

# CY1001

# BASIC CONCEPTS

Lecture 1

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## Atomists and ionists

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

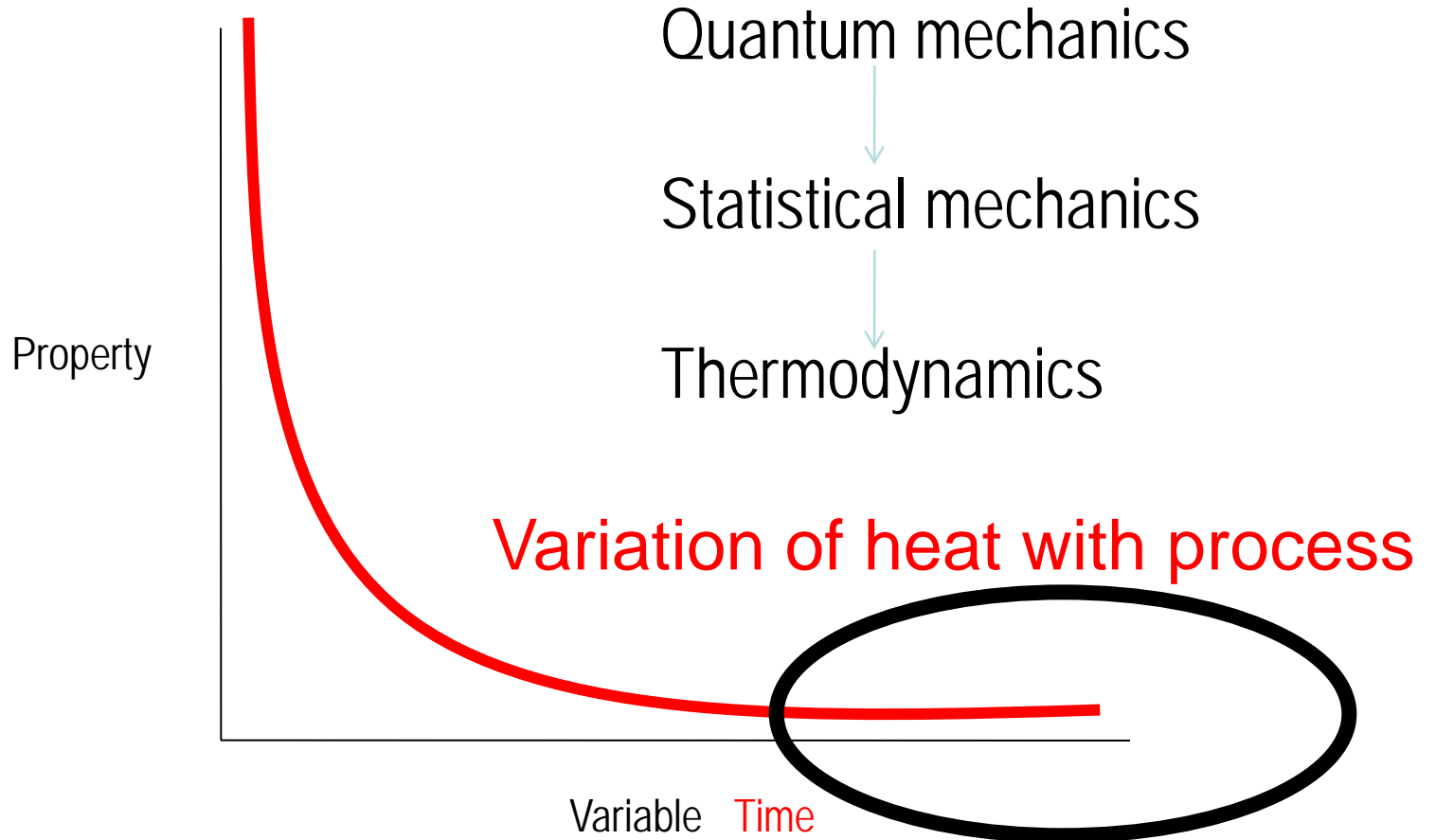
#### Books:

