# Classical Thermodynamics

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# Fundamental Laws

# Early Experimental Laws


# Boyle-Mariotte's law (1662)

***Isothermal process:***

**The *pressure* of an ideal gas at *constant temperature* varies *inversely* with the volume.**

$$P \cdot V = \text{constant}.$$

$$P_1 \cdot V_1 = P_2 \cdot V_2.$$

**Robert Boyle (1627 – 1691), Irish-born British physicist;**

**Edme Mariotte (1620 -- 1684) , French physicist.**



# Charles' law

**[The law of Charles (1787) and Gay-Lussac (1802)]**

***Isobaric process:***

**At *constant pressure*, the *volume* of a given mass of a gas increases or decreases by the same factor as its *temperature* (in kelvins) increases or decreases.**

**Jacques Alexandre César Charles (1746 – 1823), French physicist and inventor;**

**Joseph Louis Gay-Lussac (1778 -- 1850) , French chemist and physicist.**

$$\frac{V}{T} = \text{constant.}$$

$$\frac{V_1}{T_1} = \frac{V_2}{T_2}.$$


# Gay-Lussac’s law (1809)

***Isochoric process:***

**The *pressure* of a fixed amount of gas at *fixed volume* is directly proportional to its *temperature* in kelvins.**

$$\frac{P}{T} = \text{constant}.$$

$$\frac{P_1}{T_1} = \frac{P_2}{T_2}.$$

**Joseph Louis Gay-Lussac (1778 -- 1850) , French chemist and physicist.**


# Avogadro's law
# [State equation (1811)]

Equal ***volumes*** of gases, at the ***same temperature and pressure***, contain the ***same number*** of molecules.

$$\frac{P_1V_1}{T_1} = \frac{P_2V_2}{T_2}$$

$$P \cdot V = n \cdot R \cdot T.$$

**Amedeo conte di Quaregna Avogadro (1776 -- 1856), Italian chemist and physicist.**

$$1\ \mathrm{mol} = 6.02 \times 10^{23}$$

# Formal Thermodynamic Laws

# Zeroth law of thermodynamics

**If two thermodynamic systems *A* and *B* are in thermal equilibrium, and *B* and *C* are also in thermal equilibrium, then *A* and *C* are in thermal equilibrium.**

**It is often claimed that this law proves that we can define a temperature function, or more informally, that we can "construct a thermometer".**

- ***Reflexivity*** **- a system is in thermal equilibrium with itself.**
- ***Symmetry*** **- if system *A* is in thermal equilibrium with system *B*, then system *B* is in thermal equilibrium with system *A*.**

**The term *zeroth law* was coined by *Ralph H. Fowler* in 20th century.**

# First law of thermodynamics

**The increase in the *internal energy* of a system is equal to the amount of *energy* added to the system by *heating*, minus the amount lost in the form of *work* done to the system on its surroundings.**


**Rudolf Julius Emanuel Clausius (1822 -- 1888) , German mathematical physicist.**

$$dU = \bar{d}Q + \bar{d}W,$$

**general**

$$dU = T\,dS - p\,dV,$$

$$\mathrm{d}U = T\mathrm{d}S - p\mathrm{d}V + \sum_i \mu_i \mathrm{d}N_i$$

**reversible process**

# Second law of thermodynamics

**A system operating in a cycle can*<u>not</u>* produce a *<u>positive heat flow</u>* from a *<u>colder body</u>* to a *<u>hotter body</u>*.**

**The *<u>entropy</u>* of a closed system will *<u>not decrease</u>* for any sustained period of time.**


$$\bar{d}Q \leq T dS,$$

$$\frac{dS}{dt} \geq 0 \qquad (1)$$

**Rudolf Julius Emanuel Clausius (1822 -- 1888) , German mathematical physicist.**

# Third law of thermodynamics (Nernst theorem)

**As a system approaches *absolute zero* of temperature all processes *cease* and the *entropy* of the system approaches a *minimum* value or *zero* for the case of a perfect crystalline substance.**

