \cos \theta$

When $\theta = 180^\circ$, Work, $w = -Fd$

$$dw = -F.dz$$

But, $F = \text{Pressure} \times \text{Area} = P.A$



Therefore, $dw = -P.A.dz$

Now, $A.dz = dV$

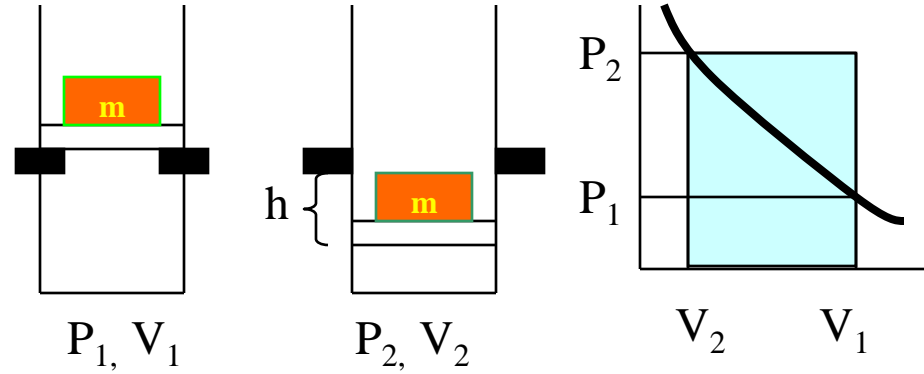
$$dw = -P.dV \quad w = -\int_{V_1}^{V_2} P dV$$

Concept of reversibility

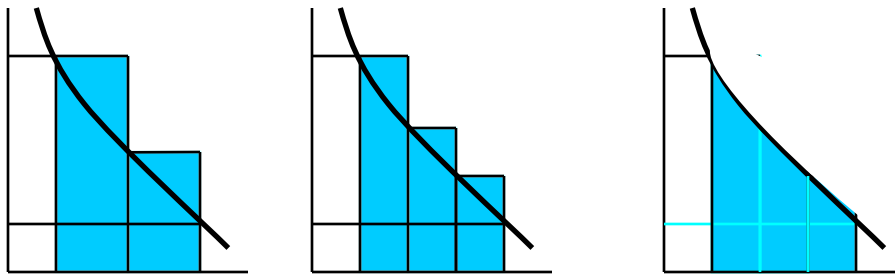
SINGLE STEP COMPRESSION

$$P_2 = \frac{mg}{A}$$

$$w = mgh = -P_2(V_2 - V_1)$$



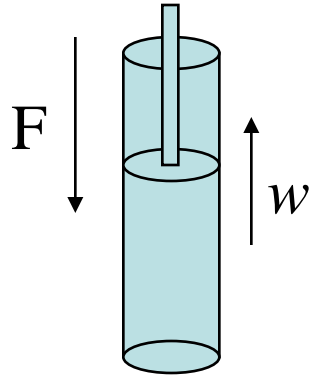
Two, three and infinite number of steps



Same compression can be Done with less work !

$$w = \int \partial w = - \int_{V_1}^{V_2} P dV$$

Different situations



- Free expansion
- Expansion against constant pressure

If P is constant,

$$w = -P(V_2 - V_1)$$

- Isothermal reversible expansion

$$w = -nRT \int_{V_1}^{V_2} \frac{dV}{V} \quad \Rightarrow \quad w = -nRT \ln \frac{V_2}{V_1}$$

HEAT CAPACITY

$$\frac{\partial q}{\partial T} = C \quad \xrightarrow{\text{Path dependant}} \quad \text{Path dependant (constant V or T)}$$

U as a function of T and V

$$dU = \left(\frac{\partial U}{\partial T} \right)_V dT + \left(\frac{\partial U}{\partial V} \right)_T dV$$

Since, $dU = \partial q - P_{ext} dV$

$$\partial q = \left(\frac{\partial U}{\partial T} \right)_V dT + \left[P_{ext} + \left(\frac{\partial U}{\partial V} \right)_T \right] dV$$

At constant volume, $\partial q_V = \left(\frac{\partial U}{\partial T} \right)_V d$

$$\frac{\partial q_V}{\partial T} = \left(\frac{\partial U}{\partial T} \right)_V = C_V$$

