

# Frederick Thomas Trouton: The Man, the Rule, and the Ratio

**Jaime Wisniak**

*Department of Chemical Engineering, Ben-Gurion University of the Negev, Beer-Sheva, Israel 84105,  
wisniak@bgumail.bgu.ac.il*

*Received July 12, 2000. Accepted October 17, 2000*

**Abstract:** Trouton was a multifaceted theoretician and experimentalist who left his name in several fields. Here, his many contributions to science are described and analyzed with particular emphasis on Trouton's rule and its further development, his contributions to rheology (Trouton's ratio), and the famous Trouton–Noble experiment, which is related to the absolute movement of the Earth through the æther.

Chemists and chemical engineers are familiar with Trouton through the rule that carries his name. Trouton's rule states that at the normal boiling temperature the entropy of vaporization is constant. They are generally unaware of his rich contributions in other scientific areas, such as rheology, osmotic pressure, and physics. Here we describe his personal life and career, his scientific achievements, and, in particular, how his rule has been further developed by others.

## Life and career [1–3]

Frederick Thomas Trouton was born in Dublin, Ireland, on November 24, 1863, the youngest son of Thomas Trouton. He came from a very wealthy and well-known family. He was educated at Dungannon Royal School and then went to Trinity College, Dublin, where he gave evidence of the versatility and quickness of grasp that would characterize his career. He studied both engineering and physical sciences. Before graduating, he had already taken a leading part in surveying for a railroad and enunciated the relation between molar latent heat and temperature that would become known as Trouton's rule. In recognition of this work, he was awarded the coveted Large Gold Medal, an honor rarely bestowed for work in the physical sciences. He graduated in 1884 and was immediately appointed assistant to Professor George Francis FitzGerald (1851–1901). In 1897, Trouton was elected a Fellow of the Royal Society; in 1901, he was appointed Lecturer of Experimental Physics; and in 1902, Quain professor of physics at the University College of London. Trouton and FitzGerald remained the closest of colleagues until FitzGerald's death in 1901. The influence of FitzGerald seems to have been decisive in Trouton's more abstract research. Together they carried out many experiments, including the ones that confirmed to a high degree of accuracy Ohm's law for electrolytes.

FitzGerald was a professor of natural and experimental philosophy whose studies on radiation, based on Maxwell's theory, led him to conclude that an oscillating electric current would produce electromagnetic waves, thus helping to lay the basis for wireless telegraphy. FitzGerald's finding was verified experimentally in 1893 by Heinrich Rudolph Hertz (1857–1894) of Germany. FitzGerald also developed a theory, now known as the Lorentz–FitzGerald contraction, which Einstein used in his own special theory of relativity. Trouton used this theory in his work to determine æther drift by the torque on a charged condenser.

In London, Trouton pursued his interests in both engineering and physics. His main research areas were the viscosity of pitch and molten glass as a function of

temperature and mode of deformation; the dynamics of the condensation of water vapor on glass, glass wool, and related substances; the effect of surface moisture on the conductivity of glass; and the relationship between the concentration and the adsorption of dyestuffs on sand.

A particularly outstanding piece of research that he performed was a test of Stoke's theory by following, using X-rays, the falling (at the rate of 3.6 cm/month) of a ball-bearing through a block of wax. Here he demonstrated, once again, his clever ability to transform complex theory into a simple experiment.

In 1897 Trouton married Annie Fowler and with her had four sons and three daughters. His two eldest sons: Eric, a physics student at Trinity College, Cambridge, and Desmond, an engineering student at University College, London, were killed in World War I. He was a friendly and helpful man, and his scientific friends remembered him particularly for his simultaneous interest in theoretical and practical work.

In 1912 Trouton was struck by a severe illness that led to permanent paralysis in both legs and to the end of his active scientific career. He retired from the University and moved to Tilford on Surrey and afterwards to Downe in Kent. His spirit was not broken, and the wit and charm for which he was noted were not dampened, even after the loss of his two sons. He continued to advise students and colleagues until his death at the age of 58 (September 21, 1922), in Downe, Kent.