1. Kuhn Hans, Försterling Horst-Dieter and Waldeck David H, *Principles of Physical Chemistry*, 2<sup>nd</sup> Ed., Wiley(2009).
2. Atkins P W and de Paula Julio, *Physical Chemistry*, Oxford University Press, 8<sup>th</sup> Ed., (Indian Student Edition) (2009).
3. Silbey Robert J, Alberty Robert A, Bawendi Mounqi G., *Physical Chemistry*, (4<sup>th</sup> Ed.), Wiley (2006).

Lecture schedule

Tutorials

Evaluation



UNIVERSE

SYSTEM

SURROUNDING

OPEN    CLOSED    ISOLATED

## **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 }

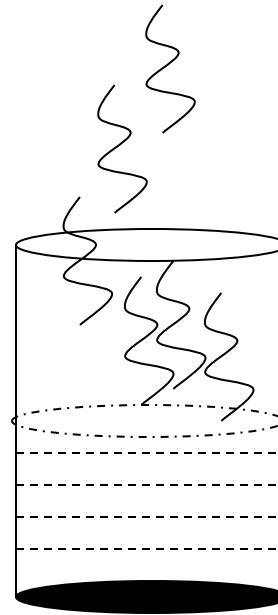
## First Law

Law of conservation of energy



Work, heat  
Exothermic, endothermic

# First Law



$$dU = dq - dw$$

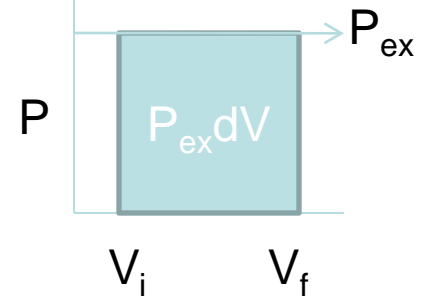
Internal energy of an isolated system is constant

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

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

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

(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

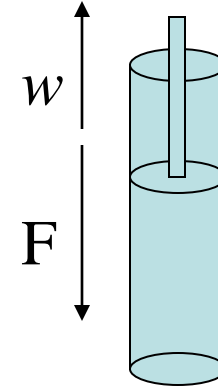
# The General Expression for Work

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,  $A.dz = dV$

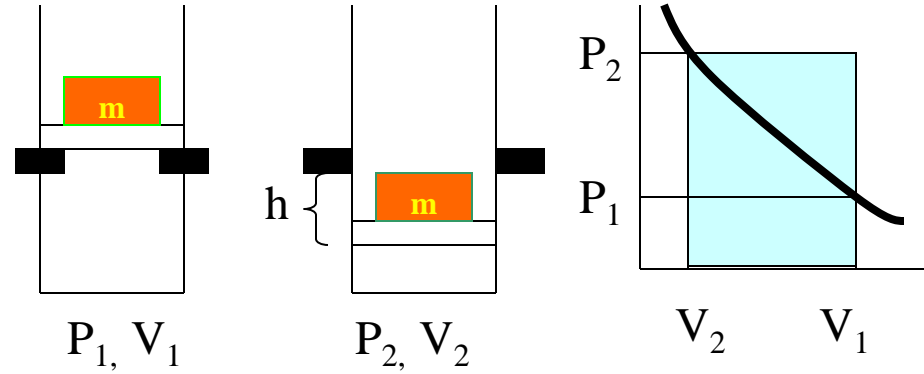
$$dw = -P.dV \quad w = -\int_{V_1}^{V_2} P dV$$