**Walther Hermann Nernst**

Germany

Berlin University
Berlin, Germany

b. 1864
d. 1941

$$\lim_{T \to 0} (\Delta S)_T = 0,$$

**It is *impossible* by any procedure, no matter how idealised, to reduce any system to the *absolute zero* of temperature in a finite number of operations.**

**Walther Hermann Nernst (1864 -- 1941), Polish-German physicist and chemist.**

# A little summary in terms of a joke

**Zeroth law:** *"You must play the game."*

**First law:** *"You can't win."*

**Second law:** *"You can't break even."*

**Third law:** *"You can't quit the game."*

# Maxwell's Relations

$$\left(\frac{\partial T}{\partial V}\right)_S = -\left(\frac{\partial p}{\partial S}\right)_V, \quad \left(\frac{\partial T}{\partial p}\right)_S = \left(\frac{\partial V}{\partial S}\right)_p,$$

$$\left(\frac{\partial S}{\partial V}\right)_T = \left(\frac{\partial p}{\partial T}\right)_V, \quad \left(\frac{\partial S}{\partial p}\right)_T = -\left(\frac{\partial V}{\partial T}\right)_p$$

John Dalton (1766 -- 1844), British chemist and physicist.

**Investigations on the *atomic theory* in chemistry.**

- **All matter is composed of extremely small particles called atoms.**
- **All atoms of a given element are identical, having the same size, mass, and chemical properties. Atoms of a specific element are different from those of any other element.**
- **Atoms cannot be created, divided into smaller particles, or destroyed.**
- **Different atoms combine in simple whole-number ratios to form compounds.**
- **In a chemical reaction, atoms are separated, combined, or rearranged.**

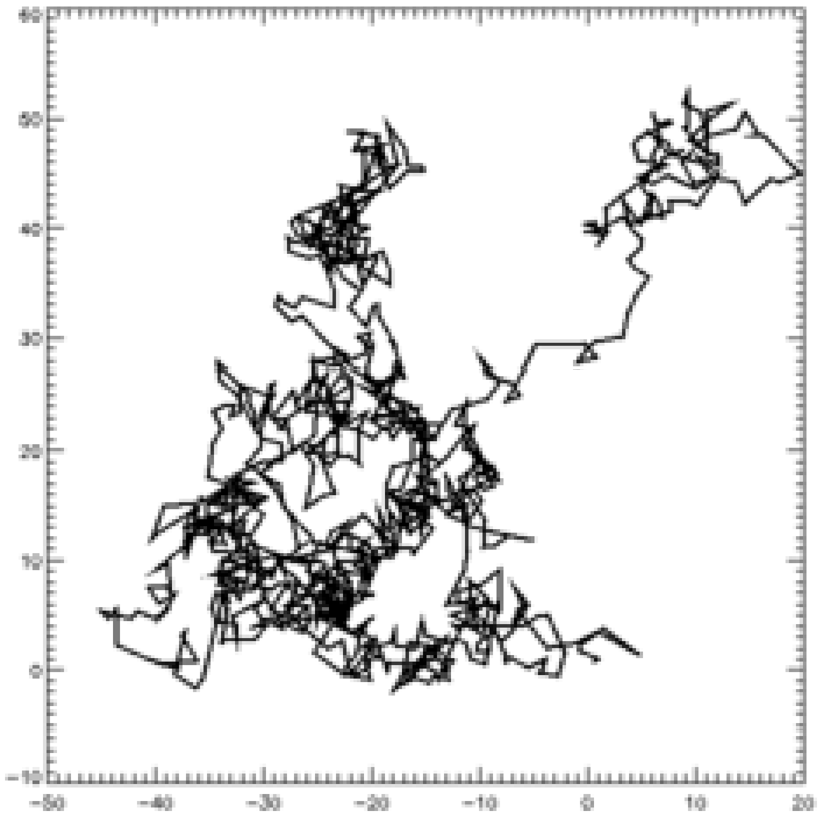
Jean Baptiste Joseph Fourier (Baron) (1768 -- 1830), French mathematician and physicist.