## Trouton's Rule

Chemists, particularly physical chemists, become acquainted with Trouton through Trouton's rule, which relates the enthalpy of vaporization to the temperature of phase change. Trouton presented his ideas on the subject in the shortest two papers he ever wrote and while still an undergraduate student at University College [4, 5]. These publications contained no experimental material or theoretical considerations. In the first one, he reported his findings that the ratio of the latent heat of vaporization (gasification) divided by the product of the relative volume of the gas and the specific heat of the body

was approximately 0.8 for the 24 compounds for which he had calculated it. He observed that he was not quite sure of the value of this observation and that he submitted it "not without considerable diffidence to the readers of *Nature*." The second paper opened with the alternative statement that when comparing the "quantities of heat necessary to evaporate at constant pressure quantities of different liquids taken in the ratio of their molecular weights, it is found that the amount of heat required by any body is approximately proportional to its absolute temperature at the point of ebullition" (nowadays, Trouton's rule). He illustrated this statement by comparing the value of this quantity for compounds of the same chemical family, like alcohols (including water), fatty acids, organic iodides, and chlorides. For fatty acids he considered that their vapor densities were abnormal. He remarked that his finding had a striking similarity with Dulong and Petit's law, namely, that the specific heat multiplied by the atomic weight was a constant quantity. We should mention that Trouton used molar density instead of molecular weight to determine the value of the constant to be 12 (about one-half of the modern value of 21). For example, he gave the heat of vaporization of water as  $537 \text{ cal mol}^{-1}$  and its density as 9, hence a ratio of 12.95 for water.

Trouton's rule is expressed in modern terms as follows

$$\frac{\Delta H_{\text{vap}}}{T_{\text{boil}}} = 21 \text{ cal mol}^{-1} \text{ K}^{-1} \text{ (or } 88 \text{ J mol}^{-1} \text{ K}^{-1}) \quad (1)$$

or even better, in dimensionless form

$$\frac{\Delta H_{\text{vap}}}{RT_{\text{boil}}} = \frac{\Delta S_{\text{vap}}}{R} = 10.63 \quad (2)$$

An interesting and unexplained fact is that in his two publications Trouton made no reference whatsoever to very similar expressions reported by others before. For example, in a paper by Raoul Pictet [6], the same relation is derived analytically and in a communication by William Ramsay to the Chemical Section of the Philosophical Society of Galsgow (1877) it is derived empirically. Pictet used a Carnot cycle operating within the liquid-vapor saturation dome to demonstrate that the ratio  $\alpha\lambda/(274 + T)$  is a constant for all liquids. In Pictet's equation  $\alpha$  is the atomic weight and  $\lambda$  the internal latent heat.

We will now discuss Trouton's rule from several different points of view and, in particular, the attempts that have been made over the years to improve its application.

First, is there any physical basis to Trouton's rule? The equation contains the change of enthalpy for the phase transition and the normal boiling temperature; thermodynamically their ratio represents the change of entropy of the phase change

$$\frac{\Delta H_{\text{vap}}}{T_{\text{boil}}} = \Delta S_{\text{vap}} \quad (3)$$

These thermodynamic parameters reflect the structure of the material and the physical and chemical forces that operate within it. In addition, the entropy of vaporization reflects the

change in order (or disorder) that takes place when going from the liquid to the vapor phase. Physical chemistry textbooks analyze the variation of the boiling points and enthalpy of vaporization of organic compounds in relation to their molecular structures and intermolecular attractive forces. It is stated that if stronger intermolecular forces must be broken to accomplish the phase change (requiring a larger value of  $\Delta H$  for the transition), then the temperature and the energy required for the change are higher. We should expect that the increase of disorder caused by the vaporization of liquids without interactions be approximately the same, independent of the nature of the liquid. This will not be the case for melting. Here, entropy changes vary considerably from one compound to another, and they represent a significant factor in the variations of melting points. In spite of this, students are frequently provided with molecular explanations of melting point differences that are based entirely on differences in enthalpy changes.