# Concept of reversibility

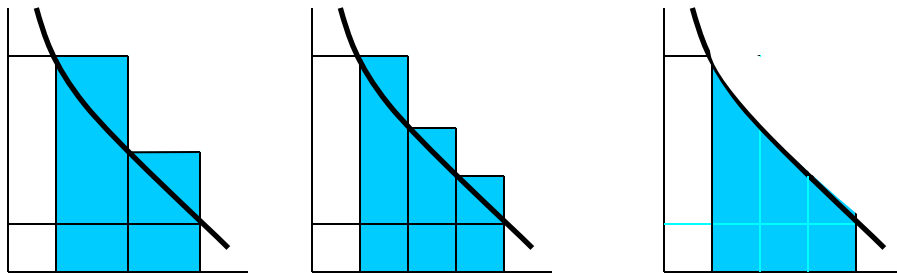
## SINGLE STEP COMPRESSION

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

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



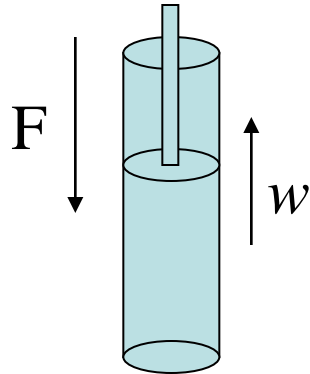
## Two, three and infinite number of steps



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

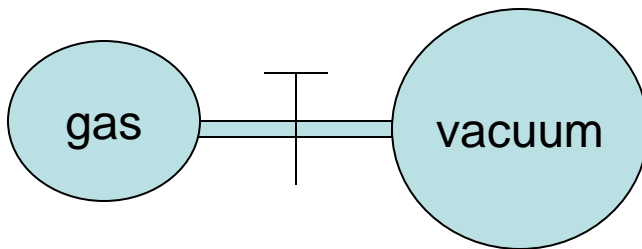
$$C_V = \left( \frac{\partial U}{\partial T} \right)_V \implies \Delta U_V = \int_{T_1}^{T_2} C_V dT$$

