

Physics

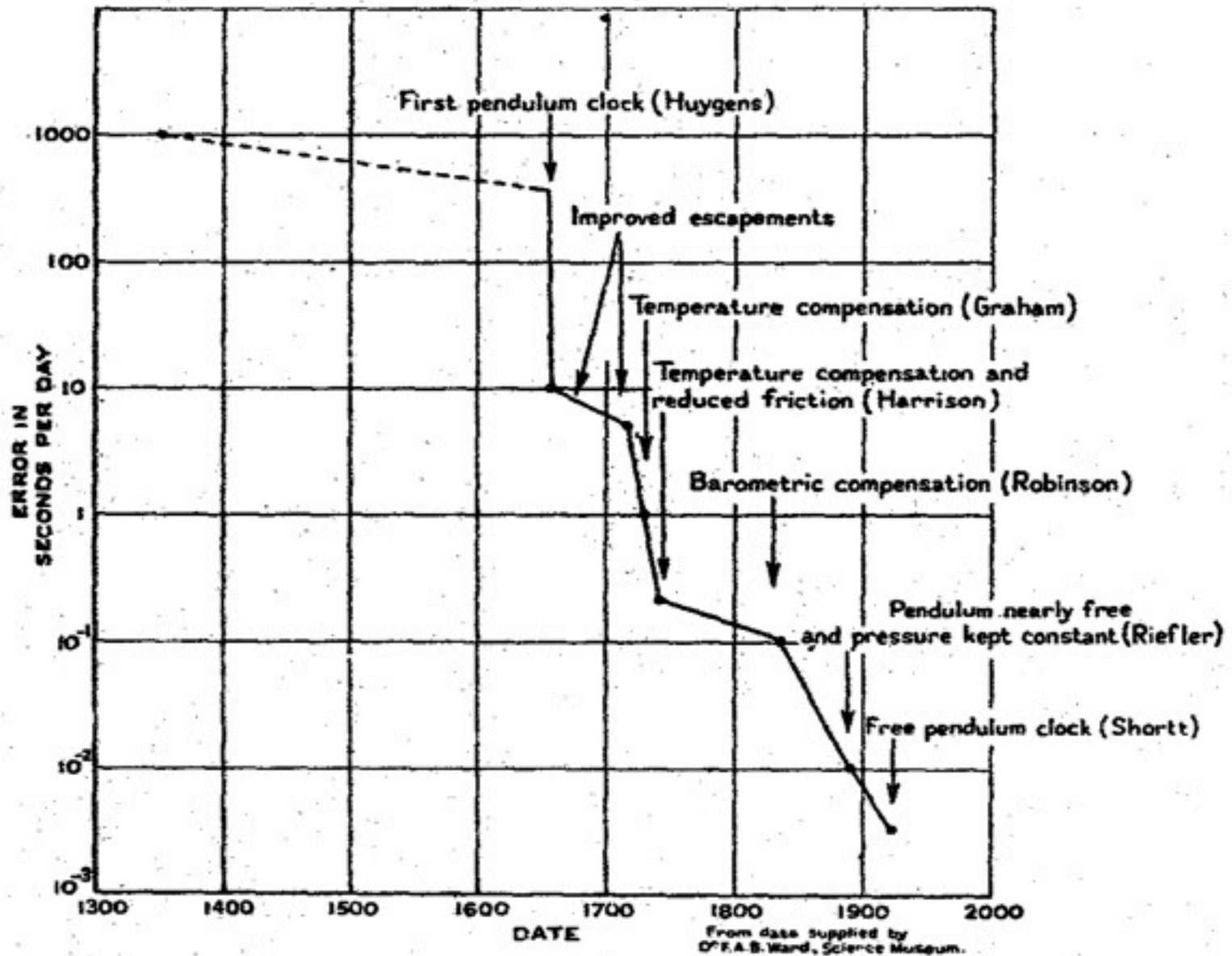
in the Enlightenment

part 1

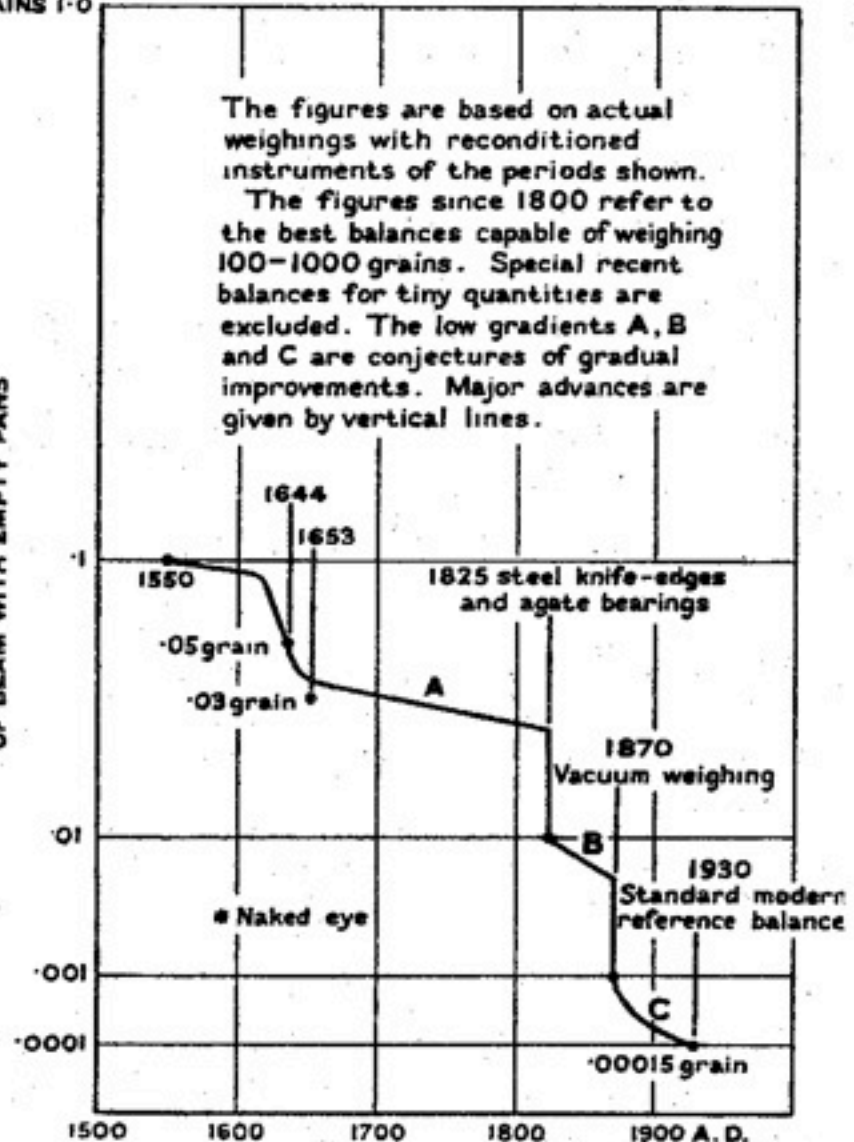
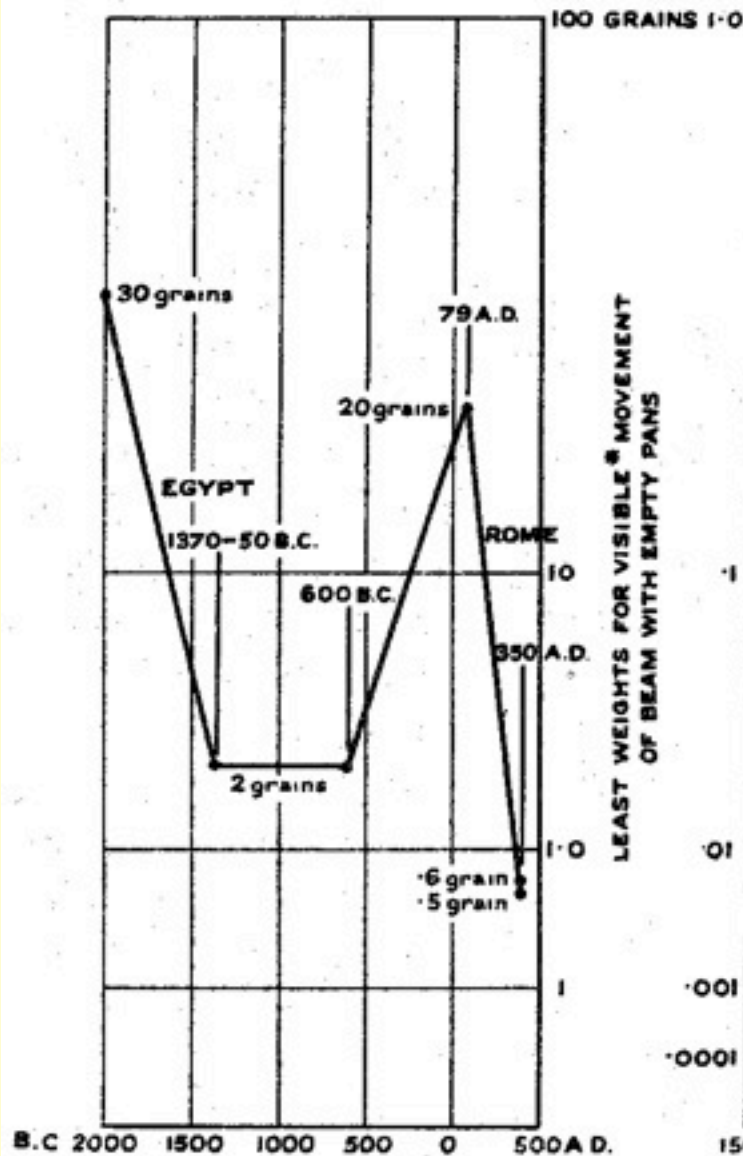
XVIIth century – “century of scientific instruments”

**termometer,
barometer,
telescope with lenses,
mirror telescope,
microscope,
hygrometer,
vacuum pump,
pendulum clock,
electrostatic machine,
electroscope,
.....**

Accuracy of time measurement

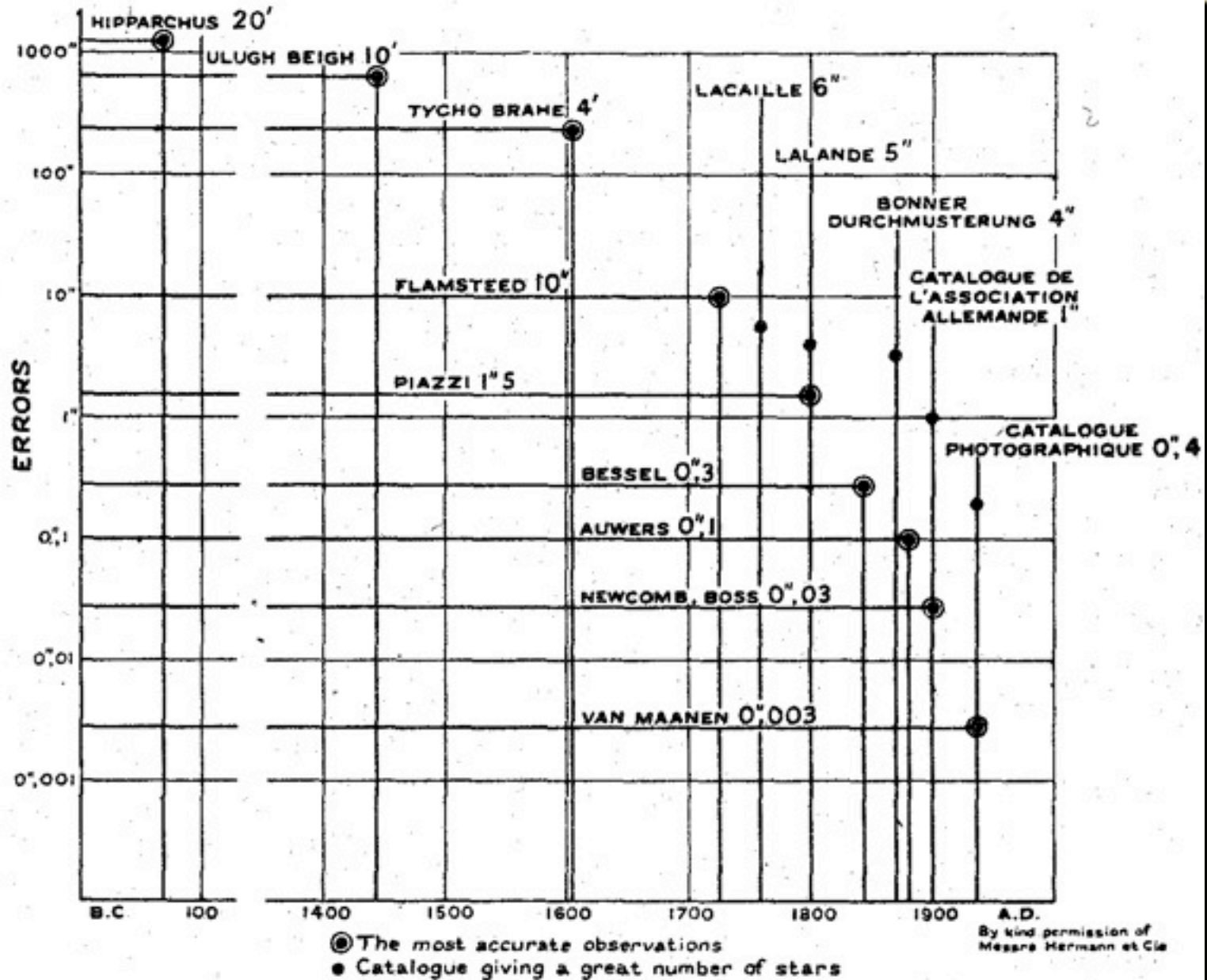


Accuracy of mass measurement



From data supplied by
F G Skinner, Science Museum

Accuracy of angle measurement





Peter Brueghel the Elder



ENCYCLOPÉDIE, OU DICTIONNAIRE RAISONNÉ DES SCIENCES, DES ARTS ET DES MÉTIERS,

PAR UNE SOCIÉTÉ DE GENS DE LETTRES.

Mis en ordre & publié par M. *DIDEROT*, de l'Académie Royale des Sciences & des Belles-Lettres de Prusse; & quant à la PARTIE MATHÉMATIQUE, par M. *D'ALEMBERT*, de l'Académie Royale des Sciences de Paris, de celle de Prusse, & de la Société Royale de Londres.

*Tantum series juncturaque pollet,
Tantum de medio fumptis accedit honoris! HORAT.*

TOME PREMIER.



A PARIS,

Chez { *BRIASSON*, rue Saint Jacques, à la Science.
 DAVID l'aîné, rue Saint Jacques, à la Plume d'or.
 LE BRETON, Imprimeur ordinaire du Roy, rue de la Harpe.
 DURAND, rue Saint Jacques, à Saint Landry, & au Griffon.

M. DCC. LL

AVEC APPROBATION ET PRIVILEGE DU ROY.



Physics in the Enlightenment is also called **the physics of the weightless fluids**

The concept of energy did not yet exist, hence changes in the state of bodies caused by heating, magnetisation, or charging with electricity were explained by presence of the subtle, weightless fluids of heat, magnetism, and electricity. Later, animal electricity and animal magnetism were also discussed in similar context.