Small differences in  $\Delta S_{\text{vap}}$  for various nonpolar compounds are assumed to be due to intermolecular forces (e.g., van der Waals forces) operating in the liquid phase. Substances with little intermolecular interaction in the liquid will have an entropy of vaporization of about  $88 \text{ J mol}^{-1} \text{ K}^{-1}$ . A more ordered state in the liquid, which results from hydrogen bonding or large dipole-dipole interactions, results in larger values for the entropy of vaporization because the order in the liquid must be randomized to form a mole of gas from a mole of liquid. Hydrogen bonding is the single most important factor that causes the entropy of boiling to deviate substantially from Trouton's rule. For polar liquids, especially those with hydrogen bonding, such as alcohols, ammonia, water, and amines, the tendency to orient in the liquid phase is greater than for nonpolar liquids. This is because hydrogen bonding is very directional and produces partial alignment in the liquid. Their entropies of vaporization may vary between 90 and  $120 \text{ J mol}^{-1} \text{ K}^{-1}$ . For example, in carboxylic acids hydrogen bonding is so strong that dimers are formed in the gas phase; the increased ordering in the gas phase lowers their entropy and markedly reduces  $\Delta S_{\text{vap}}$ . The strong effect of hydrogen bonding can also be illustrated by comparing the heat of vaporization of the two isomers: dimethyl ether ( $18.6 \text{ kJ mol}^{-1}$ ) and ethanol ( $42.6 \text{ kJ mol}^{-1}$ ). Hydrogen bonding occurs only in ethanol and this is reflected in its higher enthalpy of vaporization. Associating liquids, therefore, show the greatest deviations from Trouton's rule. Hence, on the one hand, the entropy of vaporization can be used as an indicator of intermolecular forces in liquids and, on the other, Trouton's rule may be used to indicate the absence of strong intermolecular bonds in the liquid phase. It would seem then that if a compound follows Trouton's rule, its molar mass is correct (no association effects), and the compound has little intermolecular interactions in the liquid state. Unfortunately, deviations from Trouton's rule are not that conclusive. Compounds with very low boiling points, such as  $\text{H}_2$  and He, exhibit very low entropies of vaporization, which must be corrected for the difference in volume of the gas at these temperatures. Hydrogen and helium are known to deviate strongly from Trouton's rule. The properties of hydrogen depend strongly on quantum-mechanical effects; thus, it is not surprising that they agree poorly with Trouton's rule. Silicon has strong directional bonds that stabilize the liquid and, therefore, increase the latent heat of vaporization. Iron's

conduction electrons delocalize in the liquid and thus add to the liquid's entropy, decrease its Gibbs energy, and increase the latent heat of vaporization. Larger and comparatively nonreactive molecules like Freon and benzene adhere most closely to Trouton's rule.

In a paper published in 1915, Hildebrand [7] analyzed the role of entropy as a tool for distinguishing normal liquids and provided an improved version of Trouton's rule. According to Hildebrand, the entropy of vaporization was not constant, as implied by eq 2, it actually increased with the boiling temperature. He illustrated this point by plotting the vapor pressure of different substances as a function of temperature and using the Clausius–Clapeyron equation,  $d \log P / d \log T = \Delta H / RT$ , to show that the slope of the curve at the value  $P = 1$  atm was not constant but increased regularly with temperature. In spite of this fact, he made the remarkable observation that the tangents to the curves at points cut by *any line* of unit slope had the same slope. The meaning of this fact becomes clear if we recall that at pressures low enough to assume ideal gas behavior the equation of state for an ideal gas yields  $P = RTc$ , where  $c$  denotes concentration, so that  $\log P = \log T + \log(Rc)$ . Hence, Hildebrand's conclusion that the entropy of vaporization for normal liquids is the same when evaporated to the *same concentration* (e.g., when the mean distance between molecules of vapor is the same). Hildebrand completed his analysis by noting that associating liquids, as well as hydrogen and helium, deviate strongly from his correlation.

Hildebrand's relationship remained essentially a graphical one until Everett turned it into an equation [8] by the simple artifice of retaining the normal boiling point as the appropriate temperature at which to compare substances and considering the result of evaporation to be to a vapor having a *chosen molar volume*  $v^*$  (hence, not necessarily saturated).