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

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

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



$$q_P = H_2 - H_1$$

$$H = U + PV$$

$$\partial q_P = dH$$

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,  $\Delta_f H^\circ$**

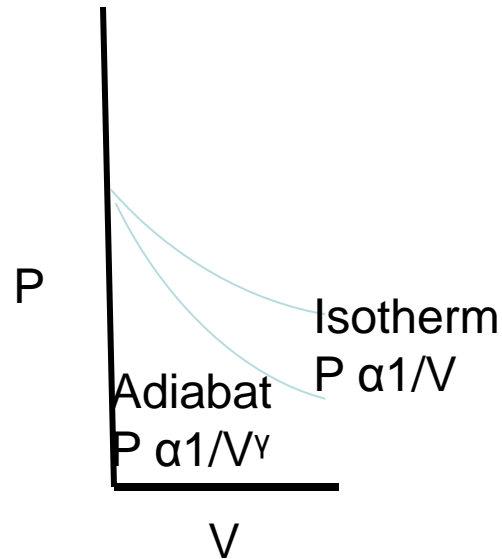
**Hess's Law**

**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

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

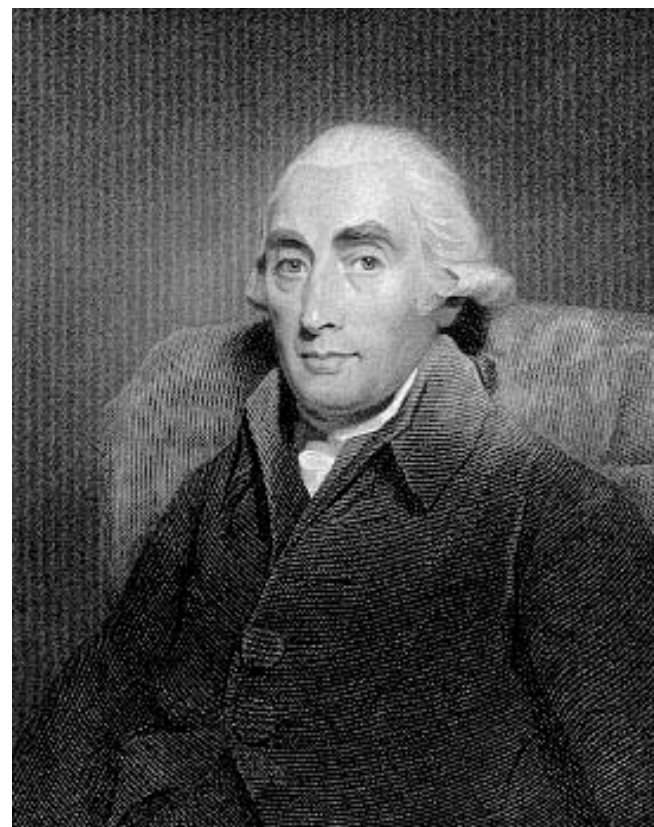
Just to know

It is all about heat....