**Gases in the atmosphere might increase the surface temperature of the Earth, this effect was later called *greenhouse effect*.**

**Established the concept of *planetary energy balance*: That planets obtain energy from number of sources that causes temperature increase. Planets also lose energy by *infrared radiation* with the rate increasing with temperature. A balance is reached between *heat gain* and *heat loss*; the atmosphere shifts the balance toward the higher temperatures by slowing the heat loss. Although Fourier understood that rate of infrared radiation increases with temperature, the Stefan-Boltzmann law which gives the exact form of this dependency (a fourth-power law) was discovered 50 years later.**

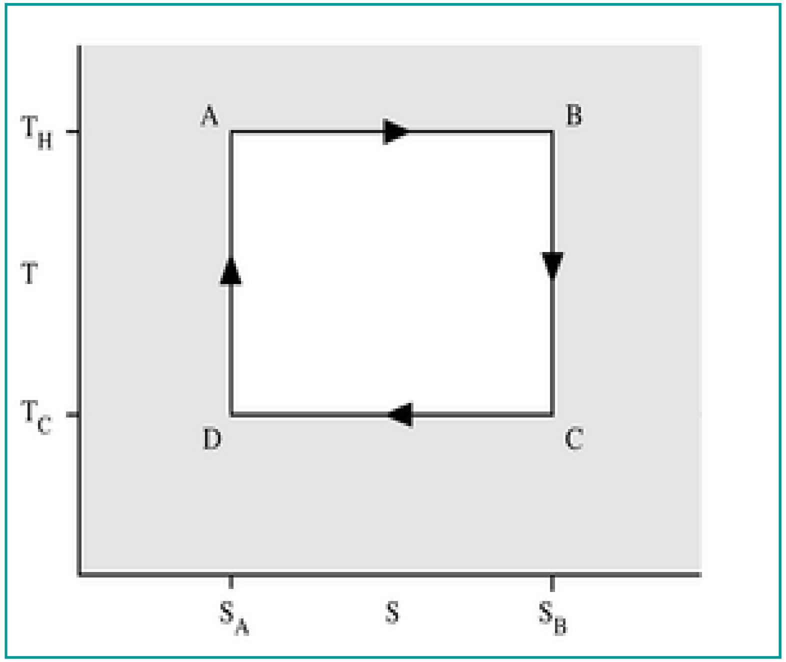
# Brownian motion

Robert Brown (1773 -– 1858),
British botanist.




An example of 1000 simulated steps of Brownian motion in two dimensions. The origin of the motion is at [0,0] and the *x* and *y* components of each step are independently and normally distributed with variance 2 and mean 0. The mathematical model posits motion in which the steps are not discrete.

# ***Carnot cycle*** and ***Carnot heat engine***

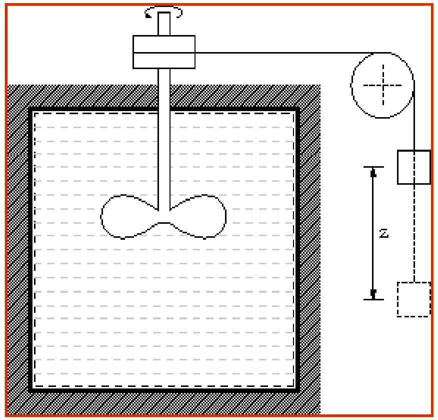



**Nicolas Léonard Sadi Carnot (1796 -- 1832), French physicist and engineer.**

**Carnot devised an ideal engine in which a gas is allowed to expand to do work, absorbing heat in the process, and is expanded again without transfer of heat but with a temperature drop. The gas is then compressed, heat being given off, and finally it is returned to its original condition by another compression, accompanied by a rise in temperature. This series of operations, known as Carnot's cycle, shows that even under ideal conditions a heat engine cannot convert into mechanical energy all the heat energy supplied to it; some of the heat energy must be rejected. This is an illustration of the second law of thermodynamics. Carnot's work anticipated that of Joule, Kelvin, and others.**

Discovered the ***first law of thermodynamics***, which is a form of the ***law of conservation of energy***.