Heat capacity at constant volume

HEAT CAPACITY

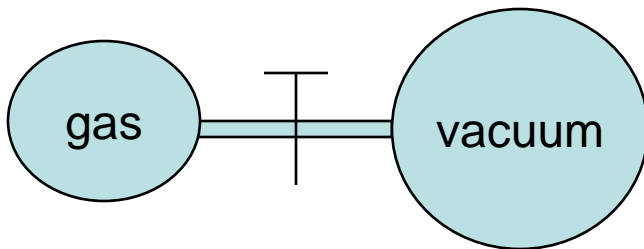
$$C_V = \left(\frac{\partial U}{\partial T} \right)_V \implies \Delta U_V = \int_{T_1}^{T_2} C_V dT$$

If C_V is constant over a small range of temperature,

$$\Delta U_V = C_V \Delta T$$

We have seen that,

$$dU = \left(\frac{\partial U}{\partial T} \right)_V dT + \left(\frac{\partial U}{\partial V} \right)_T dV$$



$$dU = \left(\frac{\partial U}{\partial V} \right)_T dV = 0$$

Since Joule Found that

$$\partial q = 0; \text{ and } \partial w = 0$$

Since $dV \neq 0$,

$$\left(\frac{\partial U}{\partial V} \right)_T = 0$$

Internal Pressure

This is not correct for real gases.

Change of state at constant pressure

Enthalpy

$$\Delta U = U_2 - U_1 = q_P - P\Delta V = q_P - P(V_2 - V_1)$$

$$q_P = (U_2 + PV_2) - (U_1 + PV_1)$$



$$q_P = H_2 - H_1$$

$$H = U + PV$$

$$\partial q_P = dH$$

H as a function of T and P $dH = \left(\frac{\partial H}{\partial T}\right)_P dT + \left(\frac{\partial H}{\partial P}\right)_T dP$

Since $\partial q_P = dH$ and at constant P, $\partial q_P = \left(\frac{\partial H}{\partial T}\right)_P dT$

$$\Rightarrow \frac{\partial q_P}{dT} = \left(\frac{\partial H}{\partial T}\right)_P = C_P$$

Heat capacity at constant pressure

If C_P is independent of temperature, $\Delta H = C_P \Delta T$

$$C_P - C_V = nR$$

$$\partial q_P = \left(\frac{\partial U}{\partial T} \right)_V dT + \left[P_{ext} + \left(\frac{\partial U}{\partial V} \right)_T \right] dV$$

divide by dT and setting $\frac{dq_P}{dT} = C_P$

$$C_P - C_V = \left[P + \left(\frac{\partial U}{\partial V} \right)_T \right] \left(\frac{\partial V}{\partial T} \right)_P$$

For an ideal gas, $\left(\frac{\partial V}{\partial T} \right)_P = \frac{nR}{P}$ and $\left[\left(\frac{\partial U}{\partial V} \right)_T \right] = 0$