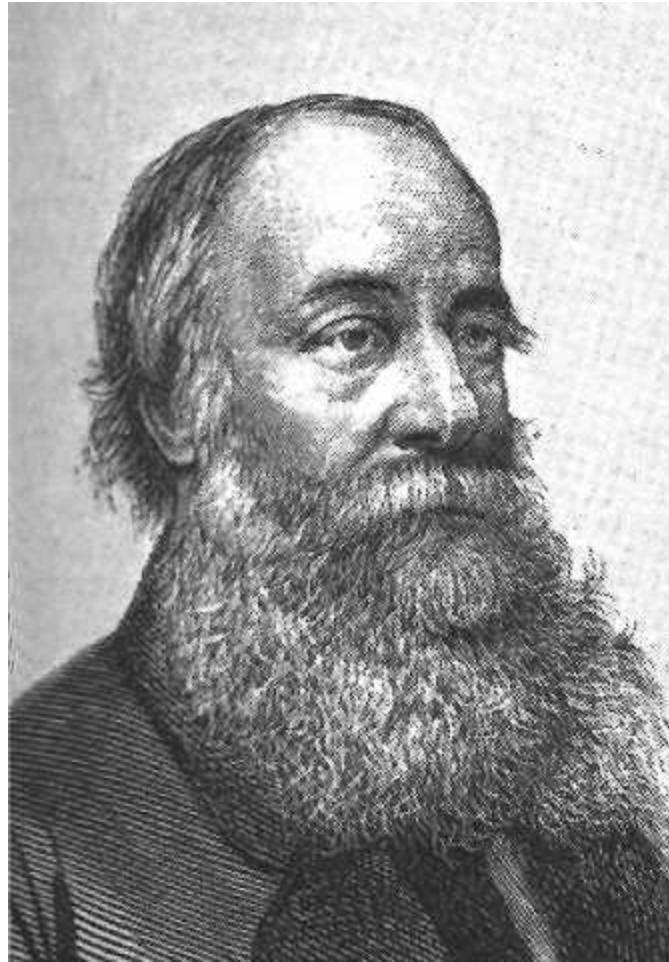


**Galileo Galilei 1564-1642**

Thermodynamics, History

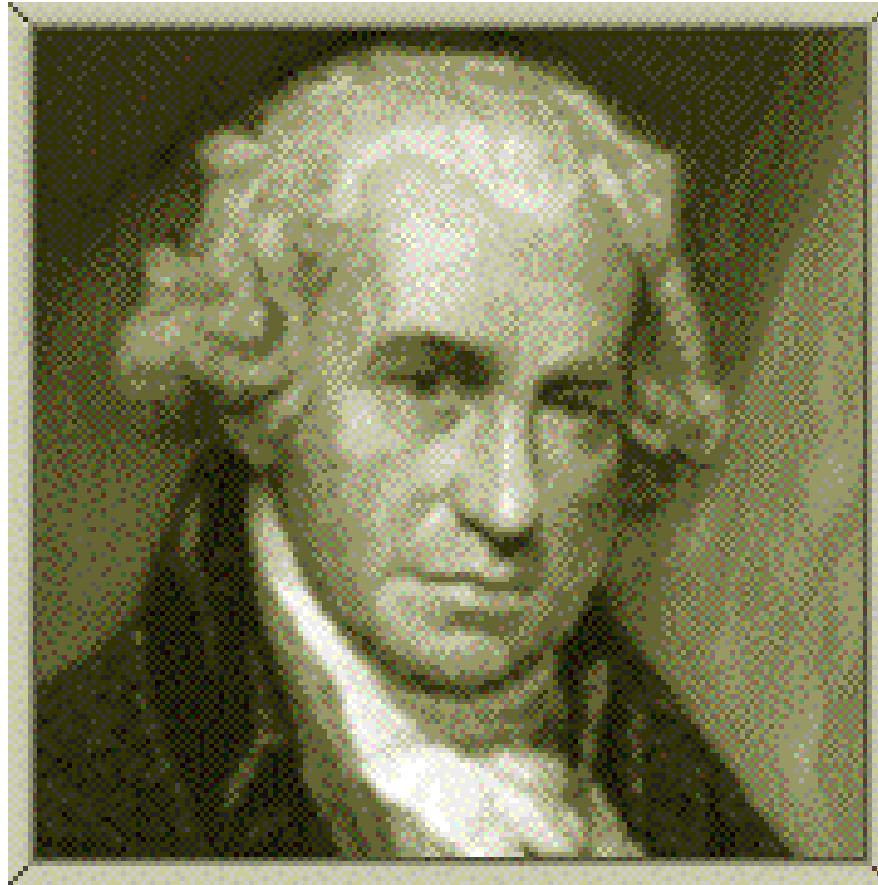


**Francis Bacon 1561-1626 Joseph Black, 1728 - 1799**



**James Prescott Joule 1818-1889**