Everett split then the overall change in entropy for the process in two, first the liquid was evaporated at the saturation temperature and then the volume of the vapor was changed from the saturated value ( $v^{\text{sat}}$ ) to the final one ( $v^*$ ) using an isothermal path. From the  $TdS$  equation [9]

$$TdS = c_v dT + T \left( \frac{\partial P}{\partial T} \right)_v dv \quad (4)$$

and assuming the vapor to be an ideal gas, we get

$$dS = R \frac{dv}{v} \quad (5)$$

$$\Delta S^* = \Delta S_{\text{boil}} + R \ln \frac{v^*}{v^{\text{sat}}} \quad (6)$$

Choosing  $v^* = 22,414 \text{ cm}^3 \text{ mol}^{-1}$  yields

$$\Delta S^* = \frac{\Delta H_{\text{vap}}}{T_{\text{boil}}} + R \ln \frac{273.15}{T_{\text{boil}}} \quad (7)$$

Everett now proceeded to examine the data available for saturated hydrocarbons up to  $C_{14}$  (90 in total) and concluded that for them  $\Delta S^* = 19.7 \pm 0.7 \text{ cal mol}^{-1} \text{ K}$ . In addition, he

found that the more symmetrical the molecule the lower the value of  $\Delta S^*$ . For this reason he selected twelve *spherical* hydrocarbons to represent a standard molecular liquid having  $\Delta S^* = 19.16 \pm 0.15 \text{ cal mol}^{-1} \text{ K}^{-1}$ . Replacement of this value in eq 7 yields, finally

$$\Delta S^* = 8.0 + R \ln T_{\text{boil}} \quad (8)$$

or

$$\frac{\Delta H_{\text{vap}}}{RT_{\text{boil}}} = \frac{\Delta S_{\text{vap}}}{R} = 4.0 + \ln T_{\text{boil}} \quad (9)$$

Equations 8 and 9 are known as the *Trouton–Hildebrand–Everett rule* (or equation). The Trouton–Hildebrand–Everett equation implies that although the boiling point is a relevant parameter it is the quantity  $\Delta S_{\text{boil}} - R \ln T_{\text{boil}}$  that is expected to be constant. Alternatively, it asserts that, for a range of substances,  $\Delta S_{\text{boil}}$  should vary with  $R \ln T_{\text{boil}}$  (Shinoda [10] has demonstrated that this is so with a slope of 1.0).

It is interesting to note that in 1923 Kistiakowsky [11] developed the following semi-empirical relation, very similar to that of Everett

$$\frac{\Delta H_{\text{boil}}}{RT_{\text{boil}}} = 4.40 + \ln T_{\text{boil}} \quad (10)$$

In eqns 9 and 10, the term  $RT_{\text{boil}}$  may be considered the molar volume of the vapor at its normal boiling point ( $P = 1$  atm).

The Trouton–Hildebrandt–Everett rule is clearly superior to that of Trouton in thermodynamic significance. Trouton's rule was derived on a generalized observation as to the mutual relationship between the molar change of enthalpy of vaporization and the normal boiling point, mainly for many liquids. In this sense Trouton's rule can even be considered as a very specific play of numbers, Trouton–Hildebrandt–Everett's rule is, however, implemented with the important  $RT_{\text{boil}}$  term that represents the molar volume of the vapor at the normal boiling point and, in this way, introduces a certain amount of thermodynamic relevance and, undoubtedly, also a greater accuracy to the equation.

Héberger and Kowalska used the Trouton–Hildebrandt–Everett rule to develop a more exact thermodynamic interpretation of the empirical correlations between retention parameters of solutes in gas chromatography [12].

Before closing we should mention that Eyring and Hirschfelder [13] and Lennard-Jones [14] have used statistical mechanics arguments to give a molecular foundation to Trouton's rule.