**James Prescott Joule (1818 -- 1889), British physicist.**




Determine the ***relationship*** between ***heat energy*** and ***mechanical energy*** (the ***mechanical equivalent of heat***).

**"... the mechanical power exerted in turning a magneto-electric machine is converted into the heat evolved by the passage of the currents of induction through its coils; and, on the other hand, that the motive power of the electro-magnetic engine is obtained at the expense of the heat due to the chemical reactions of the battery by which it is worked.“ (1842)**

The mechanical ***SI unit*** of ***work*** and ***energy***.

## Clapeyron equation

$$P \cdot V = n \cdot R \cdot T.$$

**Émile Clapeyron (1799 -- 1864), French physicist and engineer.**

**First law of thermodynamics (1847)**

$$dU = \bar{d}Q + \bar{d}W,$$

**Proposed the idea of "Heat death of the universe" (1854), the "father" of the formal second law of thermodynamics, proposed by Clausius later**

$$A = U - TS$$

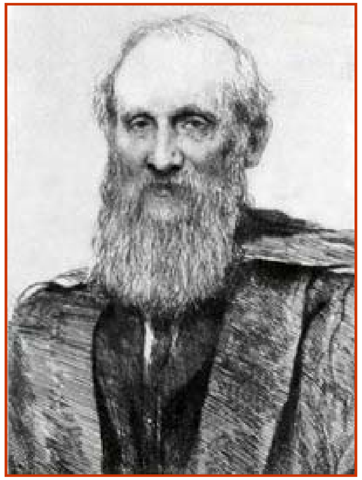
**Helmholtz free energy**

**A thermodynamic potential which measures the "useful" work obtainable from constant temperature, constant volume thermodynamic systems.**

**Hermann Ludwig Ferdinand von Helmholtz (1821 -- 1894), German physicist and physician.**

$$dF = -S\,dT - p\,dV,$$


**William Thomson (Baron Kelvin) (1824 -- 1907), British physicist and mathematician.**



**Independently recognized the _*first*_ and _*second laws*_ of thermodynamics.**

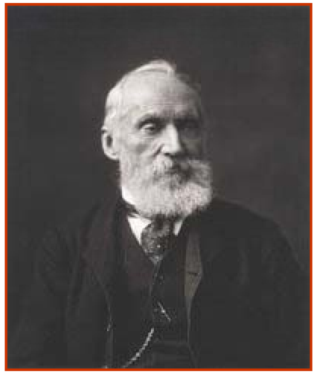
**Develop the idea of _*absolute zero degree*_ in temperature and construct the _*absolute temperature scale*_ (1848).**

**Discovered that gases cool when allowed to expand, the _*Joule-Thomson effect*_.**

**Designed a _*telegraph receiver*_, called a _*mirror galvanometer*_, for use on the cable (1958).**

**Supervised the laying of a _*trans-Atlantic cable*_ (1866).**

**Invented a _*compass*_, an instrument for measuring tides and calculating tide tables.**



Joseph Stefan (Slovene Jožef Stefan) (1835 -- 1893), Austrian (Slovene) physicist, mathematician and poet.