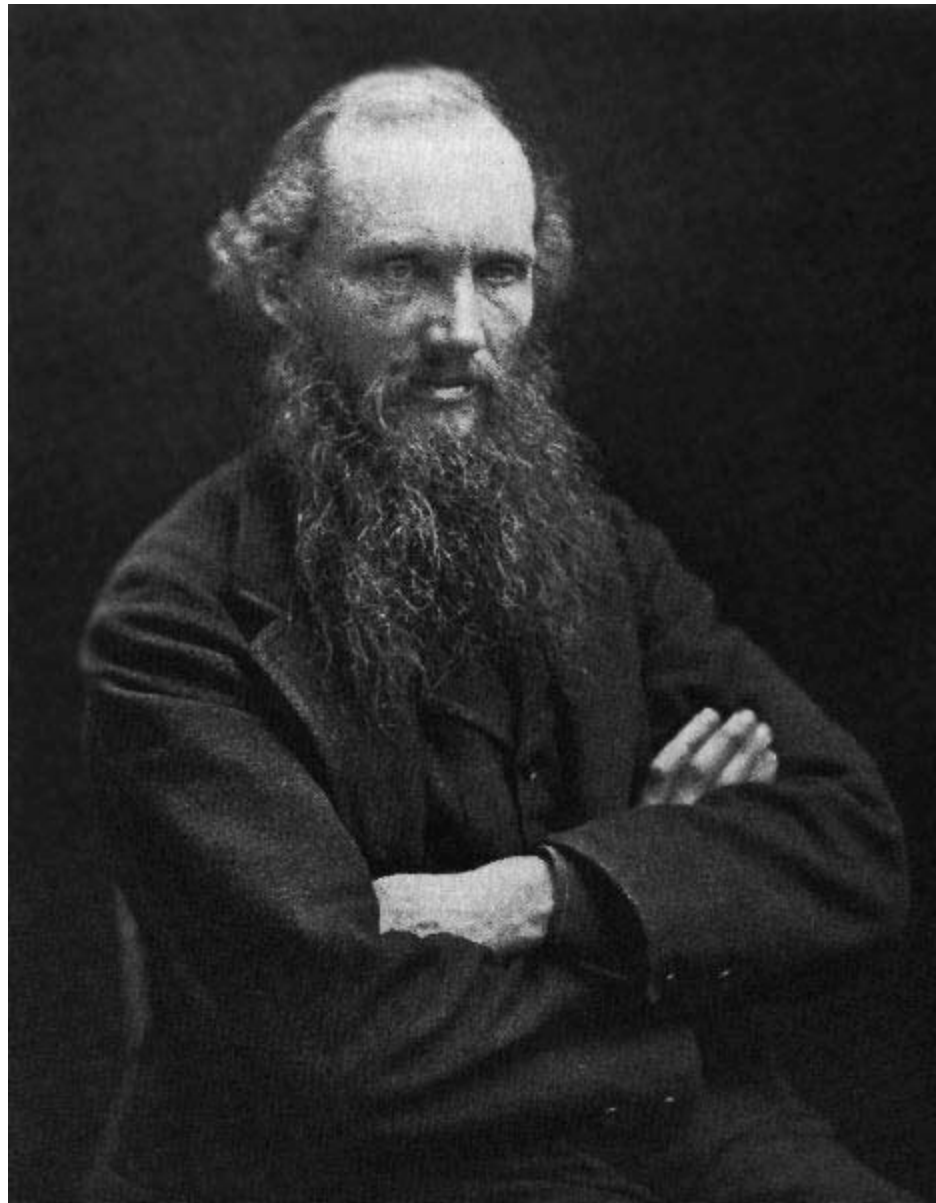
**James Watt 1736 - 1819**



**Sadi Carnot 1796-1832**



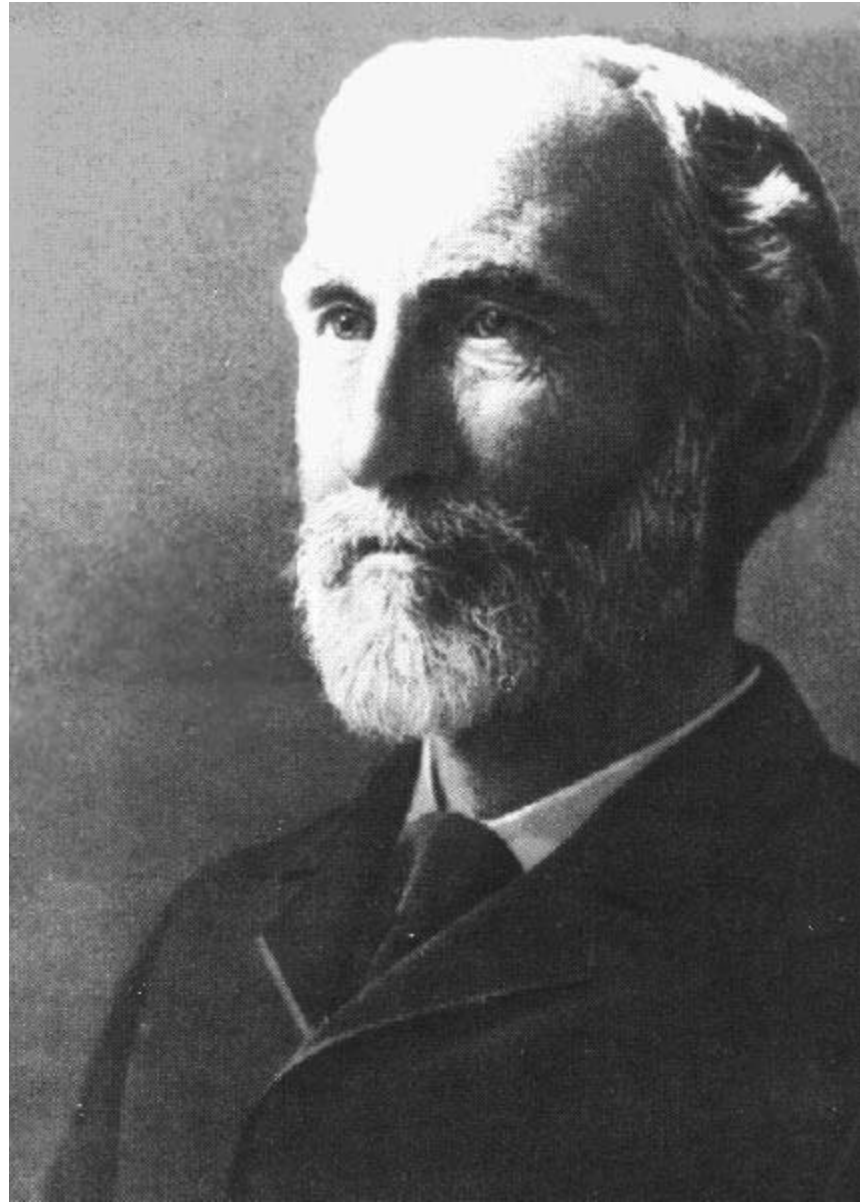
**Rudolf Clausius 1822 - 1888**



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