There was great advancement in mechanics which was developed almost to the modern form.

There was no progress in optics. The ideas of Newton concerning light were accepted because of his great authority.

Mechanics

from Newton to Laplace

**Newton had built the fundament
of mechanics and indicated proper
direction of its development,
but almost the entire mechanics,
which we know now, was the work
of famous mathematicians and
physicists of the XVIIIth century**

Royal Society Prize competition (1668) for a treatise on collisions of bodies

John Wallis – central collisions; (mass \times speed = *momentum*)

Christopher Wren – only elastic collisions

Christiaan Huygens – most complete results

”At the end I wish to stress an admirable law of nature which I can prove for spherical bodies and which seems to apply also to all other hard and soft bodies which collide centrally or obliquely: the common centre of gravity of two, three or any number of bodies moves always uniformly along a straight line in the same direction before and after their collision”

Huygens (1669)

Quantity of motion

Descartes: quantity of motion = mass \times speed

"...when a part of matter moves twice as rapidly as another part, and this other part is twice as great as the first part, we have a right to think that there is as much motion in the smaller body as in the larger..."

Principia philosophiae (1644)



Leibniz: quantity of motion = mass \times speed squared
(later named *vis viva*)

"A short demonstration of a remarkable error made by Descartes and others", *Acta Eruditorum* (1686)

d'Alembert (1743) – "a quarrel about words"

A gallery of great founders of mechanics



Jacob
Bernoulli



Johann
Bernoulli



Daniel
Bernoulli



Leonhard
Euler



Jacob
Hermann



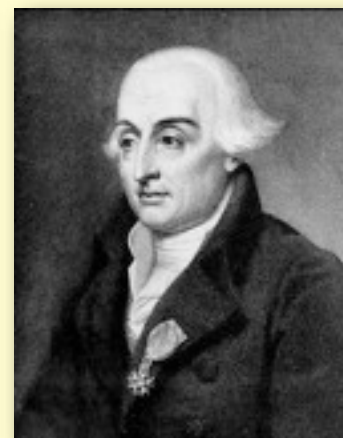
Jean Rond
d'Alembert



Alexis
Clairaut



Pierre Louis
Maupertuis



Joseph Louis
de Lagrange



Pierre Simon
de Laplace

The Bernoulli family

Nicolaus
(1623-1708)

Nicolaus
(1662-1716)

Jacob I
(1654-1705)



Johann I
(1667-1748)



Nicolaus I
(1687-1759)



Nicolaus II
(1695-1726)



Daniel I
(1700-1782)



Johann II
(1710-1790)

Johann III
(1744-1807)



Daniel II
(1754-1834)

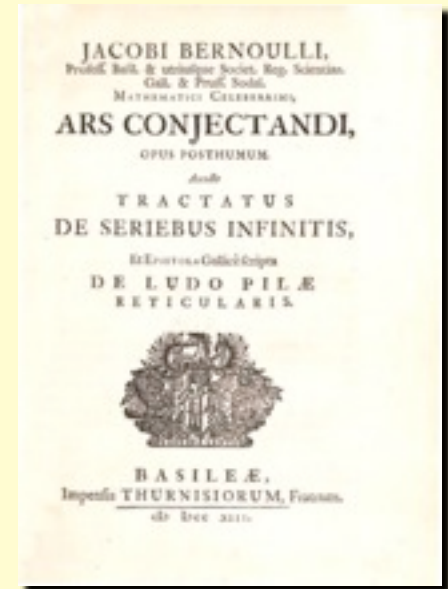
Jacob II
(1759-1789)





Jacob I Bernoulli

Integral calculus
Theory of probability



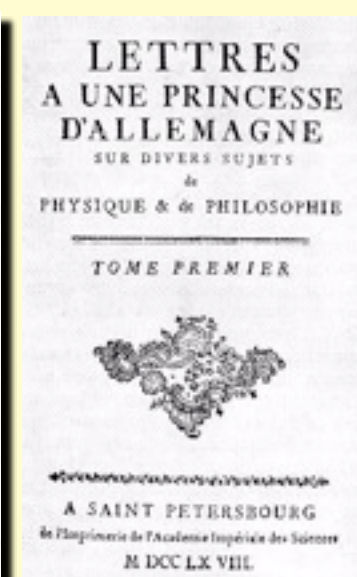
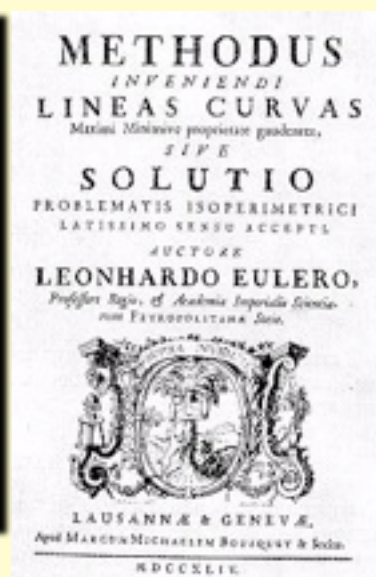
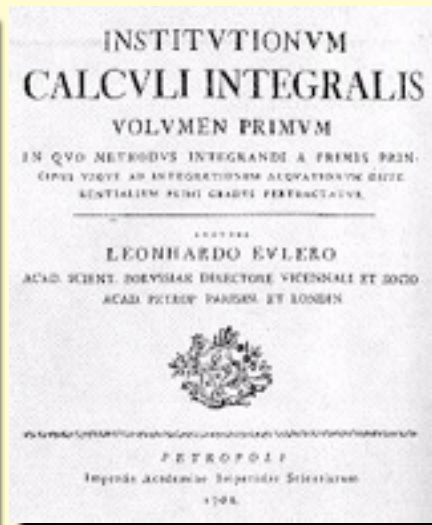
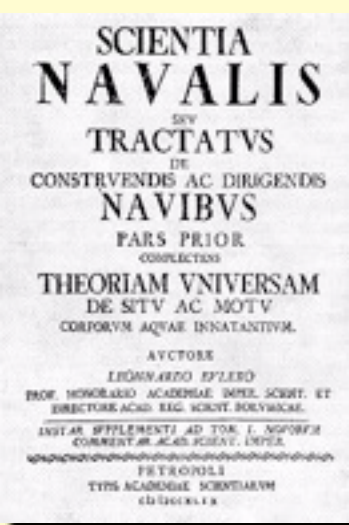
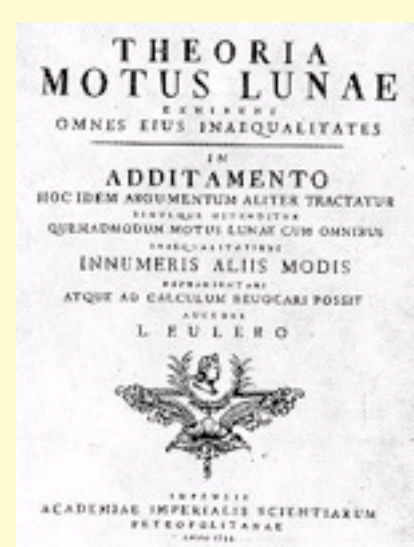
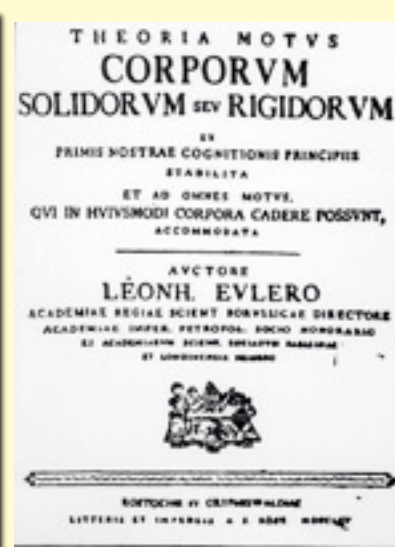
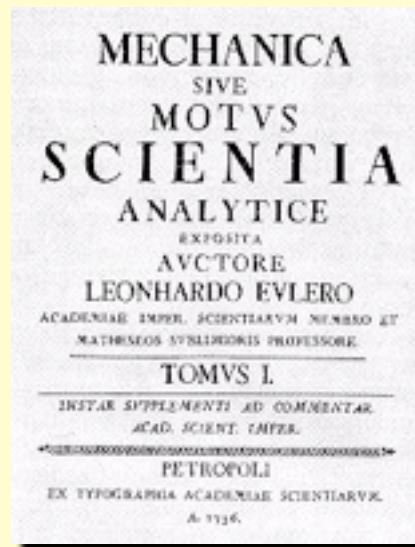
Johann I Bernoulli

Differential equations
Brachistochrone





Leonhard Euler
(1707-1783)

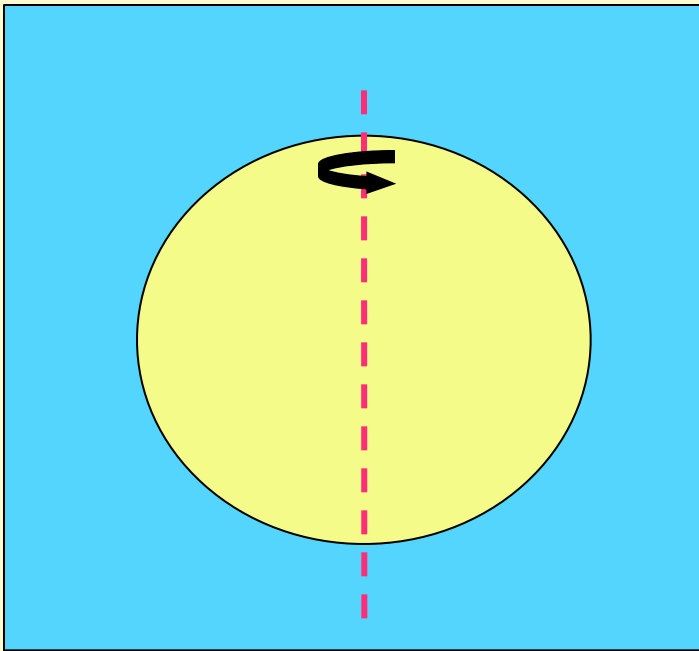


Euler's contribution to mechanics:

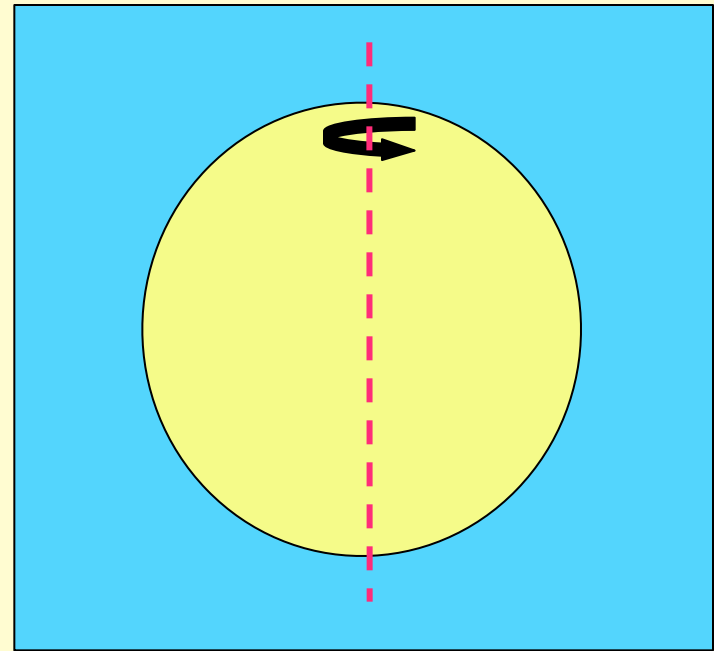
- first exposition of analytical mechanics (*Mechanica sive scientia motus analytice exposita*, 1736)
- introduction of precisely defined *material points* (Newton considered the motion of vaguely defined *bodies*)
- *acceleration* considered as kinematical quantity in motion along a trajectory
- introduction of directed quantities (later named *vectors*)
- first differential equation of transverse vibrations of an elastic rod (independently of, and simultaneously with Daniel Bernoulli, 1734)
- first analysis of a harmonic oscillator (1739)
- first use of „Newton's equations" $F_x = m a_x$ etc. (1752)
- first exposition of mechanics of rigid bodies with equations of motion, Euler's angles etc. (*Theoria motus corporum solidorum seu rigidorum*, 1765)
- development of methods of hydrodynamics (*Scientia navalis*, 1749, *Principia motus fluidorum*, 1752, *Continuation des recherches sur la théorie du mouvement des fluides*, 1757)
- new calculation methods in celestial mechanics (*Theoria motuum planetarum et cometarum*, 1744, *Theoria motus lunae*, 1753)

Newtonianism or Cartesianism?

Newton



Descartes



Expeditions to Lapland and to the equatorial region of South America (1735)

Newtonianism or Cartesianism?

Academie de Sciences in Paris: 1748 Prize competition for a treatise on the motion of the moon

Three papers sent in by d'Alembert, Clairaut, and Euler

Results of calculations in disagreement with observations !

"I can give you a number of proofs that the forces which act on the moon are not strictly subject to the Newton's law... because the observed deviations can not be attributed to observation error, I have no doubt that their probable cause is certain '*derangement*' of forces which are assumed theoretically.

I am inclined to think that these forces are due to vortices or some other material causes because it is easy to understand that these forces should be changing if carried by some other vortex."

Euler in a letter to Clairaut, September 1747

Newtonianism or Cartesianism?



D'Alembert: perhaps a "*derangement*" of Newton's law is caused by a magnetic force, (look for correlation of moon's positions and changes of the earth's magnetic field ?)

The law of gravitation should be modified by adding a term proportional to $1/r^3$ or $1/r^4$



Georges-Leclerc de Buffon:

"you better look for errors in your calculations!"

and indeed Buffon was right...

A. Clairaut, *Theorie de la Lune, deduite du seul principe de l'attraction reciproquement aux quarrés des distances*, Petersburg 1752



Jacob Hermann (1678-1733)

Force G acts difformly.

In an indefinitely small time dT (*temporis tractum indefinite parvum* dT) a body acquires an infinitesimal speed dV (*celeritas infinitorum* dV); under these conditions

$$G = M \cdot dV/dT, \text{ or } dT = M \cdot dV/G$$

here G stands for the weight (*pondus*) or gravity (*gravitas*) however variable of mass M

PHORONOMIA,
SIVE
DE VIRIBUS ET MOTIBUS
CORPORUM
SOLIDORUM ET FLUIDORUM

LIBRI DUO,

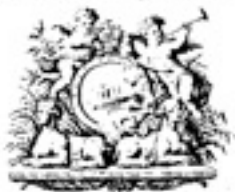
AUTORE

JACOBO HERMANNO Bafil.

antehac in Illustri Patavino Lyceo; nunc vero

in Regio Vindobono Math. Prof. Ord.

& Reg. Scientiarum Societatis, quae Berochini est, Socii.