**Stefan-Boltzmann law**

$$u = aT^4$$

$$a = \frac{8\pi^5 k^4}{15 c^3 h^3}$$

**Wien coefficient**

**Stefan constant**

$$\sigma = ac^4$$


**Ludwig Boltzmann, (1844 - – 1906), Austrian physicist.**

**Boltzmann equation**

$$\frac{\partial f}{\partial t} + \frac{\partial f}{\partial \mathbf{x}} \cdot \frac{\mathbf{p}}{m} + \frac{\partial f}{\partial \mathbf{p}} \cdot \mathbf{F} = \left.\frac{\partial f}{\partial t}\right|_{\mathrm{coll}}.$$

**Boltzmann constant**

$$k = 1.3807 \times 10^{-23} \mathrm{J} \cdot \mathrm{K}^{-1}$$

**Boltzmann's H theorem**

$$H \equiv \int P \log P d^3\vec{v}; \quad S = -Nk_B H.$$

$$\Longrightarrow \Delta S \geq 0$$

**Stefan-Boltzmann law**

$$u = aT^4$$

$$f_{\mathbf{v}}(v_x, v_y, v_z) = \sqrt{\left(\frac{m}{2\pi kT}\right)^3} \exp\left[\frac{-m(v_x^2 + v_y^2 + v_z^2)}{2kT}\right], \qquad (8)$$

**Maxwell-Boltzmann distribution**

Wilhelm Wien (1864 –- 1928), German physicist.