Wilson [15] followed a procedure somewhat similar to that of Everett to calculate the value of  $\Delta H_{\text{boil}}/RT_{\text{boil}}$  for a wide variety of nonpolar and polar compounds. His method is based on calculating the difference between the actual entropy of vaporization and an ideal entropy for the change in volume in going from the liquid phase to the vapor phase. This residual entropy of vaporization,  $\Delta S^{\text{dev}}$  is, by definition

$$\frac{\Delta S^{\text{dev}}}{R} = \frac{s^0 - s^L}{R} - \left( \frac{s^0 - s^L}{R} \right)^{\text{ideal}} \quad (11)$$

were  $s$  and  $s^0$  represent the actual molar entropy and the molar entropy in the ideal state, respectively. After some algebra, eq 11 becomes

$$\frac{\Delta S^{\text{dev}}}{R} = \frac{\Delta H_{\text{boil}}}{RT_{\text{boil}}} - \ln \frac{RT_{\text{boil}}}{Pv^L} \quad (12)$$

where  $v^L$  is the molar volume of saturated liquid. Its value can be calculated using Rackett's equation [16]

$$v^L = v_c z_c^{(1-T_r)^{0.2857}} \quad (13)$$

where  $v_c$  and  $z_c$  are the critical volume and compressibility factor, respectively, and  $T_r$  is the reduced boiling temperature.

Significantly, a plot of  $\Delta S^{\text{dev}}/R$  versus the boiling point of many compounds yields a straight line.

In a more sophisticated approach Zhao et al. [17] correlated the entropy of boiling by means of molecular parameters and group contribution methods, to derive the following expression

$$\Delta S_{\text{boil}} = 84.53 - 0.11\sigma + 0.35\tau + 0.05\omega^2 + \sum n_i X_i \quad \text{J mol}^{-1} \text{K}^{-1} \quad (14)$$

where  $\sigma$ ,  $\tau$ , and  $\omega$  are the molecular rotational symmetry number, the effective number of torsional angles, and the molecular planarity, respectively;  $n_i$  the occurrence of group  $i$  in the compound; and  $X_i$  the contribution of group  $i$  to the entropy of boiling.

Zhao et al. claimed that the improved accuracy of their method was the result of using molecular parameters that reflect both geometrical features ( $\sigma$ ,  $\tau$ , and  $\omega$ ) and intermolecular association ( $X_i$ ).

Several accurate and relatively simple equations have been developed in the last 40 years or so for calculating the heats of vaporization of pure substances. They are either empirical, based on the principle of corresponding states, or based on group contribution methods. Two of the most accurate of the empirical equations are probably the following:

(a) Riedel [18]

$$\frac{\Delta H_{\text{boil}}}{RT_{\text{boil}}} = \frac{1.0929(\ln P_c - 1.013)}{0.930 - T_{\text{boil}}/T_c} \quad (15)$$

where  $P_c$  is the critical pressure in bars and  $T_c$  the critical temperature and

(b) Watson [19]

$$\frac{\Delta H_{\text{vap},2}}{\Delta H_{\text{vap},1}} = \left( \frac{1 - T_{2,r}}{1 - T_{1,r}} \right)^{0.38} \quad (16)$$

where  $T_r$  is the reduced boiling temperature. Watson's equation allows calculating the heat of vaporization at a pressure different from the normal.

There are many procedures for predicting the heat of vaporization based on group-contribution methods. The one of Basarova and Svodova [20] is probably the most accurate.

### Determination of the Osmotic Pressure

In a paper published in 1912 [21], Trouton discussed the experimental limitations of using semipermeable membranes for determining the osmotic pressure of salts at high pressures. In order to solve this problem he suggested using a *liquid membrane* instead. His theoretical arrangement consisted of an aqueous solution of sugar separated from water by a layer of ether. Sugar is insoluble in ether and water has a small solubility in ether. In order to eliminate gravity problems Trouton suggested an alternative arrangement where the sugar solution was separated from the water by an impervious vertical partition reaching to a certain height. Ether was then poured to cover it all and act as the membrane separating the solution from the water.