AMSTELÆDAMI,

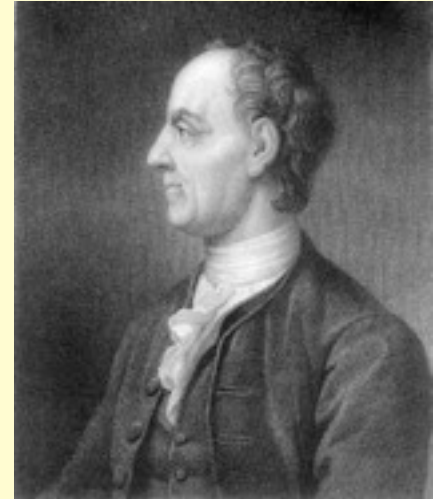
Apud ROD. & GERH. WETSTENIOS HFF.

M. D. CCXVI.

The first known example of Newton's law in an algebraic form

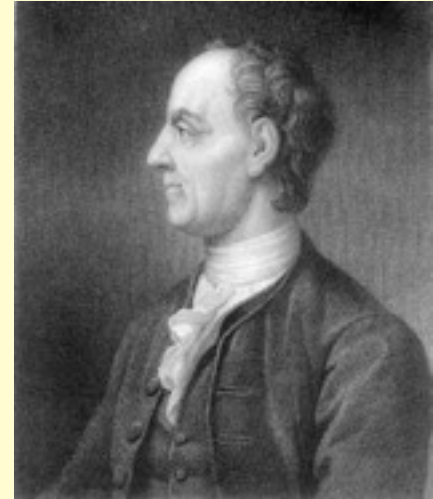
"If Analysis is to become indispensable, it is just in Mechanics. The reader admittedly becomes convinced as to the correctness of solutions, but he does not acquire clear and precise understanding of the problems, so when they are slightly changed, he is not able to solve them by himself without turning to an analytic method.

This was the case when I began to get acquainted with Newton's *Principia* and Hermann's *Phoronomia*; though I seemed to understand the solution of many problems clearly enough, yet I was not able to solve problems which were slightly different."



Leonhard Euler, *Mechanica sive motus scientia...*, Preface

„Thus I tried, as well as I could, to solve these problems once again by using analytic methods which helped me to considerably improve my insight. Then I treated in a similar way other problems scattered in various places but related to this science and, for myself, explained their solutions by a uniform method and put them in a proper order. While doing it I not only encountered many problems earlier unsolved, which I managed to resolve, but I also found many other methods which greatly enriched the mechanics and likewise the analysis itself. Such was the origin of the present treatise on motion in which I expounded by the analytic method in the proper order all what I found in other works about the motion of bodies and also my own results obtained in the course of this consideration.”



Leonhard Euler, *Mechanica sive motus scientia...*, Preface

"If the speed is such that a body covers a distance of three feet in one second, then this speed is expressed by the number 3... A body which covers 48 feet in 6 seconds has a speed of 8 – this number tells us that the body covers 8 feet in one second."

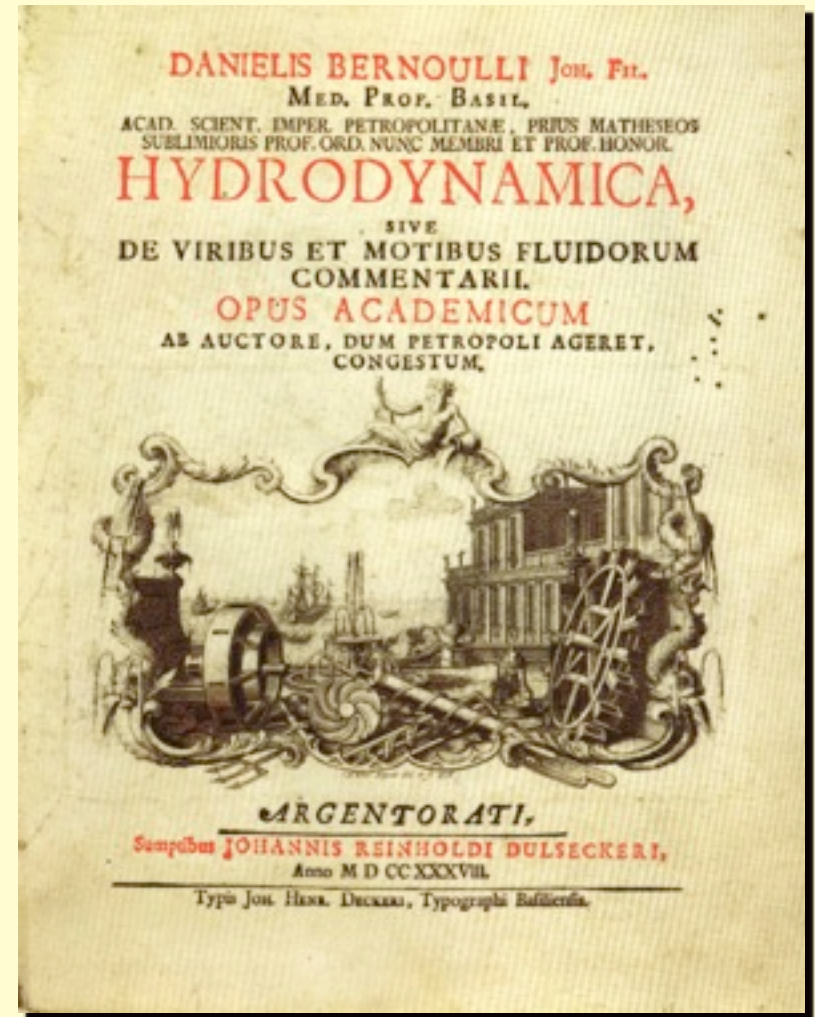
"A doubt may arise how a distance can be divided by a time, because they are not quantities of the same kind and it is not possible to tell, for example, how many times a time of 10 minutes fits into a path of 10 feet ."

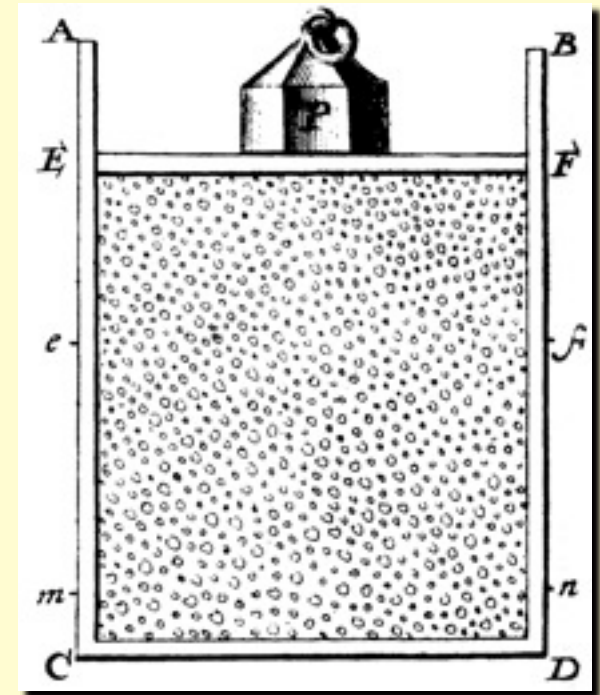
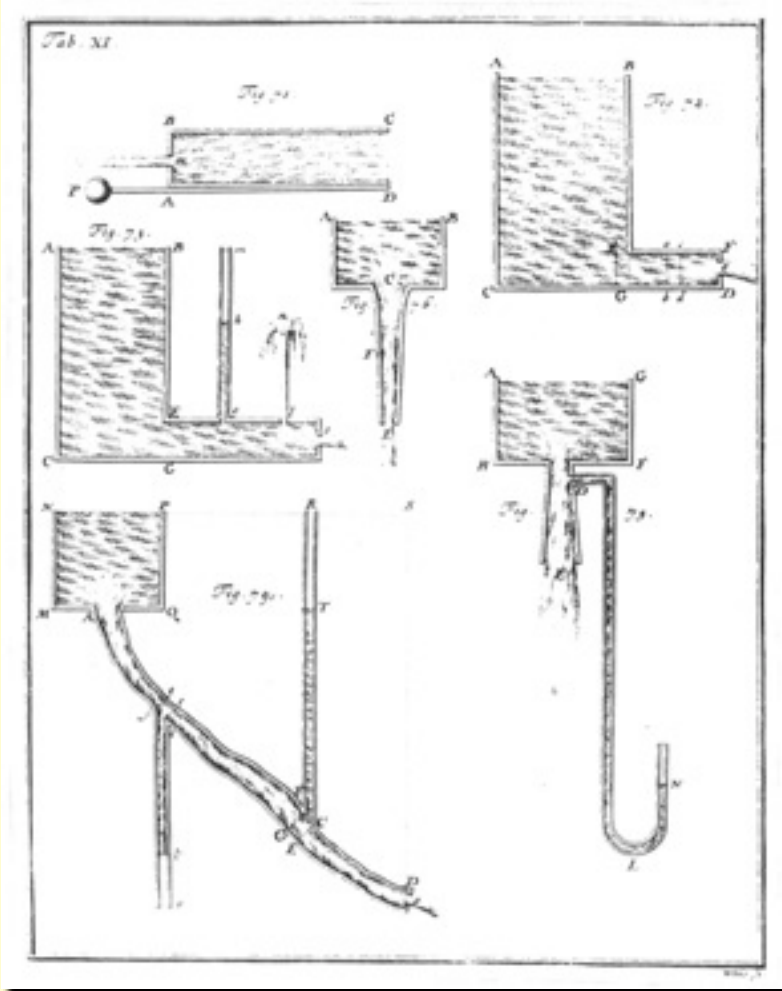
" d^2s/dt^2 represents a distance, which is covered by the body in addition to the distance which would be covered if its speed did not change... This additional segment is directly proportional to the force and inversely proportional to the mass of the body."

Euler, *Mechanica sive motus scientia analytice exposita*



Daniel Bernoulli - *Hydrodynamica* (1738)





Illustrations from *Hydrodynamica* by Daniel Bernoulli

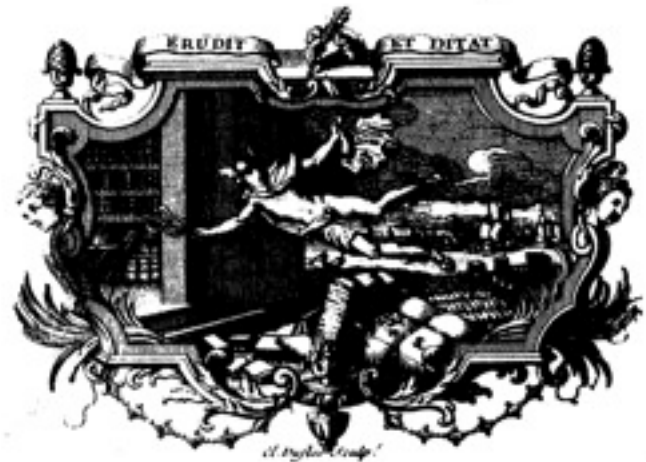


(1717-1783)

TRAITÉ DE *DYNAMIQUE,*

DANS LEQUEL LES LOIX DE L'EQUILIBRE
& du Mouvement des Corps sont réduites au plus petit nombre possible, & démontrées d'une manière nouvelle, & où l'on donne un Principe général pour trouver le Mouvement de plusieurs Corps qui agissent les uns sur les autres, d'une manière quelconque.

Par M. d'ALEMBERT, de l'Académie Royale des Sciences.



A PARIS,

Chez DAVID l'aîné, Libraire, rue Saint Jacques, à la Plume d'or.

MDCCXLIII.

AVEC APPROBATION ET PRIVILEGE DU ROI.



d'Alembert – *Traité de dynamique* (1743)

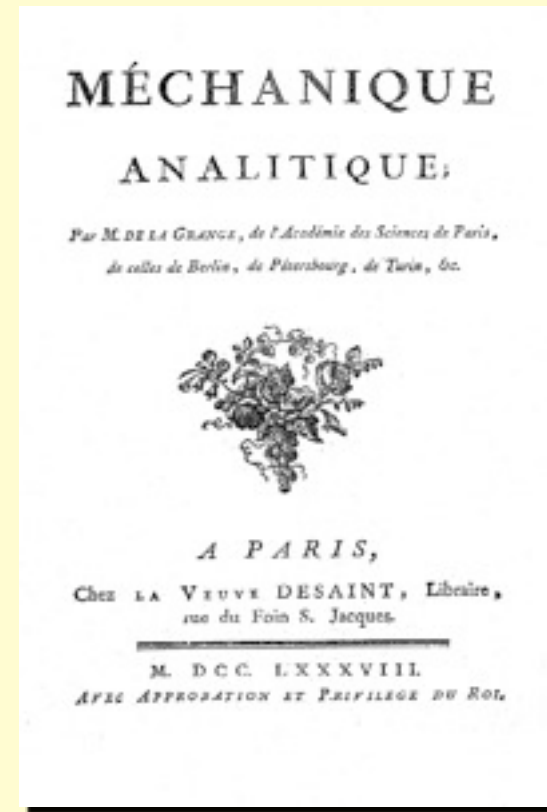
"Following Newton, I call force of inertia the property which bodies have of remaining in the state in which they are; now a Body is necessarily in either a state of rest or a state of motion...

1st Law: A Body at rest will persist at rest unless an external cause draws it out of that state. For a Body cannot of itself put itself into motion.

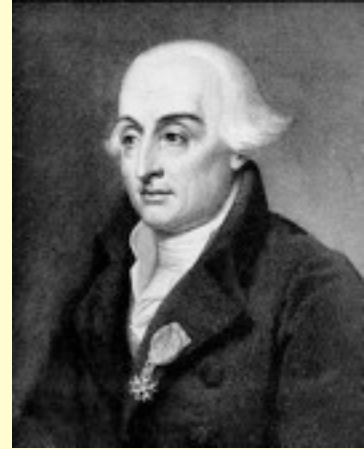
2nd Law: A Body once put into motion by any cause whatsoever must ever persist in motion that is uniform and in a straight line, if indeed a new cause, different from the former one which put the body in motion, does not act on it, that is to say, unless an outside force that is different from the cause of the motion acts on this Body, and it will move continually in a straight line and will traverse equal spaces in equal times."



Joseph Louis de la Grange (1736-1813)



"There are many treatises on mechanics, but the plan of this book is entirely new. My aim was to reduce the theory of mechanics, and the art of solving the associated problems, to general formulae, whose simple development provides all the equations necessary for the solution of each problem."



"This work will bring yet another advantage; it will unite, and present from one point of view, the different principles which have, so far, been found to assist in the solution of problems of mechanics; by showing their mutual dependence and making a judgement of their validity and scope possible. I divided this treatise into two parts: Statics or the Theory of Equilibrium, and Dynamics, or Theory of Motion. Rigid bodies and fluids are treated separately in each of these parts. **No diagrams will be found in this work.** The methods that I explain in it require neither constructions nor geometrical or mechanical arguments, but only the algebraic operations inherent to a regular and uniform process. Those who love Analysis will, with joy, see mechanics become a new branch of it and will be grateful to me for thus having extended its field."