$$\therefore C_P - C_V = nR$$

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

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

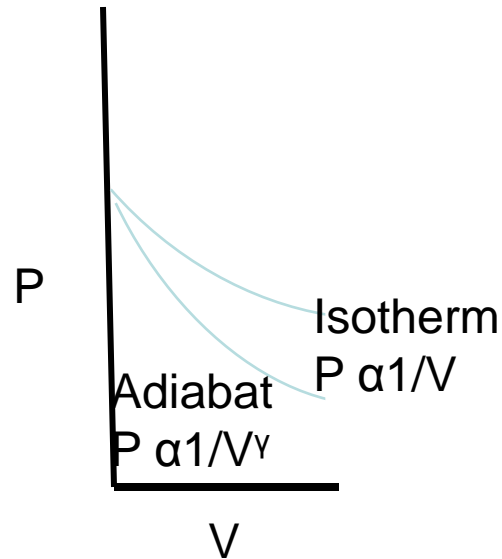
Hess's Law

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

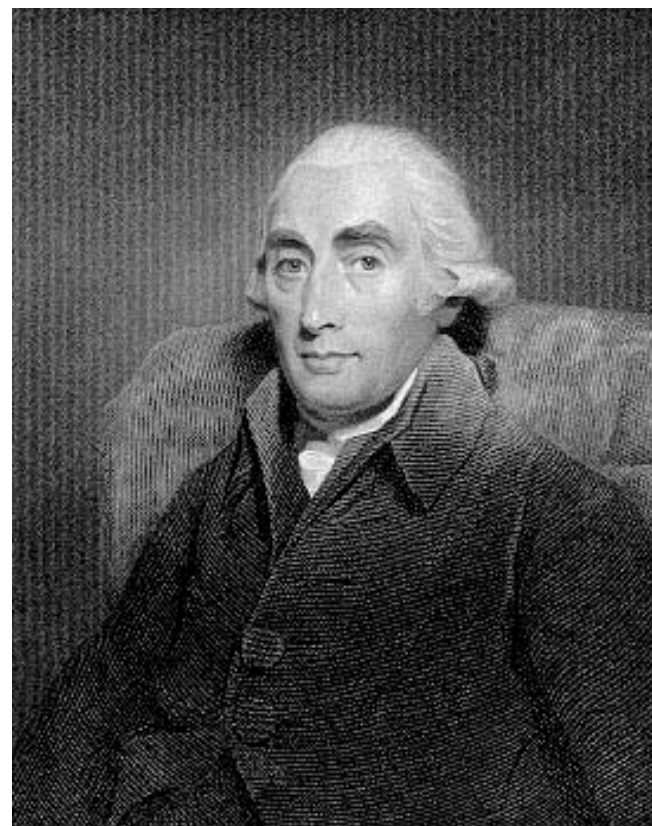
$$\mu = (\partial T / \partial P)_H$$

It is all about heat....