**Ludwig Boltzmann 1844-1906**



**Josiah Willard Gibbs 1839-1903**

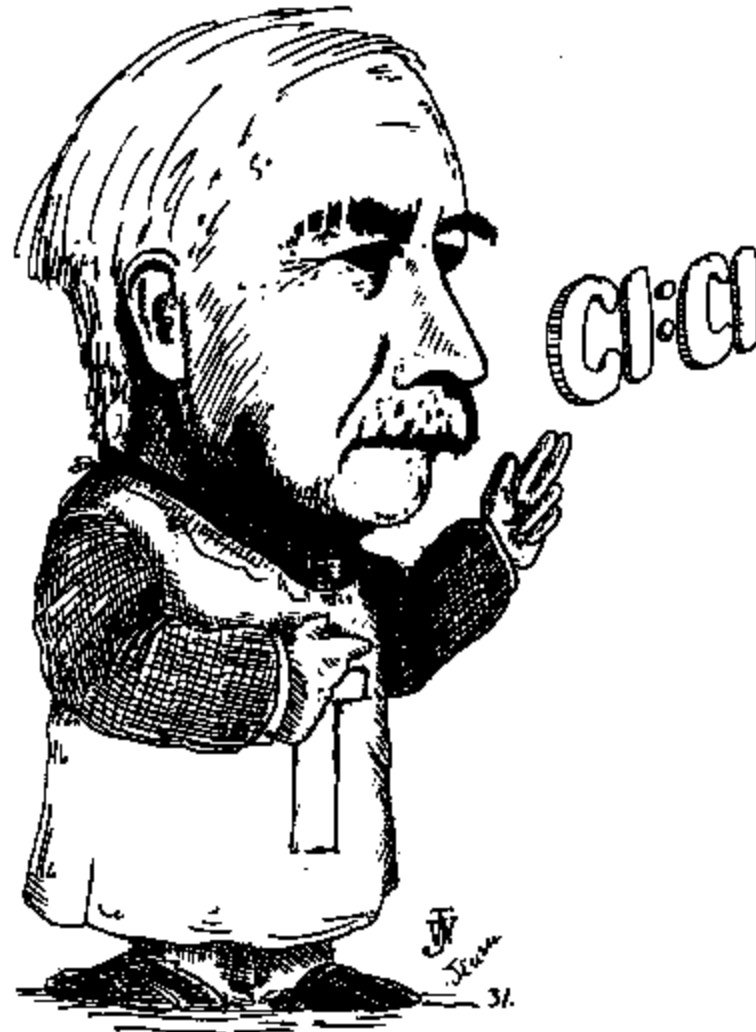


**Jacobus Henricus van 't Hoff 1852-1911**



**Walther Hermann Nernst 1864 - 1941**





**Gilbert Newton Lewis 1875-1946**