A page from
Lagrange's *Mécanique analytique*
with the 'Lagrange equations'

9. De cette manière la formule générale du mouvement $\Gamma + \Delta = 0$ (art. 2) sera transformée en celle-ci,

$$\pi \delta \xi + \varphi \delta \downarrow + \phi \delta \phi + \&c = 0,$$

dans laquelle on aura

$$\pi = d. \frac{\partial T}{\partial d \xi} - \frac{\partial T}{\partial \xi} + \frac{\partial V}{\partial \xi}$$

$$\varphi = d. \frac{\partial T}{\partial d \downarrow} - \frac{\partial T}{\partial \downarrow} + \frac{\partial V}{\partial \downarrow}$$

$$\phi = d. \frac{\partial T}{\partial d \phi} - \frac{\partial T}{\partial \phi} + \frac{\partial V}{\partial \phi}$$

&c,

en supposant

$$T = S \left(\frac{dx^2 + dy^2 + dz^2}{2 dt^2} \right) m, V = S \Pi m,$$

$$\& d \Pi = P dp + Q dq + R dr + \&c.$$

Si donc dans le choix des nouvelles variables $\xi, \downarrow, \phi, \&c$, on a eu égard aux équations de condition données par la nature du système proposé, en sorte que ces variables soient maintenant tout-à-fait indépendantes les unes des autres, & que par conséquent leurs variations $\delta \xi, \delta \downarrow, \delta \phi, \&c$, demeurent absolument indéterminées, on aura sur le champ les équations particulières $\pi = 0, \varphi = 0, \phi = 0, \&c$, lesquelles serviront à déterminer le mouvement du système; puisque ces équations sont en même nombre que les variables $\xi, \downarrow, \phi, \&c$, d'où dépend la position du système à chaque instant.

Mais quoiqu'on puisse toujours ramener la question à cet état, puisqu'il ne s'agit que d'éliminer par les équations de condition, autant de variables qu'elles permettent de le faire, & de prendre ensuite pour $\xi, \downarrow, \phi, \&c$, les variables

Pierre Simon de Laplace (1749-1827)

TRAITÉ DE MÉCANIQUE CÉLESTE,

PAR P. S. LAPLACE,

Membre de l'Institut national de France, et du Bureau
des Longitudes.

TOME PREMIER.

DE L'IMPRIMERIE DE CRAPELET.

A PARIS,

Chez J. B. M. DUPRAT, Libraire pour les Mathématiques,
quai des Augustins.

AN VII.



according to the revolutionary calendar
introduced in 1792

”Given for one instant an intelligence which could comprehend all the forces by which nature is animated and the respective situation of the beings who compose it - an intelligence sufficiently vast to submit these data to analysis - it would embrace in the same formula the movements of the greatest bodies of the universe and those of the lightest atom; for it, nothing would be uncertain and the future, as the past, would be present to its eyes. The human mind offers, in the perfection which it has been able to give to astronomy, a feeble idea of this intelligence...”



Laplace, *A philosophical essay on probabilities* (1812)

„mixed” mathematics: all physics problems which could be treated with the use of mathematics

An example: Ch. Wolff, *Elementa Matheseos Universae*, Geneva 1743:

Tomus I. De Methodo mathematica brevis commentatio. Elementa Arithmeticae. Elementa Geometriae. Elementa Trigonometriae planae. Elementa Analyseos finitorum. Elementa Analyseos infinitorum.

Tomus II. Elementa Mechanicae & Staticae. Elementa Hydrostaticae. Elementa Aërometriae. Elementa Hydraulicae.

Tomus III. Elementa Opticae. Elementa Perspectivae. Elementa Catoptricae. Elementa Dioptricae. Elementa Sphaericorum & Trigonometriae Sphericae. Elementa Astronomiae.

Tomus IV. Elementa Geographiae & Hydrographiae. Elementa Chronologiae. Elementa Gnomonicae. Elementa Pyrotechnicae. Elementa Architecturae militaris. Elementa Architecturae civilis.

Tomus V. De praecipuis scriptis mathematicis brevis Commentatio. Commentatio de studio mathematico recte instituendo

How far are the stars?

4. That Light takes up more time in Travelling from the Stars to us, than we in making a *West-India* Voyage (which is ordinarily performed in six Weeks.) That a Sound would not arrive to us from thence in 50000 Years, nor a Cannon-Bullet in a much longer time. This is easily computed, by allowing (according to Mr. *Newton*) Ten Minutes for the Journey of Light from the Sun hither, and that a Sound moves about 1300 Foot in a Second.

Roberts, *Phil. Trans.* (1694)



James Bradley (1693-1762)

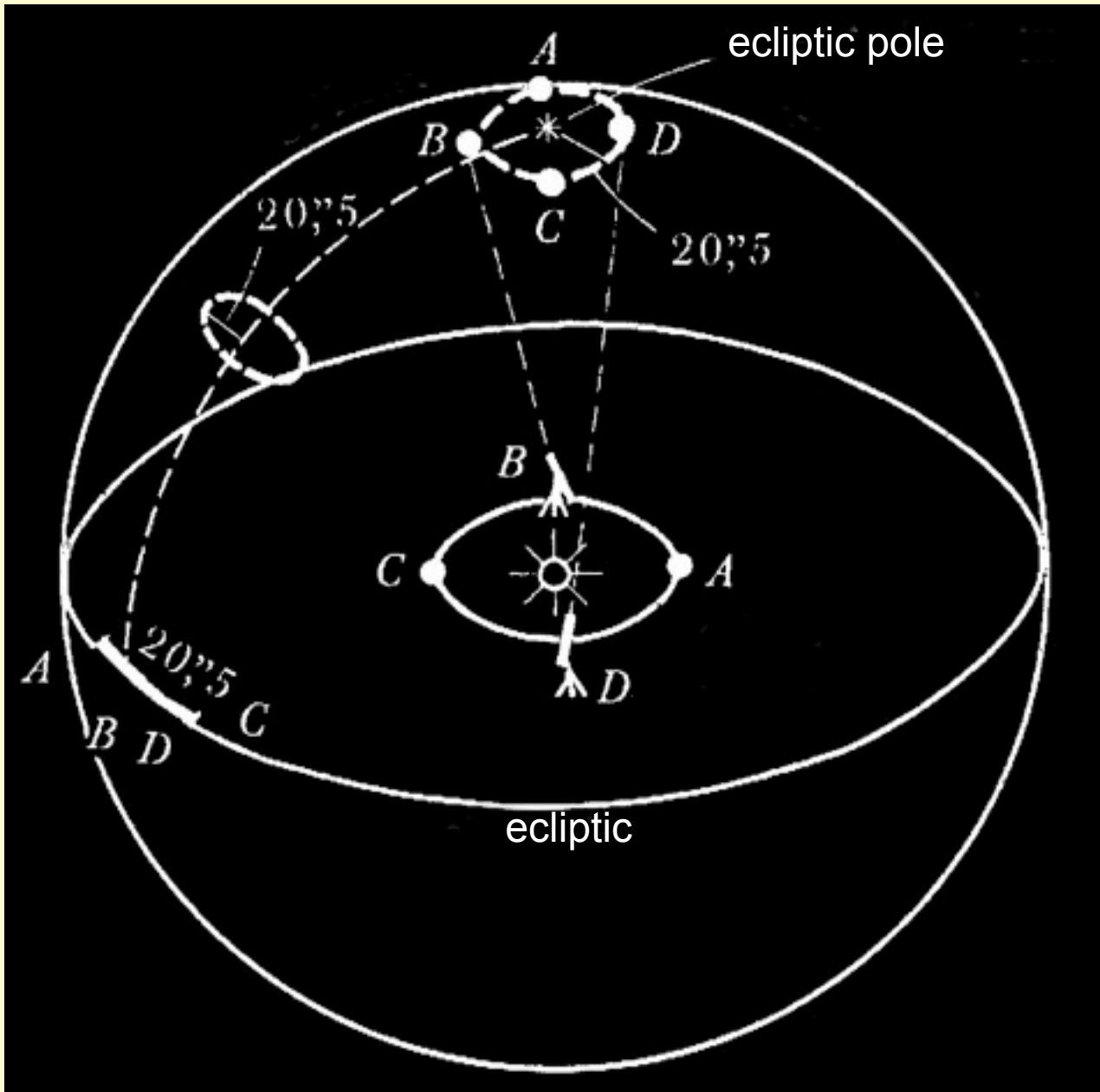
Discovery of the aberration of starlight

(Philosophical Transactions, 1729)

"...the Velocity of Light to the velocity of the Earth's annual Motion [is] as 10210 to One, from whence it would follow, that Light moves, or is propagated as far as from the Sun to the Earth in 8'12"... It must be granted, that the Parallax of the fixt stars is much smaller, that hath been hitherto supposed by those who have pretended to deduce it from their Observations...

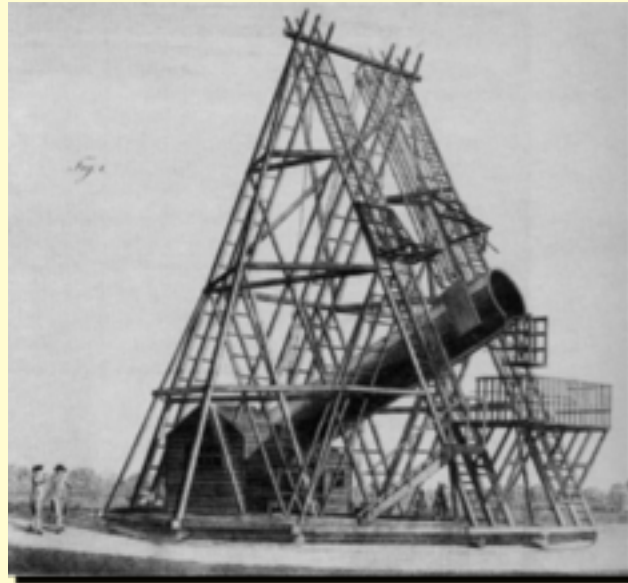
I am of the Opinion, that if it were 1", I should have perceived it, in the great number of Observations that I made especially of *γ Draconis*... it seems very probable that the Parallax of it is not so great as one single Second, and consequently that it is above 400000 times farther from us than the Sun."

Aberration of starlight





William Herschel (1738-1822)



Herschel's
great telescope;
diameter 147 cm
length 22 m

1781 Discovery of Uranus (13 III)

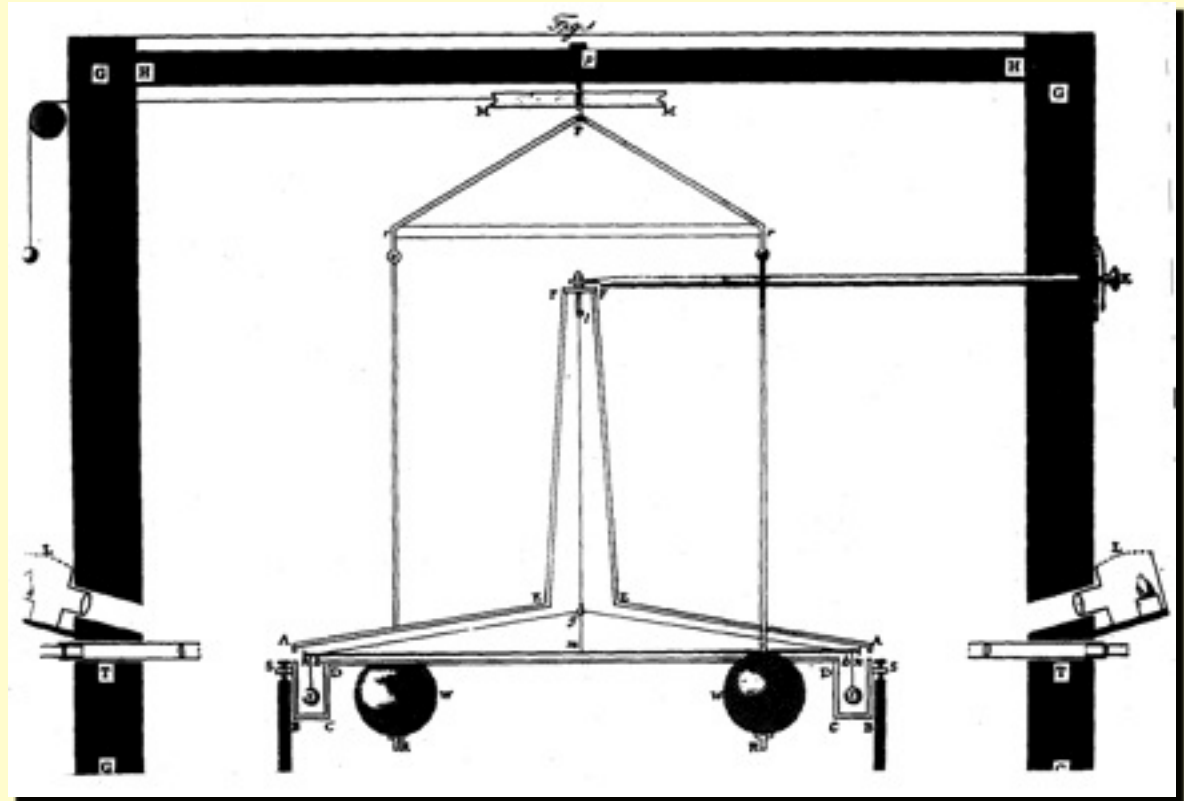
1783 Determination of the apex of the Sun (λ Her)

1785 Shape and dimensions of the Galaxy

Determination of the mass of the earth



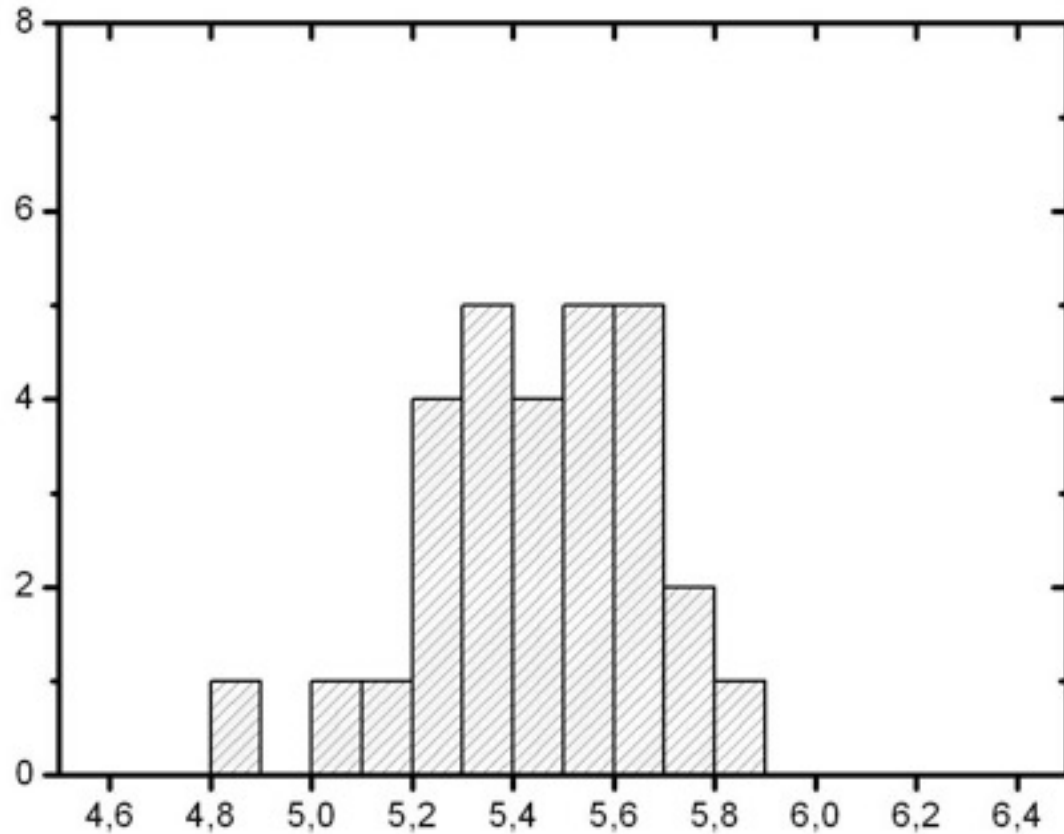
Henry Cavendish
(1731-1810)