**Wilhelm Wien**

Germany

Würzburg University
Würzburg, Germany

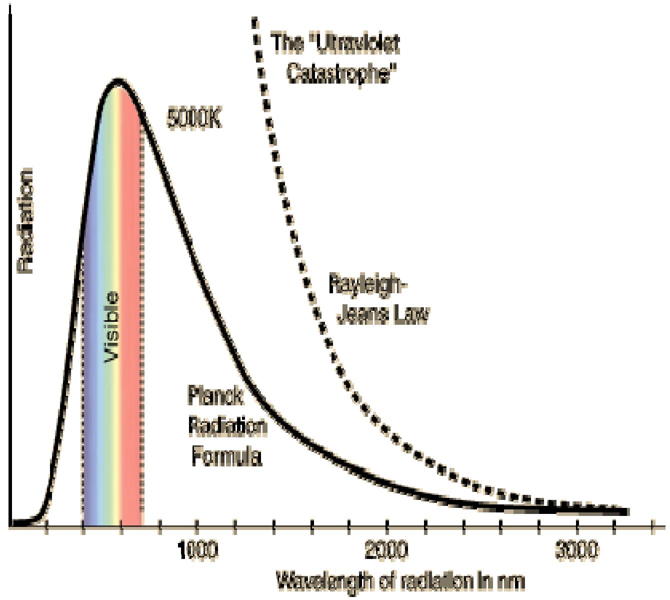
b. 1864
d. 1928

# Wien's Displacement Law

$$\lambda_{max} = \frac{2.898\ldots \times 10^6 \ \mathrm{nm \cdot K}}{T}$$

$$u_\nu d\nu = \nu^3 \phi\left(\frac{\nu}{T}\right) d\nu,$$

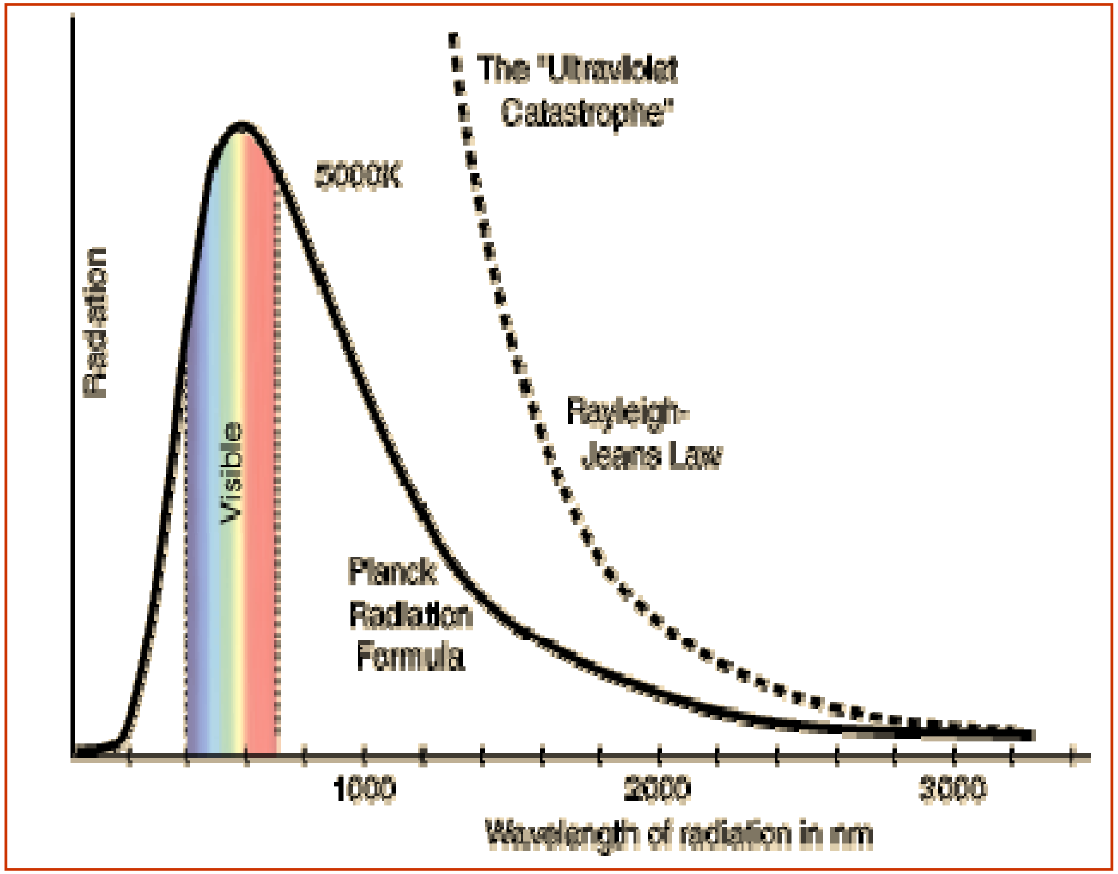
$$u_\nu d\nu \propto \nu^3 e^{-c_2/\lambda T} d\nu.$$

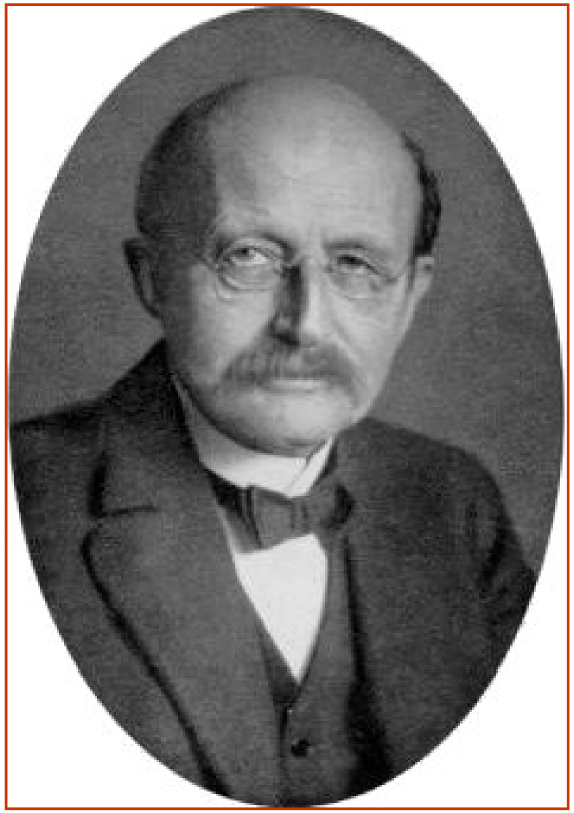


The Right Honourable, John William Strutt, 3rd Baron Rayleigh (1842 -– 1919), British physicist.