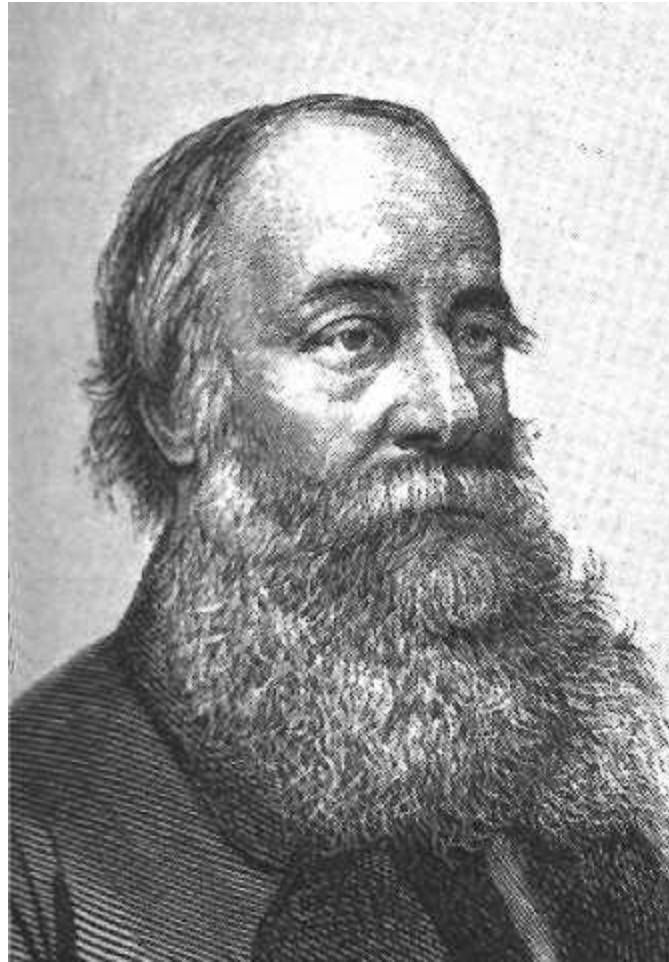


Galileo Galilei 1564-1642

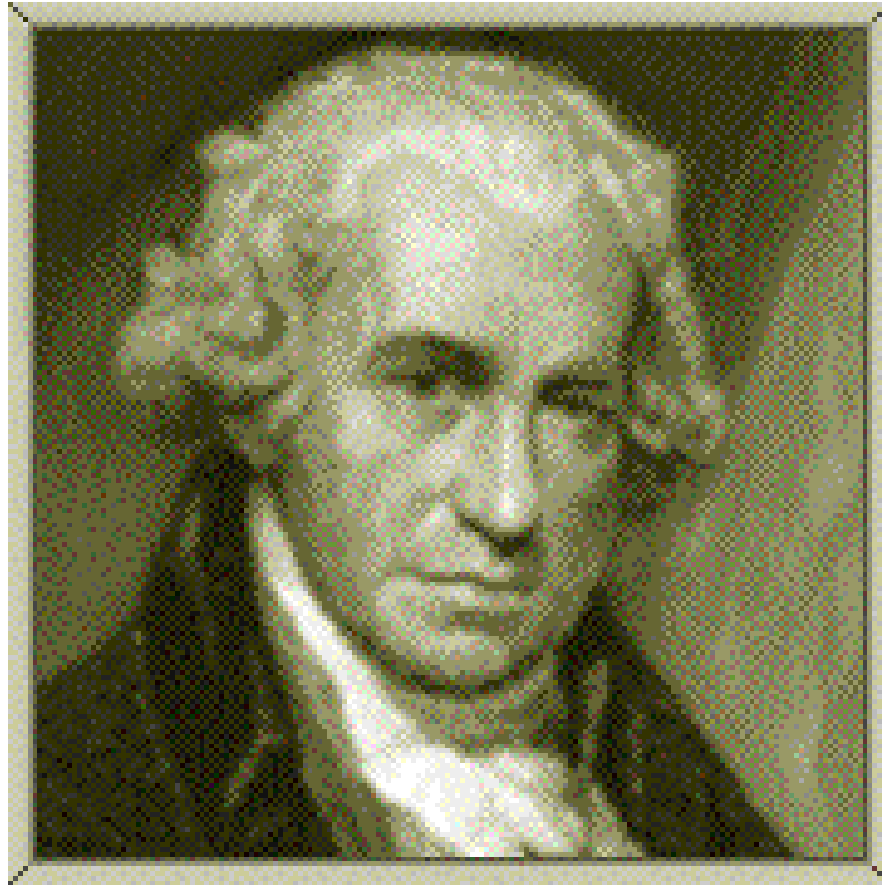
Thermodynamics, History



Francis Bacon 1561-1626 Joseph Black, 1728 - 1799



James Prescott Joule 1818-1889



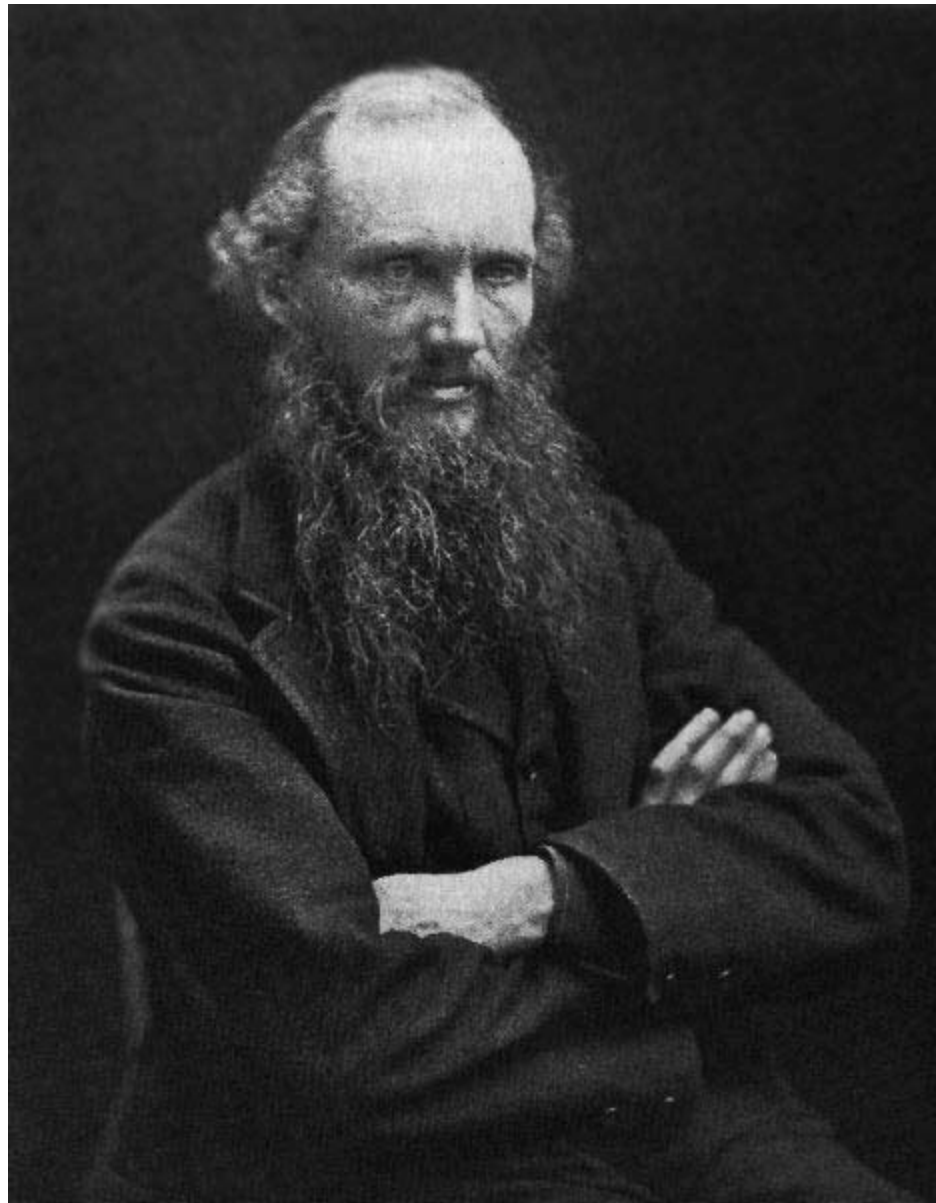
James Watt 1736 - 1819