Torsion balance used by Cavendish
(1798)

Cavendish's results

Number
of
measurements



Density of the earth in g/cm³

Final result: $5,48 \pm 0,39$

Physics of the phenomena of heat

Heat and cold were long regarded as **separate entities**,
i.e. cold was not conceived as a low degree of heat

For example, Pierre Gassendi, Peter van Musschenbroek
even discussed ***frigorific particles***

Example: Jean Baptiste Morin (1583-1656) thought that heat and cold had a certain maximum degree, which it could not exceed, and a certain minimum degree, below which it could not fall

An arbitrary assumption:

$$\text{degree of heat} + \text{degree of cold} = 8$$

For example: certain amount of water which had 2 degrees of heat and 6 degrees of cold was mixed with equal amount of water. According to Morin the mixture would have $2\frac{4}{5}$ degrees of heat and $5\frac{1}{5}$ degrees of cold



Temperature of mixtures

Comparison of some thermometric scales

Newton 1701	Roemer 1702	Amontons 1702	Fahrenheit 1717	Reaumur 1730	Delisle 1733	Celsius 1742	Sweden 1745	Deluc 1772	
34	60	73	212	80	0	0	100		Boiling water
12,5	22,5	59,2	96	30,8	96,5	64,3	35,5	28,5	Human body
0	7,5	51,5	32	0	150	100	0	0	Melting ice
	0								
-5,5		46	0	-14,2	176,2	117	-18		

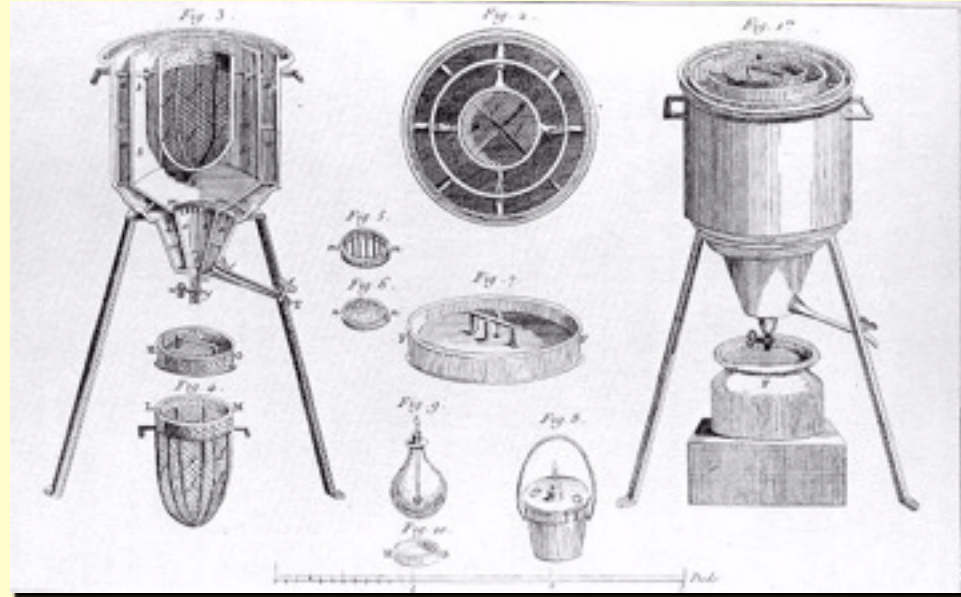
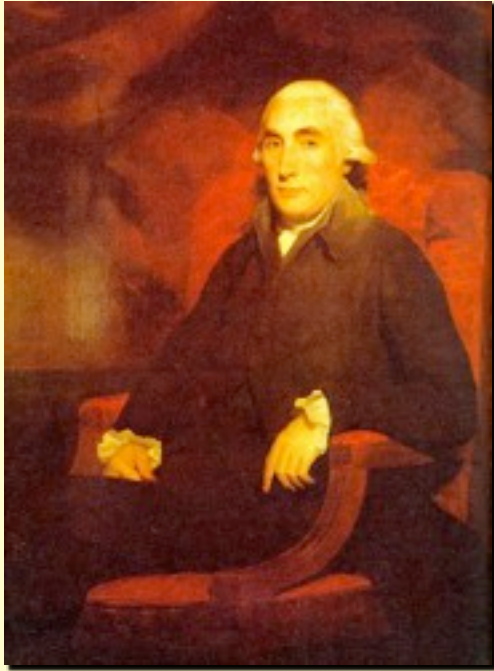
Thermometers measured 'heat'

(temperature from Latin *temperatura* - blending)

In equilibrium heat was thought to be simply proportional to volume or proportional to mass (e.g. Boerhaave, Musschenbroek) which was found by experiment **not** to agree with thermometric formulae of mixtures



Beginnings of calorimetry



Calorimeters
Laplace and Lavoisier (1783)

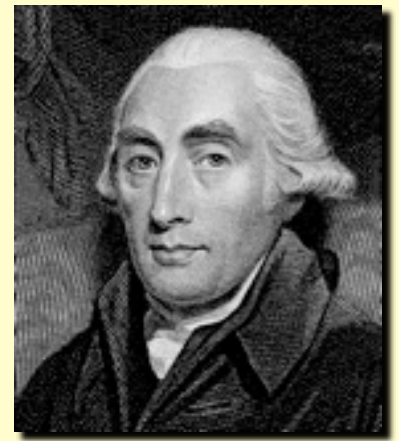
Joseph Black (1728-1799)

Found the difference between the amount of heat and temperature and discovered the latent heat (ca. 1760)



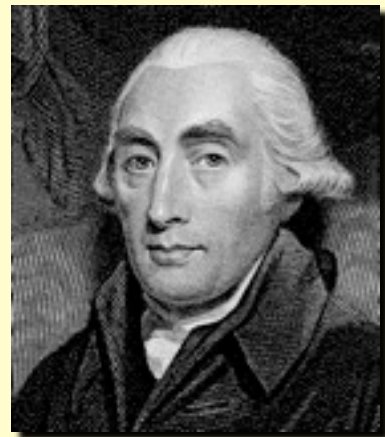
"First then it appears that true elementary fire is corporeal; since under the name corporeal is included any thing geometrically measurable by three lines, drawn perpendicularly to each other from the same centre...For suppose a solid silver globe suspended by a thread, and almost ignited; let it fall gently into cold water... the fire will distribute itself through the measurable spaces of such water... In effect, the whole history of fire evidently proves, that fire is extended as truly as body or space itself... The particles of fire, which have already been shown to be corporeal, appear further to be the smallest of all the bodies yet known; for if they be corporeal, they must necessarily be exceedingly subtle, as they readily penetrate all, even the densest bodies..."



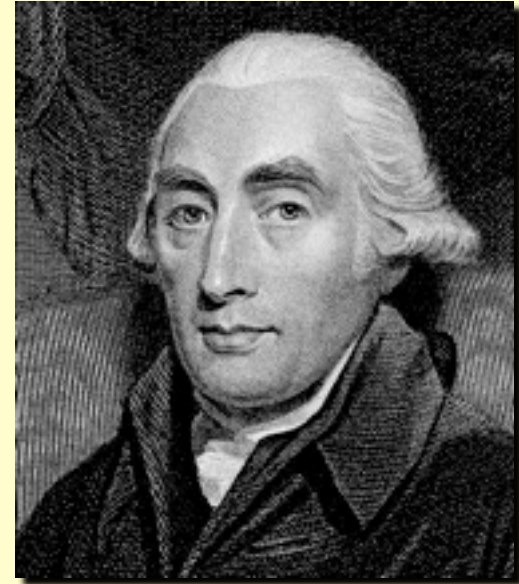


"By the use of thermometers we have learned that, if we take a thousand, or more, different kinds of matter – such as metals, stones, salts, woods, cork, feathers, wool, water and a variety of other fluids – although they be at first of different temperatures, and if we put them in a room... the heat will be communicated from the hotter of these bodies to the colder, during some hours perhaps, or the course of a day, at the end of which time, if we apply a thermometer to them all in succession, it will give precisely the same reading."

"This is what has been commonly called an 'equal heat', or the 'equality of heat among different bodies'; I call it the equilibrium of heat. The nature of this equilibrium was not well understood until I pointed out a method of investigating it. Dr. Boerhaave imagined that when it obtains, there is an equal quantity of heat in every equal volume of space, however filled up with different bodies; and professor Musschenbroek, in his *Physica*, expressed his opinion to the same purpose that 'fire is distributed through all the bodies, not in proportion to their weight, so that in a cubic foot of gold and of air and of feathers, there will be an equal quantity of heat'. The reason they give for this opinion is that, to whichever of these bodies the thermometer be applied, it gives the same reading."



”But this is taking a very hasty view of the subject. It is confounding the quantity of heat in different bodies with its intensity [temperature], though it is plain that these are two different things, and should always be distinguished, when we are thinking of the distribution of heat.”

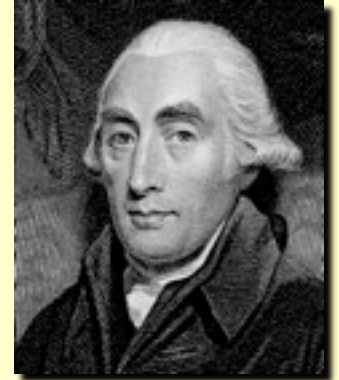


Joseph Black – *Lectures on the Elements of Chemistry*

"It was formerly a common supposition that the quantities of heat required to increase the temperatures of different bodies by the same number of degrees were directly proportional to the quantities of matter in them; and therefore, when the bodies were of equal volumes, that the quantities of heat were proportional to their densities. But very soon after I began to think on this subject (*anno 1760*), I perceived that this opinion was a mistake, and that the quantities of heat which different kinds of matter must receive to raise their temperatures by an equal amount of degrees are not in proportion to the quantity of matter in each, but in proportions widely different from this, and for which no general principle or reason could yet be assigned."

"This opinion was first suggested to me by an experiment described by Dr. Boerhaave... After relating an experiment on the mixing of hot and cold water which Fahrenheit made at his desire, Boerhaave also tells us that Fahrenheit agitated together quicksilver and water of initially different temperatures. From the Doctor's account, it is quite plain that the quicksilver, though it has more than 13 times the density of water, had less effect in heating or cooling the water with which it was mixed than would have been produced by an equal volume of water. He says expressly that the quicksilver, whether it was applied hot to cold water, or cold to hot water, never produced more effect in heating or cooling an equal volume of the water than would have been produced by water of the same initial temperature as the quicksilver, and only two-thirds of its volume. He adds that it was necessary to mix three volumes of quicksilver with two of water in order to produce the same middle temperature that is produced by mixing equal volumes of hot and cold water."

Joseph Black thus discovered that the **capacity of heat** of various substances differs;
later he discovered and measured the **latent heat** of melting and evaporation.

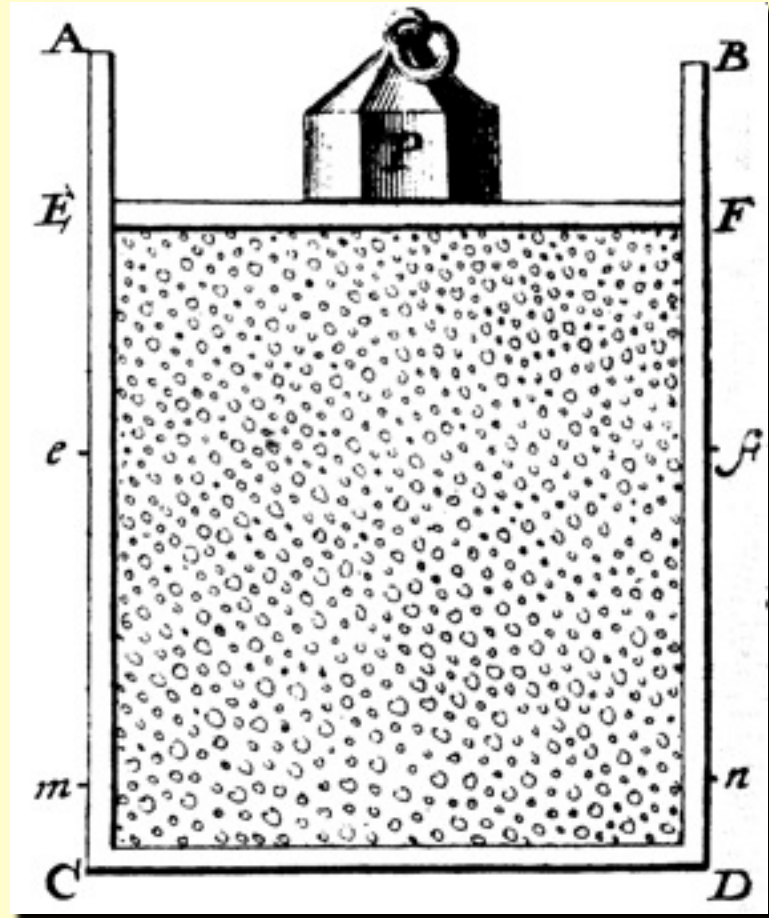
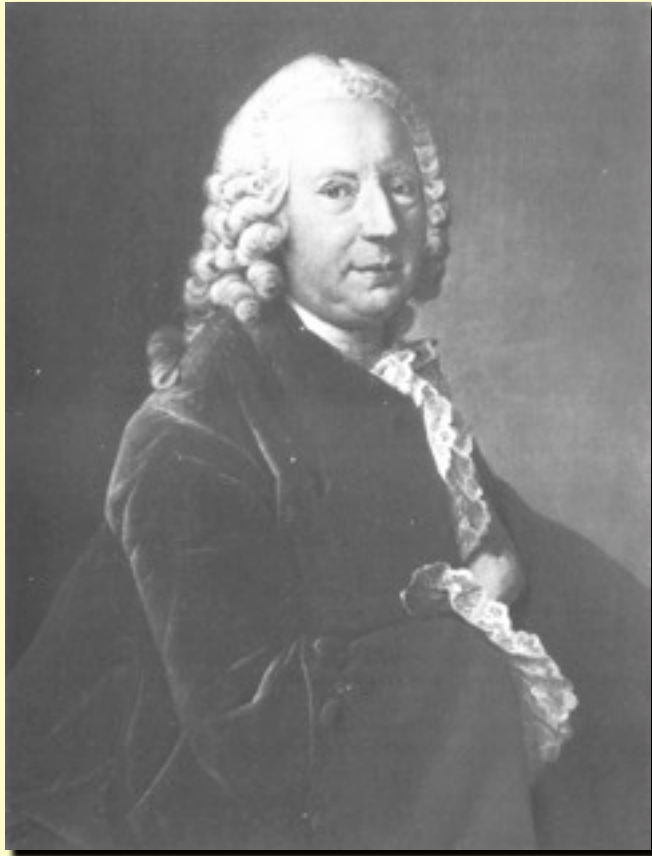


In Sweden Johann Carl Wilcke made similar discoveries independently of Black;
he proposed the term **specific heat**.