**Rayleigh-Jeans law**

$$u_\nu d\nu = \frac{8\pi\nu^2}{c^3} k_B T d\nu,$$





**Max Karl Ernst Ludwig Planck**

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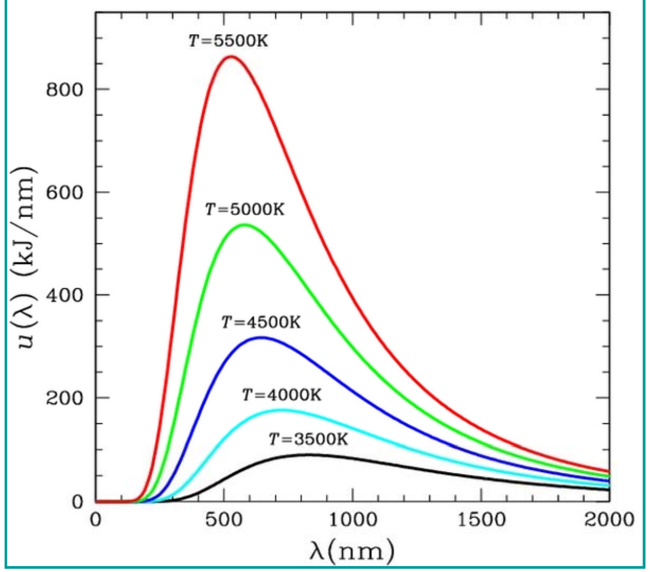
b. 1858
d. 1947



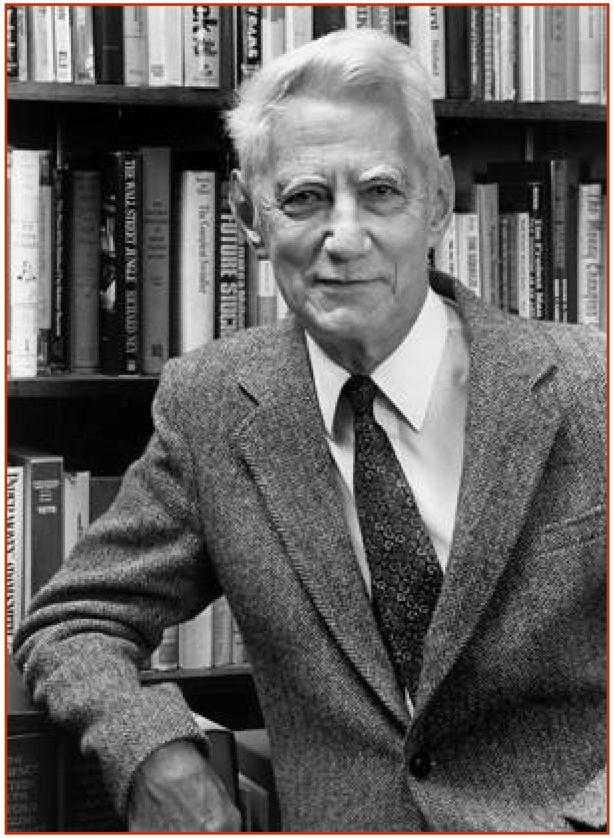

$$u(\nu, T) = \frac{8\pi h\nu^3}{c^3}\frac{1}{e^{\frac{h\nu}{kT}} - 1}$$

$$u(\lambda, T) = \frac{8\pi hc}{\lambda^5}\frac{1}{e^{hc/\lambda kT} - 1}$$

**Max Karl Ernst Ludwig Planck (1858 -- 1947), German physicist.**

**Planck's law of black body radiation (1900)**

$$u_\nu d\nu = \frac{8\pi\nu^2}{c^3}\frac{h\nu}{e^{h\nu/K_B T} - 1}d\nu$$



# Information theory

**Claude Elwood Shannon (1916 -- 2001), American applied mathematician and electrical engineer, is called the father of information science.**

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