Sadi Carnot 1796-1832



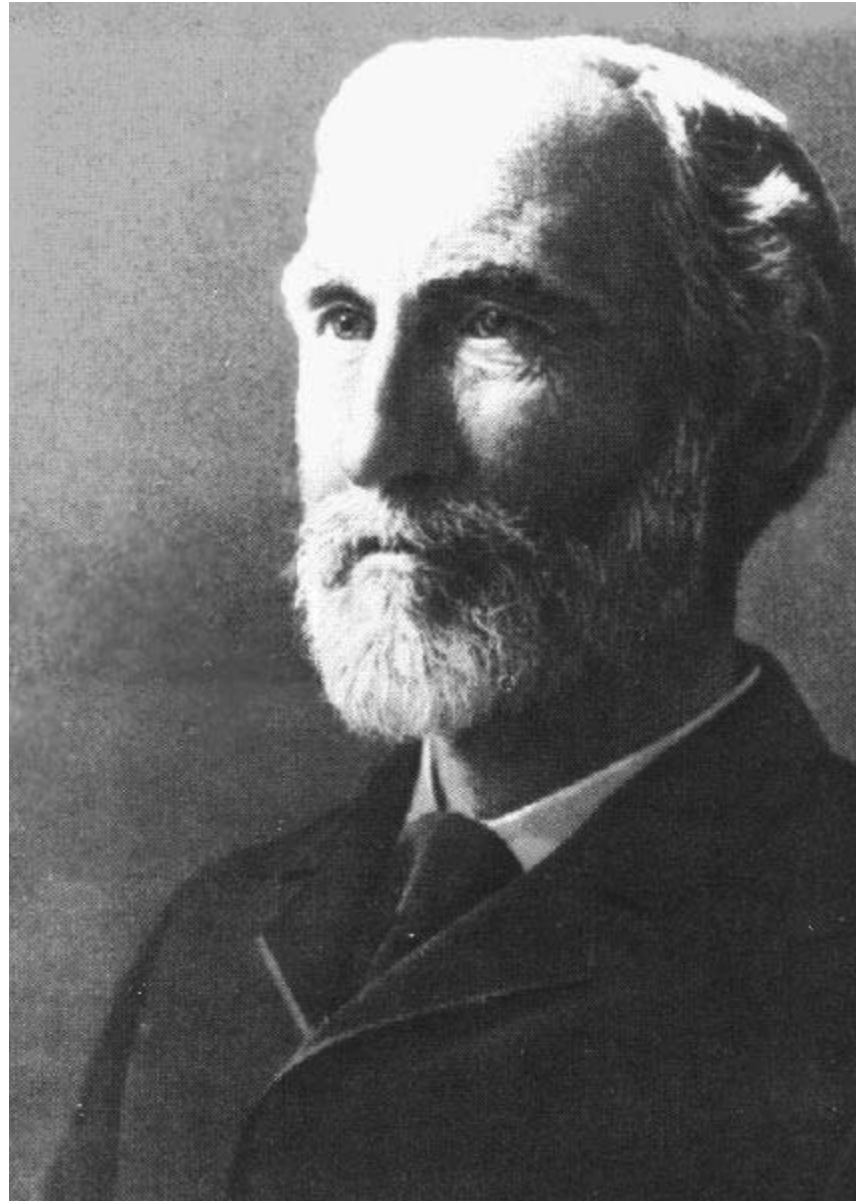
Rudolf Clausius 1822 - 1888



Lord Kelvin (William Thomson) 1824-1907



Ludwig Boltzmann 1844-1906



Josiah Willard Gibbs 1839-1903



Jacobus Henricus van 't Hoff 1852-1911



Walther Hermann Nernst 1864 - 1941



Gilbert Newton Lewis 1875-1946