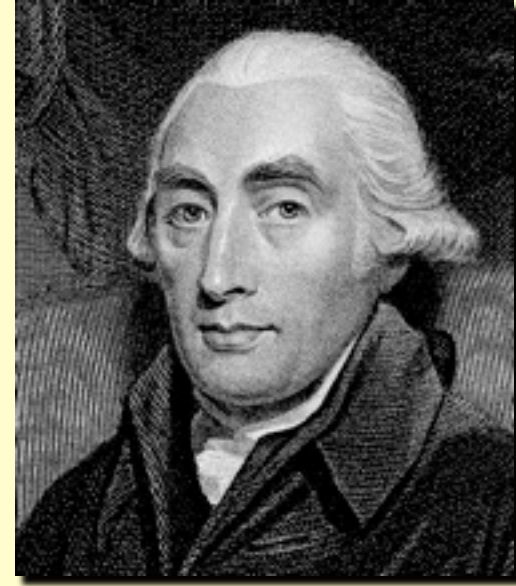
Caloric and phlogiston

Daniel Bernoulli - *Hydrodynamica* (1738)



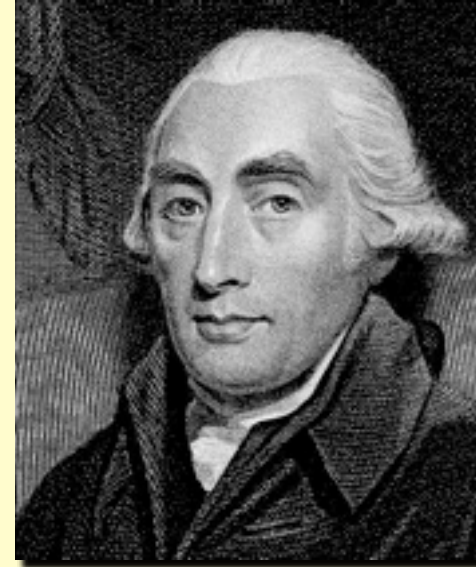
First explanation of Boyle-Mariotte's law in a kinetic theory of gases

"The greater number of French and German philosophers, and Dr. Boerhaave, have held that the motion of which they suppose heat to consist is not a tremor, or vibration, of the particles of the hot body itself, but of the particles of a subtle, highly elastic, and penetrating fluid matter, which is contained in the pores of hot bodies...Some suppose that this matter, when modified in different ways, produces light and the phenomena of electricity..."



Joseph Black, Lectures on the Elements of Chemistry

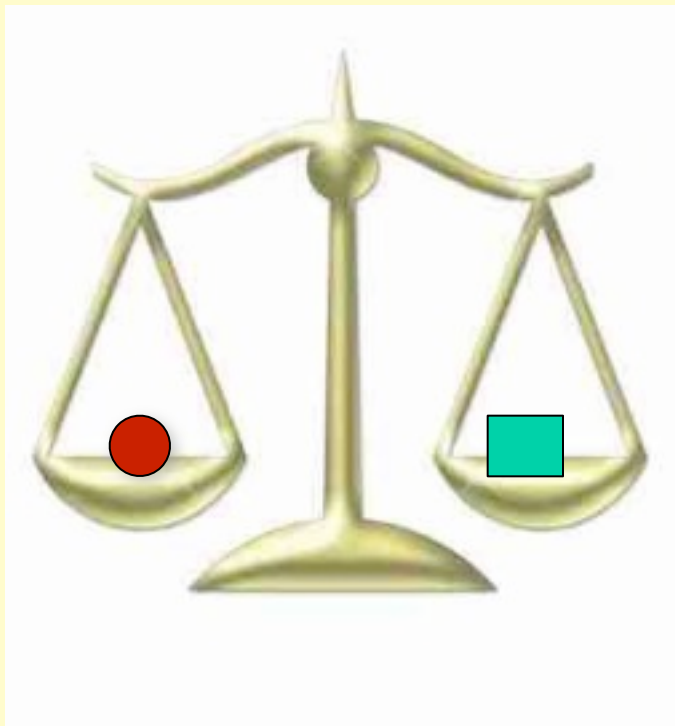
"A more ingenious attempt has lately been made...by the late Dr. Cleghorn in his inaugural dissertation on the subject of heat published here [Edinburgh, 1779]. ...other philosophers had assumed, or supposed, one property only as belonging to this subtle matter, namely, its great elasticity, or strong repulsion of its particles for one another, whereas Dr. Cleghorn has supposed it to have still another property, namely, a strong attraction for the particles of the other kind of matter in nature, which have in general more or less [gravitational] attraction to each other... Such an idea of the nature of heat is the most probable of any I know..."



Joseph Black, Lectures on the Elements of Chemistry

Basic assumptions of the theory of caloric

1. Caloric is a fluid, whose particles repel each other.
2. Particles of caloric are attracted by particles of ordinary matter; this attraction differs for different substances.
3. Caloric is a fluid which is indestructible and impossible to create. This specific 'principle of conservation of caloric' was fundamental for its theory.
4. Caloric can be free or latent. Free caloric forms an 'atmosphere' around each particle of matter; latent caloric blends with particles of matter and forms combinations similar to chemical compounds.
5. Caloric is (probably) weightless.



Numerous efforts to determine the density of the caloric by using a simple balance gave conflicting results

Herman Boerhaave (1732) – heated copper does not change weight

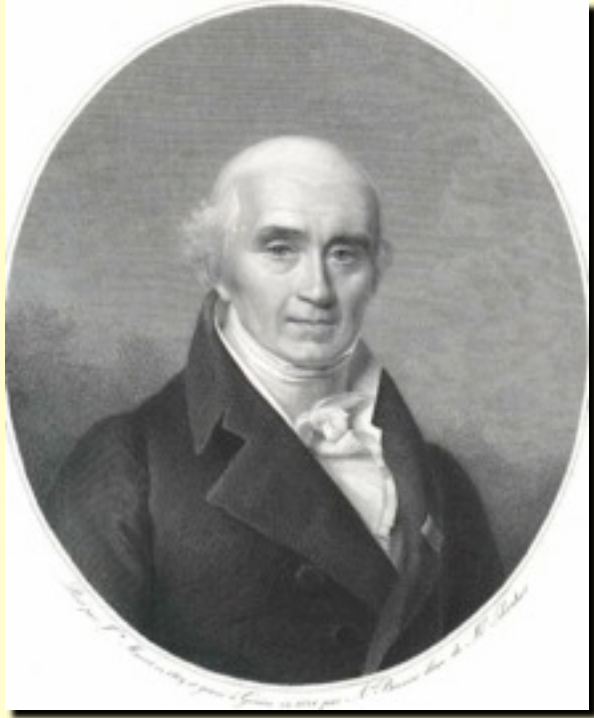
Georges Buffon (1773) – heated iron gains weight

John Roebuck (1776) – heated iron loses weight

George Fordyce (1785) – frozen water gains weight

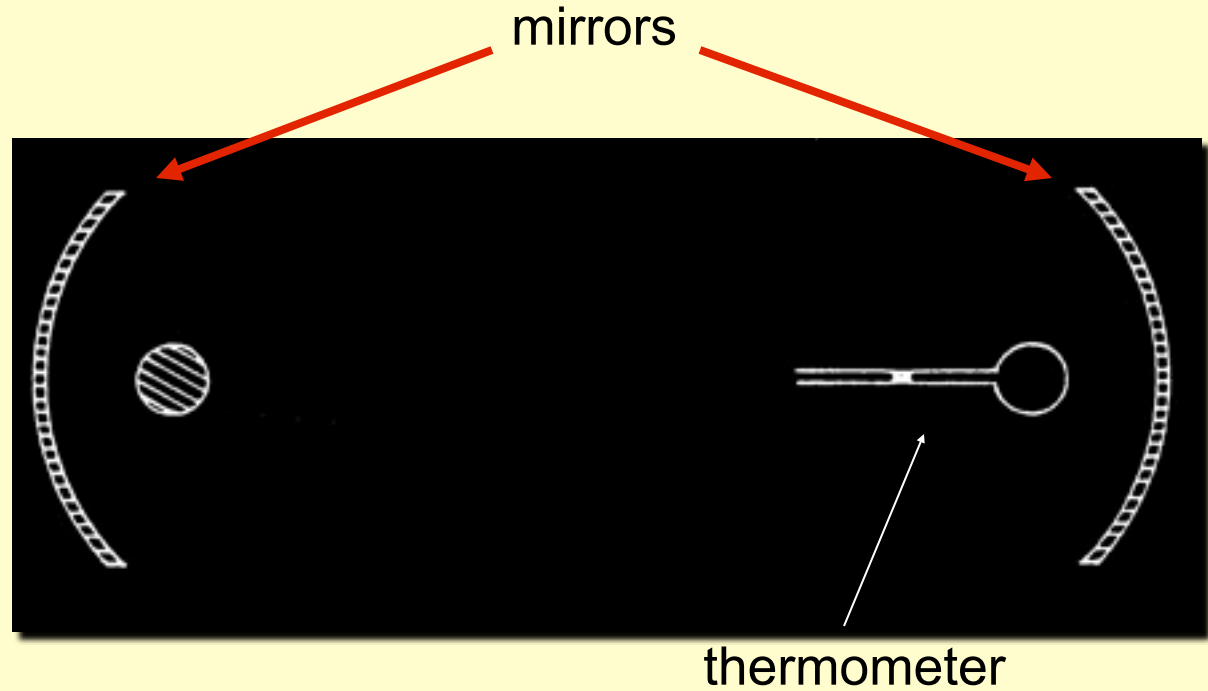
Count Rumford (1799) – no effect at all (after numerous experiments)

Radiation of heat and cold

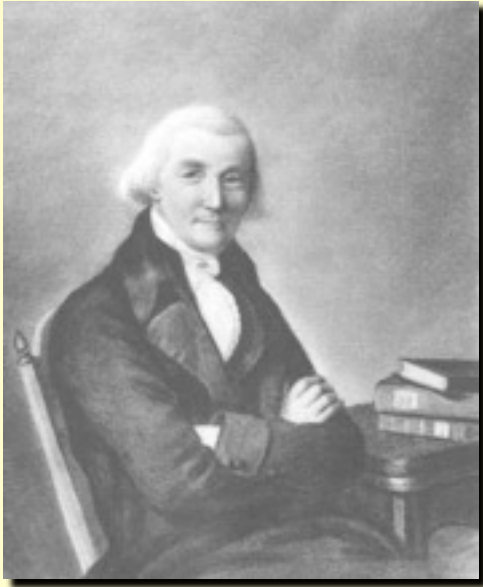


Marc-Auguste Pictet

Essai sur le feu (1790)



Explanation of Pictet's experiments



"dynamic equilibrium"
(l'équilibre mobile)
between radiated and
absorbed heat

Pierre Prevost

Mémoire sur l'équilibre du feu (1791)

"This fire material, of and by itself and apart from other things, especially air and water, is not found united and active, either as a liquid or in an attenuated state. But if once by the movement of fire, with the addition of free air, it is attenuated and volatilized, then by this in all such conditions it is lost through unrecognizable subtlety and immeasurable attenuation, so that from this point on no science known to man, no human art, can collect it together or bring it into narrow limits, especially if this occurred rapidly and in quantity..."

Georg Ernest Stahl, *Zufällige Gedanken...
von den Sogenannten Sulphure* (1718)



"From all these various conditions, therefore, I have believed that it should be given a name, as the first, unique, basic, inflammable principle... I have felt that it is most fitting to name it from its general action, which it customarily shows in all its compounds. And therefore I have chosen the Greek name *phlogiston* (inflammable)."

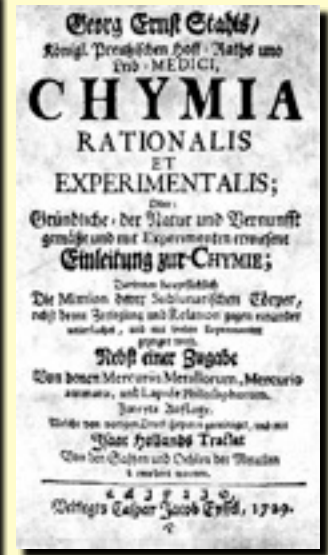
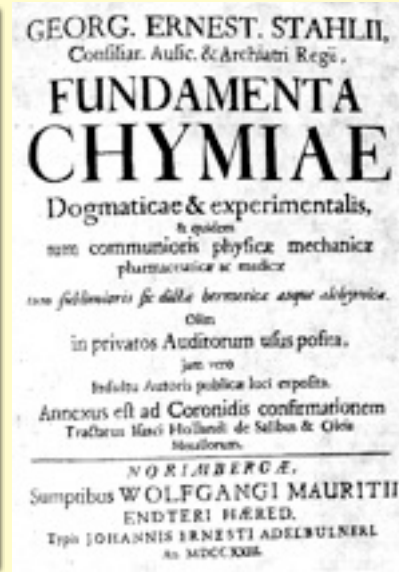
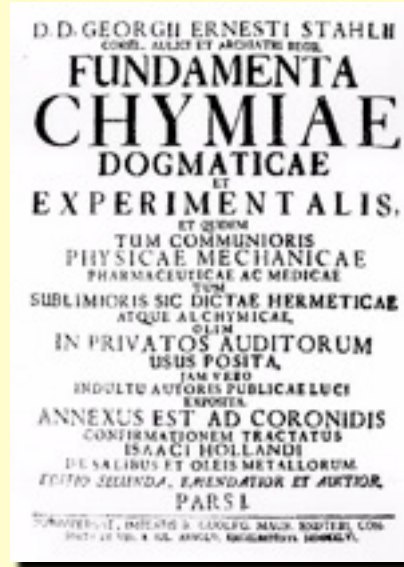


Georg Ernest Stahl, *Zufällige Gedanken... von den Sogenannten Sulphure* (1718)

The phlogiston theory

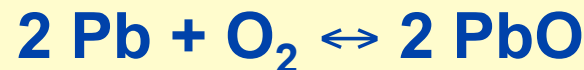


Georg Ernest Stahl
(1660-1734)



Phlogiston theory: metal \rightarrow 'calx' + phlogiston
'calx' + charcoal (*rich in phlogiston*) \rightarrow metal
Lavoisier:
metal + air \rightarrow 'calx'
'calx' + charcoal \rightarrow metal + 'fixed air'

Nowadays:



"You do not surely expect that chemistry should be able to present you with a handful of phlogiston separated from an inflammable body; you may just as reasonably demand a handful of magnetism, gravity or electricity to be extracted from a magnetic, weighty or electric body; there are powers in Nature, which cannot otherwise become the objects of sense, than by the effects they produce, and of this kind is phlogiston."

Richard Watson, *Chemical Essays* (1782)



TRAITE ÉLÉMENTAIRE DE CHIMIE,

PRÉSENTÉ DANS UN ORDRE NOUVEAU
ET D'APRÈS LES DÉCOUVERTES MODERNES;

Avec Figures:

Par M. LAVOISIER, de l'Académie des Sciences, de la Société Royale de Médecine, des Sociétés d'Agriculture de Paris & d'Orléans, de la Société Royale de Londres, de l'Institut de Bologne, de la Société Helvétique de Basle, de celle de Philadelphie, Harleux, Manchester, Padoue, etc.