The paper contains a description of an experimental apparatus built according to the above ideas and capable of supporting a pressure of 100 atm. Actual measurements were compared and shown to be equal to those reported in the literature using a semi-permeable membrane of ferrocyanide of copper on porcelain.

### Adsorption of Water

In 1906 Trouton and Pool [22] reported their results on the adsorption of water vapor by flannel and other fabrics and by glass. They were interested on the possibility of constructing a recording hygrometer based either on the change of weight, or, in the case of glass, the change of electrical resistance between two wires fused on to the surface. Although Trouton and Pool were not successful, they did notice two interesting facts. The first was that the weight of water absorbed by the material under different conditions of pressure and humidity depended only on the relative humidity of the air (today we speak of equilibrium moisture content). Second, that at a given temperature the amount of water held per weight of bone dry fabric followed a parabolic relation with the pressure.

Experiments on the adsorption of water vapor on glass showed some peculiar results that Trouton was unable to explain [23]. Application of voltage between the electrodes gave differences of almost one order of magnitude for the resistance, depending on the direction of the voltage drop. The results were found to be sensitive to the humidity of the air and to the time the current was allowed to run before reversing the voltage.

### Elongational Flow and Trouton's Ratio

Extensional deformations play a very significant role in many processing operations. For example, fiber spinning, thermoforming, blow molding, and foam production are all essentially extensional deformations. In recent years it has become very clear that shear flow measurements alone are not sufficient to characterize the deformation behavior of a fluid. In many industrially important processes like fiber spinning, thermoforming, blow molding of bottles and film, vacuum forming, and flow through porous beds, it has been recognized that elongational (extensional or tensional) rather than shear

deformation is the dominant mode of deformation. Elongational flow may be present as uniaxial, biaxial, or planar, each giving rise to a different elongational viscosity [24].

Flow in converging or diverging regions of dies and molds, as well as flow at the moving front during mold filling, can have large extensional components. Extensional flows strongly orient polymer molecules and asymmetric particles; regional flows in a particular process can have a strong effect on final product performance.

Already, in 1906, Trouton was aware that when measuring the viscous flow of pitch and other substances of similar character their rate of turning under torsion was not exactly proportional to the driving couple. On his first experimental work on the subject [25], Trouton studied the viscous flow of pitch and other similar materials under a torsional stress. His main result was that the rate of flow of the material was not strictly proportional to the driving couple. He realized that torsional experiments could not give the exact relation between the variables because the rate of flow in a twisting rod is not the same everywhere; it varies from zero at the center to a maximum at the surface of the rod. He performed another series of ingenious experiments where he eliminated the problem of uneven flow [26]. These experiments included the flow produced in a rod under traction and under axial compression and the flow of a free stream of material. Of particular interest is the ingenious procedure that Trouton devised for performing the traction experiments. He simply thickened the rod at each end so that it fit exactly into a metallic box and then he attached weights to the box to produce the desired traction. Trouton's ingenious experiments can be said to mark the beginning of extensional rheology.

Trouton found that in all cases the rate of flow (1) was faster immediately after application of the force than afterwards and (2) the time rate of elongation per unit length,  $dv/dx$ , was proportional to the force of traction per unit area,  $F/A$ . That is,

$$\lambda = \frac{F/A}{dv/dx} \quad (17)$$

where  $\lambda$ , the coefficient of viscous traction (today: elongational viscosity), was constant for a given material.

The experiments with a stream falling under its own weight allowed Trouton to determine the differential equation of the shape of the stream and that the latter corresponds to an equilateral hyperbola  $xy = K$ . The latter result was confirmed by the clever trick of casting the shadow of the stream with a distant source of light.

With this information, Trouton was able to develop the following simple equation for calculating the value of the elongation viscosity,  $\lambda$

$$\lambda = \frac{\rho g \pi K^2}{2M_1} \quad (18)$$

where  $\rho$  is the density of the material and  $M_1$  is the mass of the material falling per second.