A PARIS,

Chez CUCHET, Libraire, rue du Croc-Serpente.

M. DCC. LXXXIX.

Sous le Privilège de l'Académie des Sciences & de la Société Royale de Médecine.

	Noms nouveaux.	Noms anciens correspondans.
	Lumière.....	Lumière. Chaleur. Principe de la chaleur.
	Calorique.....	Fluide igné. Feu. Matière du feu & de la chaleur.
Substances simples qui appartiennent aux trois règnes & qu'on peut regarder comme les élémens des corps.	Oxygène.....	Air déphlogistiqué. Air empiréal. Air vital. Base de l'air vital.
	Azote.....	Gaz phlogistiqué. Mofete. Base de la mofete.
	Hydrogène.....	Gaz inflammable. Base du gaz inflammable.
	Soufre.....	Soufre.
	Phosphore.....	Phosphore.
Substances simples non métalliques oxidables & acidifiables.	Carbone.....	Charbon pur.
	Radical muriatique.	Inconnu.
	Radical fluorique.	Inconnu.
	Radical boracique.	Inconnu.
	Antimoine.....	Antimoine.
Substances simples métalliques oxidables & acidifiables.	Argent.....	Argent.
	Arsenic.....	Arsenic.
	Bismuth.....	Bismuth.
	Cobalt.....	Cobalt.
	Cuivre.....	Cuivre.
	Étain.....	Étain.
	Fer.....	Fer.
	Manganèse.....	Manganèse.
	Mercure.....	Mercure.
	Molybdène.....	Molybdène.
	Nickel.....	Nickel.
	Or.....	Or.
Substances simples salifiables terreuses.	Platine.....	Platine.
	Plomb.....	Plomb.
	Tungstène.....	Tungstène.
	Zinc.....	Zinc.
	Chaux.....	Terre calcaire, chaux.
	Magnésie.....	Magnésie, base du sel d'Epsom.
	Baryte.....	Barote, terre pesante.
	Alumine.....	Argile, terre de l'alun, base de l'alun.
	Silice.....	Terre siliceuse, terre vitrifiable.

”...in the work published by M. De Morveau, M. Berthollet, M. De Fourcroy, and myself, upon the reformation of chemical nomenclature...we have distinguished the cause of heat, or that exquisitely elastic fluid which produces it, by the name of *caloric*.

...In the present state of our knowledge, we are unable to determine whether light be a modification of caloric, or if caloric be, on the contrary, a modification of light. This, however, is indisputable, that, in a system where only decided facts are admissible, we are to avoid, as far as possible, to suppose any thing to be, that is not really known to exist, we ought provisionally to distinguish, by distinct terms, such things as are known to produce different effect. We have therefore distinguish light from caloric; though we do not therefore deny that these have certain qualities in common, and that, in certain circumstances, they combine with other bodies almost in the same manner, and produce, in part, the same effects.”

Lavoisier, *Traité élémentaire de chimie* (1789)

"What I have already said may suffice to determine the idea affixed to the word *caloric*; but there remains a more difficult attempt, which is, to give a just conception of the manner in which caloric acts upon other bodies. Since this subtle matter penetrates through the pores of all known substances; since there are no vessels through which it cannot escape, and, consequently, as there are none which are capable of retaining it, we can only come at the knowledge of its properties by effects which are fleeting, and therefore ascertainable...



We have already seen, that the same body becomes solid, or liquid, or aeriform, according to the quantity of caloric by which it is penetrated; or, to speak more strictly, according as the repulsive force exerted by the caloric is equal to, stronger, or weaker, than the attraction of the particles of the body it acts upon."

Lavoisier, Traité élémentaire de chimie (1789)

"Caloric penetrates all bodies; it separates their particles by lodging between them, and diminishes their attraction; it dilates bodies, it liquifies solids, and rarifies liquids to such a degree, as to render them invisible, give them the form of air, and convert them into elastic, compressible, aeriform fluids. Hence it follows that liquids are combinations of solids with caloric, and that gases are solutions of different bodies in caloric, which of itself is the most attenuate, subtile, light, and elastic of all natural substances; accordingly its weight cannot be estimated...



All these facts prove that caloric is a particular substance, and not a modification of all substances, as some natural philosophers have imagined; and it is far from having been shown to be the same thing with light; for the farther we advance in the science of physics, the greater differences appear in the action of these two substances."

Antoine-François de Fourcroy, The Philosophy of Chemistry (1800)

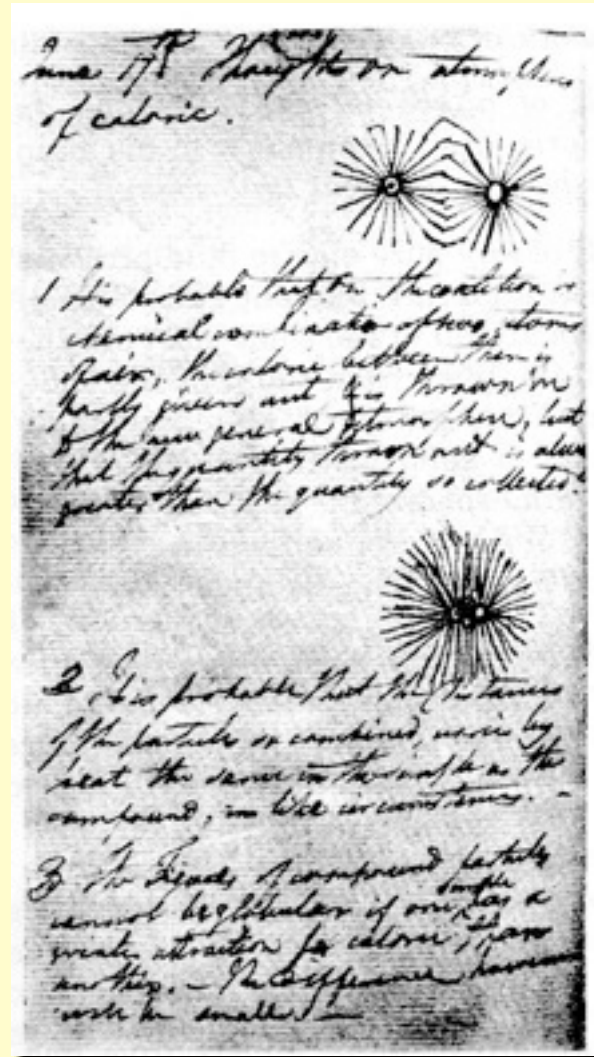
**The fluid of heat (caloric)
had properties similar
to those of the electric fluid**

Facts explained by the caloric theory

- **Existence of gases**
- **States of matter**
- **Thermal expansion and its variations**
- **Production of heat by friction**
- **Conductivity of heat (Fourier)**
- **Transfer of heat through the vacuum**
- **Differences in the specific heat**
- **C_p/C_v (Laplace, Poisson)**
- **Radiation, absorption and reflection of heat**

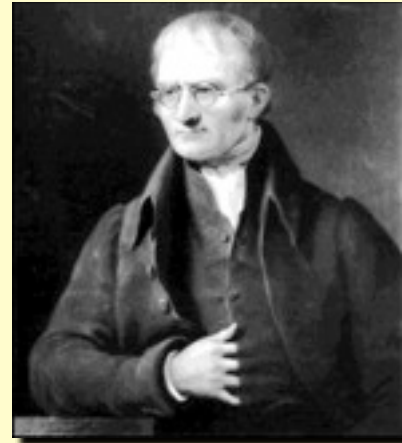


John Dalton
(1766-1844)



"Newton had demonstrated, in the 23rd Proposition of the *Principia*, that an elastic fluid is constituted of small particles or atoms of matter, which repel each other by a force increasing in proportion as their distance diminishes..."

John Dalton, 1810



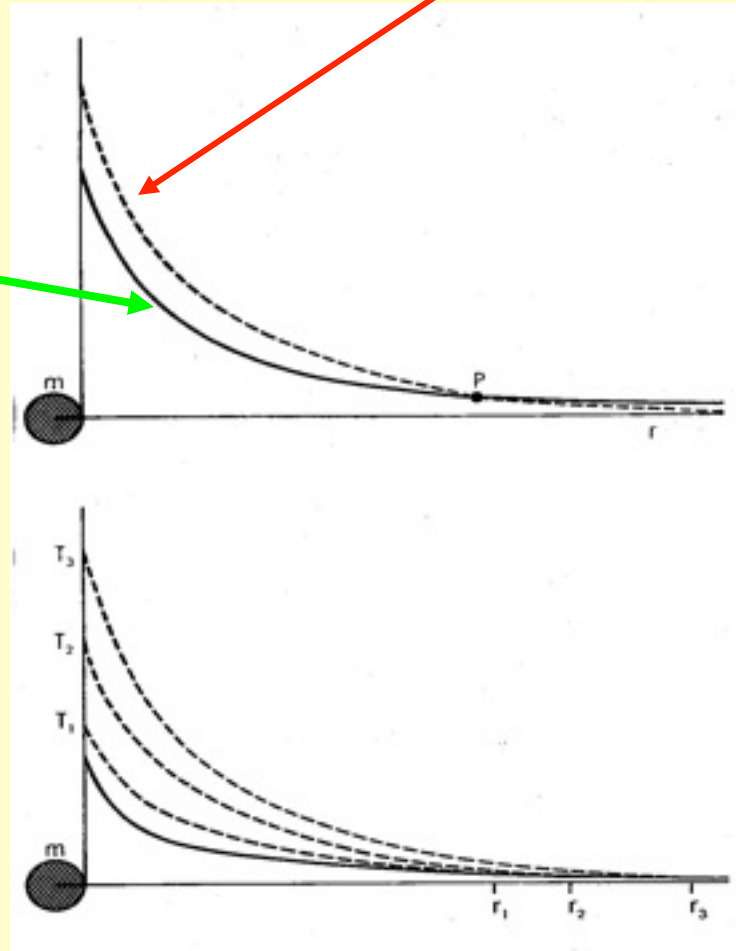
However, Newton wrote clearly:

"If a fluid be composed of particles fleeing from each other, and the density be as the compression, the centrifugal forces of the particles will be inversely proportional to the distances of their centres..."

But whether elastic fluids do really consist of particles so repelling each other, is a physical question. We have demonstrated mathematically the property of fluids consisting of particles of this kind, that hence philosophers may take occasion to discuss that question."

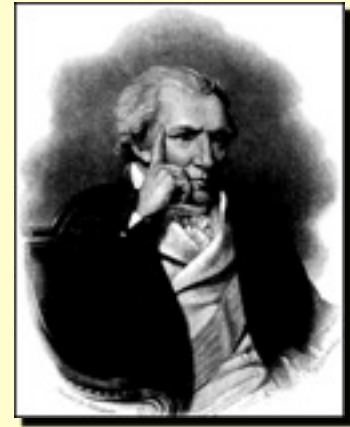
caloric repulsion

**gravitational
attraction**



Thermal expansion in the caloric theory

Experiments on boring cannons
by Benjamin Thompson (Rumford)
in 1798...



and experiments on heat produced
by friction between pieces of ice
by Humphry Davy (1799),

interpreted in favour of the mechanical interpretation
of heat, were easily disposed of by the proponents
of the caloric.

An example of criticism:

"That the quantity of heat evolved in this experiment was great cannot be disputed, yet it was by no means sufficient to warrant the conclusions that have been made... In these experiments, a very large mass of metal was submitted to an excessive pressure, and of the mass, fresh strata was continually exposed to the compression by the wearing off of the brass; hence a definite quantity of heat was separated from each stratum in succession. Now if we admit the existence of caloric in a state of great density in the metals, this cause would be quite adequate to the production of the observed effect. The gravest error appears to the assumption that the source of heat thus generated is inexhaustible; the quantity that can thus be excited is finite, but will not cease, according to this picture, until all the brass is worn away."

J. B. Emmett, *Annals of Philosophy*, 1820

Some remarks on the state of chemistry

Chemistry before Lavoisier's reform

- The theory of the four elements was still accepted, and even 'confirmed' experimentally, e.g. by van Helmont.
- The alchemists were convinced that the number of combinations of the four elements can be **infinite**. Even metals were then treated as mixtures of the elements.
- Paracelsus introduced three 'principles': quicksilver (principle of solubility), sulphur (principle of combustion), and salt (principle of stability). He tried to convince chemists to abandon fruitless search for the 'philosophical stone' and concentrate instead on finding new drugs (iatrochemistry).
- Michael Sendivogius believed in the four elements but also in the three principles of Paracelsus.
- Robert Boyle – new definition of chemical element proposed in *Sceptical Chymist* (1661).



Paracelsus
(1493-1541)



Michael Sendivogius
(1566-1636)



Jan Baptista
van Helmont
(1577-1644)



Deciphered,

1. The form of an *Athamor* or great *Furnace*.
- 2: The *Forceps* or *Tongs* and *Fork*.
3. The *Coppel* or *Test*, with *Philosophers Bellows*.
4. The *Digestive Pot* with its *Cover* and *Fire* about it.
5. A cover'd *Crucible*.
6. The long *Bell*, or *Matras-Glass* on a *Sand Furnace*.
7. The *Wind Furnace* with a *Blow-pipe*.
8. A *Furnace* with a *Copper head*, and its *Receiver*.
9. A *Furnace* with a *naked* and open *Fire*.
10. The *Pestel* and *Mortar*, with one beating the *Metals*.
11. The *Owl's Head*, or another form of a *Cover* to the *Figure 8*.
12. A *Retort*.

**A NEW LIGHT
OF
ALCHYMIE:**

Taken out of the fountaine of
NATURE, and Manuall
Experience.

To which is added a TREATISE of
SVLPHR:

Written by *Michael Sendivogius*:
i.e. Anagrammatically,
DIFI LESCHI GENVS AMO.

Also Nine Books *Of the Nature of Things*,
Written by PARACELSUS, viz.

Of the	{	Generations	}	Renewing	{	of Nature's things.
		Growth		Transmutation		
		Conservation		Separation		
		Life : Death		Signatures		

Also a Chymicall Dictionary explaining hard places
and words met withall in the writings of Paracelsus,
and other obscure Authors.

All which are faithfully translated out of the
Latin into the English tongue,

By J. F. M.D.

London, Printed by Richard Cotes, for Thomas Williams, at the
Bible in Little-Britain, 1650.

COSMOPOLITE

OV
NOUVELLE LUMIERE
de la Physique naturelle.

*Traictant de la constitution generale des
Elements simples & des composez.*

Traduit nouvellement de LATIN
EN FRANÇOIS.

Par le Sieur DE BOSNET



A PARIS.

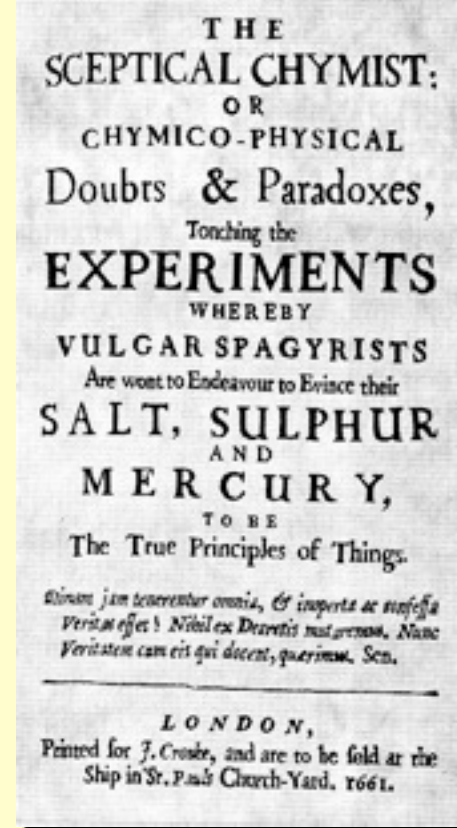
Chez ABRAHAM PACARD, rue sainte
Iacques, au sacrifice d'Abraham.

M. DC. XVIII.

The works of Michael Sendivogius were very popular and were translated into many languages. Newton had several of them in his library.



Robert Boyle



"I now mean by Elements, as those Chymists that speak plainest do by their principles, certain Primitive and simple, or perfectly unmingled bodies; which not being made of any other bodies, or of one another, are the Ingredients of which all those call'd perfectly mixt Bodies are immediatetly compounded, and into which they are ultimately resolved..."

”...if by the term ‘elements’ we mean to express those simple and indivisible molecules of which matter is composed, it is extremely probable we know nothing at all about them; but, if we apply the term ‘elements’ or ‘principles of bodies’, to express our idea of the last point which analysis is capable of reaching, we must admit, as elements, all the substances into which we are capable, by any means, to reduce bodies by decomposition. Not that we are entitled to affirm that these substances we consider as simple may not be compounded of two, or even of a greater number of principles; but, since these principles cannot be separated, or rather since we have not hitherto discovered the means of separating them, they act with regard to us as simple substances, and we ought never to suppose them compounded until experiment and observation has proved them to be so.”

Antoine Lavoisier, Traité élémentaire de chimie (1789)

TABLE OF SIMPLE SUBSTANCES.

Simple substances belonging to all the kingdoms of Nature, which may be considered as the chemical elements of bodies.

<i>English.</i>	<i>New Names.</i>	<i>Latin.</i>	<i>Correspondent Old Names.</i>
Light			Light.
			Heat.
Caloric	Caloricum		Principle or element of heat, Fire, Igneous fluid, Matter of fire and of heat.
Oxygen	Oxygenum		Dephlogisticated air, Empyrean air, Vital air, or Base of vital air.
Azot	Azotum		Phlogisticated air or gas, Mephitic, or its base,
Hydrogen	Hydrogenum		Inflammable air or gas, or the base of inflammable air.

Oxydable and Acidifiable simple Substances not Metallic.

<i>New Names.</i>	<i>Latin.</i>	<i>Correspondent old Names.</i>
Sulphur	Sulphurum	The same names.
Phosphorus	Phosphorum	
Carbon	Carbonum	The simple element of charcoal.
Muriatic radical	Murium	
Fluoric radical	Fluorum	Still unknown.
Boracic radical	Boracum	

Oxydable and Acidifiable simple Metallic Bodies.

<i>New Names.</i>	<i>Latin.</i>	<i>Correspondent old Names.</i>
Antimony	Antimonium	Antimony.
Arsenic	Arsenicum	Arsenic.
Bismuth	Bismuthum	Bismuth.
Cobalt	Cobaltum	Cobalt.
Copper	Cuprum	Copper.
Gold	Aurum	Gold.
Iron	Ferrum	Iron.
Lead	Plumbum	Lead.
Manganese	Manganum	Manganese.
Mercury	Mercurium	Mercury.
Molybdena	Molybdenum	Molybdena.
Nickel	Nickolum	Nickel.
Platina	Platinum	Platina.
Silver	Argentum	Silver.
Tin	Stannum	Tin.
Tungstein	Tungstenum	Tungstein.
Zinc	Zincum	Zinc.

Lavoisier 1789

Elements

ca. 1750

ca. 1800

fire

light
electric fluid
magnetic fluid
caloric

air

oxygen

nitrogen

water

hydrogen

oxygen

earth

iron, gold, silver, copper,
lead, carbon, sulphur, silicon,
bismuth, cobalt, nickel, platinum,
tin, zinc, mercury, antimony,
arsenic, molybdenum, manganese...

Modern atomic theory

The gas laws

1699-1702 **Guillaume Amontons** – air pressure increases approximately in proportion to its temperature

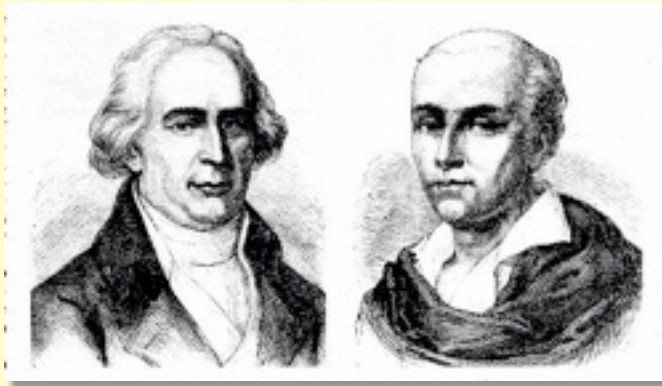
XVIIIth century – studies of thermal expansion of air made by many physicists (**Berthollet, Deluc, De la Hire, Hauksbee, Lambert, Priestley, Saussure**, and others) gave conflicting results: some found nonuniform expansion, the others - expansion uniform but with the coefficient of thermal expansion from $1/85$ to $1/235$

1787 **Jacques Charles** – thermal expansion of air, oxygen, nitrogen, hydrogen, carbon dioxide is uniform (unpublished result)

1793 **Alessandro Volta** – the coefficient of thermal expansion of air equals $1/270$ (however, Volta's paper published in *Annali di Chimica* was not known among the physicists)

1802 **John Dalton** - thermal expansion of various gases is about the same

1802 **Joseph-Louis Gay-Lussac** – measurements of thermal expansion of gases can be represented as $V = V_0(1 + \alpha t)$, where the coefficient of thermal expansion $\alpha = 1/266,66$ (**Gay-Lussac Law**)



Joseph-Michel and Jacques-Etienne Montgolfier
The first public demonstration of a hot-air balloon
4 July, 1783



The first piloted flight of
a hot-air balloon
November 21, 1783



The first piloted flight of
a hydrogen balloon
December 1, 1783

The XVIIIth century opinions of physicists concerning atoms were sometimes ironic

”Atom – small corpuscle perfectly rigid, hard, nonporous, and non-divisible. Some philosophers admitted that atoms exist as parts of all bodies. But is it reasonable to admit existence of something defined as above? Atoms are certainly matter, since otherwise they could not be parts of bodies. If they are matter, then they are composed of differing parts because the upper part differs from the lower part, the right part differs from the left part etc. But if they are composed of parts then they are divisible and not non-divisible atoms. The system of Epicurus concerning atoms is too ridiculous to be worth discussing here.”











Dictionnaire raisonné de physique (1781)

"Whether the ultimate particles of a body, such as water, are all alike, that is, of the same figure, weight, etc. is a question of some importance. From what is known, we have no reason to apprehend a diversity in these particles; if it does exist in water, it must equally exist in elements constituting water, namely, hydrogen and oxygen. Now, it is scarcely possible to conceive how the aggregates of dissimilar particles should be so uniformly the same. If some of the particles of water were heavier than others, if a parcel of the liquid on any occasion were constituted principally of these heavier particles, it must be supposed to affect the specific gravity of the mass, a circumstance not known. Similar observations may be made on other substances. Therefore we may conclude that *the ultimate particles of all homogeneous bodies are perfectly alike in weight, figure, etc.* In other words, every particle of water is like every other particle of water; every particle of hydrogen is like every other particle of hydrogen..."



John Dalton, *A New System of Chemical Philosophy* (1808)

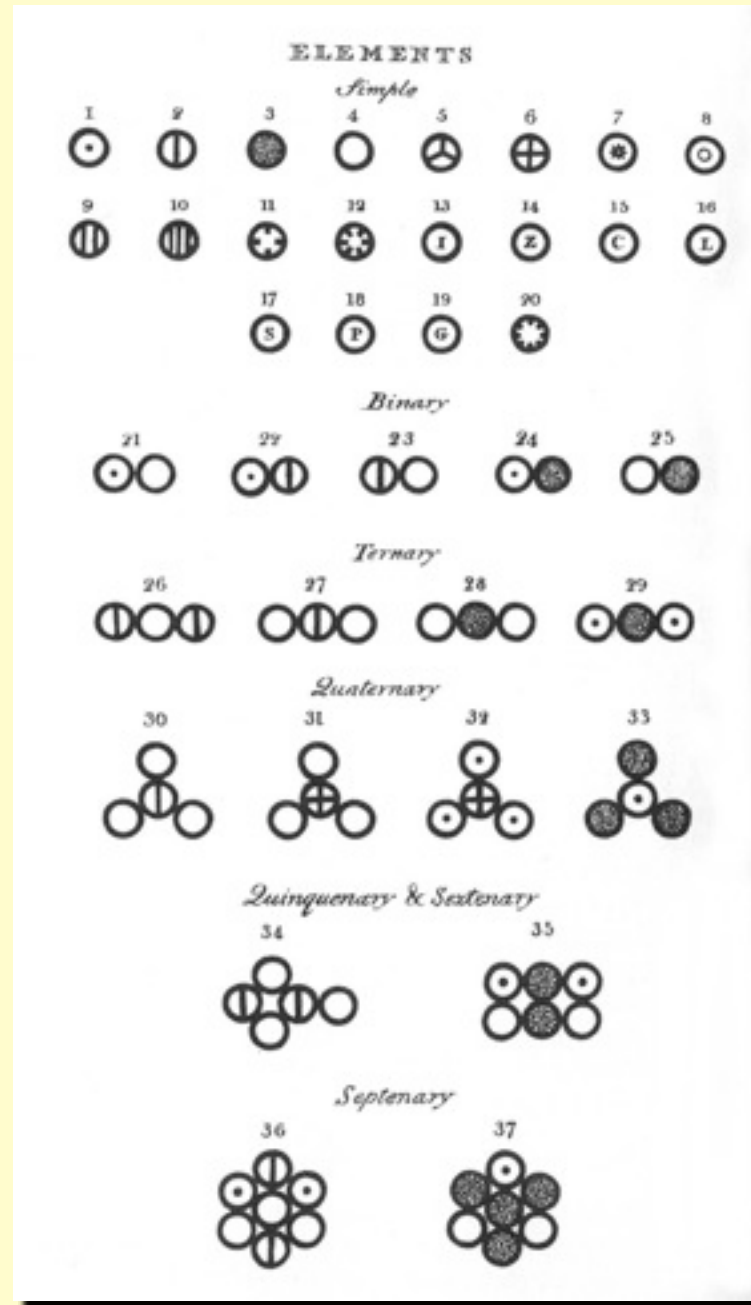
ELEMENTS

	Hydrogen	<i>wt</i> 1		Strontian	<i>wt</i> 46
	Azote	5		Barytes	68
	Carbon	5		Iron	50
	Oxygen	7		Zinc	56
	Phosphorus	9		Copper	56
	Sulphur	13		Lead	90
	Magnesia	20		Silver	190
	Lime	24		Gold	190
	Soda	28		Platina	190
	Potash	42		Mercury	167

Dalton's symbols of elements and their relative weights

"If there are two bodies, A and B, which are disposed to combine, the following is the order in which the combinations make take place, beginning with the most simple: namely,

1 atom of A + 1 atom of B = 1 atom of C
 1 atom of A + 2 atoms of B = 1 atom of D
 2 atoms of A + 1 atom of B = 1 atom of E
 1 atom of A + 3 atoms of B = 1 atom of F,
 3 atoms of A + 1 atom of B = 1 atom of G,
 etc."



"The following general rules may be adopted as guides in all our investigations respecting chemical synthesis.

- 1st. When only one combination of two bodies can be obtained, it must be presumed to be a *binary* one, unless some cause appear to the contrary.
- 2nd. When two combinations are observed, they must be presumed to be a *binary* and a *ternary*.
- 3rd. When three combinations are obtained, we may expect one to be a *binary*, and the other two *ternary*.
- 4th. When four combinations are observed, we should expect one *binary*, two *ternary*, and one *quaternary*, etc..
- 5th. A *binary* compound should always be specifically heavier than the mere mixture of its two ingredients.
- 6th. A *ternary* compound should be specifically heavier than the mixture of a binary and a simple, which, if combined, constitute it, etc.
- 7th. The above rules and observations equally apply, when two bodies such as C and D, D and E, etc. are combined.

Dalton, *A New System of Chemical Philosophy* (1808)

"From the application of these rules, to the chemical facts already well ascertained, we deduce the following conclusions;

- 1st. That water is a binary compound of hydrogen and oxygen, and the relative weights of the two elementary atoms are as 1 : 7, nearly.
- 2nd. That ammonia is a binary compound of hydrogen and azote, and the relative weights of the two atoms are as 1 : 5, nearly..."

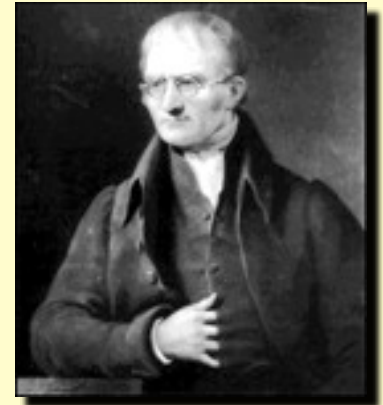
Dalton, *A New System of Chemical Philosophy* (1808)



Joseph Louis Proust
Law of constant proportions (1797)

(1754-1826)

John Dalton
Law of multiple proportions (1804)



(1760-1844)



Louis Joseph Gay-Lussac
Law of combining volumes (1808)

(1778-1850)

Proust and Dalton looked at different quantities, for example

Proust: 88.1% tin and 11.9% oxygen
and 78.7% tin and 21.3% oxygen

(difficult to see a regularity in these numbers)

Dalton: 100 g of tin combines with 13.5 g
or 27 g of oxygen

(an obvious regularity)

Gay-Lussac's results hard to reconcile with Dalton's conceptions:

2 volumes hydrogen + 1 volume oxygen
= 2 volumes water vapour

if equal volumes of gases contain the same number of atoms then:

2 atoms hydrogen + 1 atom oxygen
= 2 atoms water vapour

which leads ad absurdum (1/2 atom oxygen) for 1 atom water vapour

similarly:

2 volumes carbon monoxide + 1 volume oxygen
= 2 volumes carbon dioxide



Amedeo Avogadro (1776-1856)

Avogadro's hypothesis (1811)
Equal volumes of all gases, at the same
temperature and pressure, contain identical
numbers of molecules



Accepted by chemists only after
the lecture of Stanislao Cannizzaro
during the 1st Congress of Chemists
(1860)

Modern atomic theory



John Dalton

Matter is built of indivisible, indestructible atoms. All atoms of a pure substance are perfectly alike. Chemical compounds are formed of atoms in the simplest numerical proportions (1 : 1, 1 : 2 etc.). The atoms are large and essentially at rest, their atmospheres of caloric touching.

Static gas model !



Amedeo Avogadro

Equal volumes of all gases contain equal number of molecules (which are small compared with the total volume of a gas and are in motion)

Kinetic gas model !