A theoretical analysis of the differential equations of flow led Trouton to deduce that the coefficient of viscous traction must be equal to three times the coefficient of viscosity,  $\mu$ , that

is,  $\lambda = 3\mu$ . His results indicated that for pitches the traction method gave an elongational viscosity of  $\lambda = 4.3 \times 10^{10}$  poises against a viscosity of  $\mu = 1.4 \times 10^{10}$  poises using a torsion method, thus confirming his theoretical analysis.

Trouton's results are quite consistent with Newton's viscosity law when it is written properly in three dimensions. The theoretical result that the elongational viscosity is three times the shear viscosity is nowadays called *Trouton's ratio*. For a Newtonian liquid, Trouton's ratio is three while for non-Newtonian polymer melts, it is greater than three. Elongational viscosity is now understood as the resistance of a fluid to any elongational flow.

Polymer processes that employ elongational flows have been successfully used for shaping ceramics by using crowded (50 to 60 vol %) suspensions of ceramic particles, but the full realization of their potential rests on an understanding of the extensional-flow behavior of filled-polymer systems.

Trouton's formula can also be used to calculate the dissipation of energy that arises from the fact that every deformation, even of the most elastic rubber, is connected with frictional processes, which must be taken into consideration for the evaluation of measurements. This contribution can be estimated using Trouton's formula

$$W_{\text{friction}} = 3\eta V \left( \frac{1}{l_0} - \frac{1}{l} \right) \frac{dv}{dx} \quad (19)$$

where  $W_{\text{friction}}$  is the lost work due to friction,  $V$  the sample volume,  $dv/dx$  the rate of deformation, and  $l_0$  and  $l$  the initial and final length of the sample, respectively.

### The Trouton-Noble Experiment

In 1901, shortly before his death, FitzGerald proposed an experiment to detect the absolute motion of the Earth through the æther. His basic consideration was that if a freely suspended parallel plate capacitor is charged at high voltage, it will turn spontaneously to minimize its total energy and will seek a stable position parallel to the direction of the motion of the Earth in the æther (the zero-point field). His idea was based on the fact that a purely electric field in one reference frame can be magnetic in another and that the separation of these interactions depends on which reference frame is chosen for description. Specifically, a charged capacitor moving through the æther with its plates parallel to the direction of motion should possess magnetic energy as well as electrostatic energy because a moving charge is equivalent to a current element.

The experiments were subsequently carried out in 1903 by Trouton and H. R. Noble, one of Trouton's research students [27–29]. Their idea was to look for the turning motion of a charged plate capacitor suspended at rest in the frame of the earth. Trouton gave a simple argument to predict a torque: The energy of a capacitor at rest in the ether,  $U_R$ , is

$$U_R = \frac{1}{8\pi} \int \mathbf{E}^2 dV = \frac{1}{8\pi} \mathbf{E}^2 V \quad (20)$$

where  $\mathbf{E}$  is the electric field and  $V$  is the volume between the plates of the capacitor. When the capacitor is moving through

the ether in a direction parallel to the plates, a magnetic field  $\mathbf{B} = v_x \mathbf{E}$  appears and adds to the electric field so that the energy for parallel motion,  $U_{\parallel}$ , becomes

$$U_{\parallel} = \frac{1}{8\pi} \int (\mathbf{E}^2 + \mathbf{B}^2) dV = \frac{1}{8\pi} (\mathbf{E}^2 + v_x^2 \mathbf{E}^2) V \quad (21)$$

$$U_{\parallel} = U_R (1 + v_x^2) \quad (22)$$

Now, when the capacitor is moving perpendicular to the plates, there is no  $\mathbf{B}$  field, and the energy,  $U_{\perp}$ , is now

$$U_{\perp} = U_R < U_{\parallel} \quad (23)$$

Thus, there should be a torque tending to rotate the capacitor until the plates are aligned perpendicular to the velocity through the æther, which is the lowest energy state. Because the orientation of the capacitor with respect to the earth's motion through the æther should presumably be different at different times of the day, one may look for a rotational effect. Trouton and Noble made the prediction of this electromagnetic turning moment using the then available prerelativistic formulas for a moving charged capacitor. When the experiment was performed by Trouton [27] and then by Trouton and Noble [28, 29], they obtained a null effect. The experiment was later repeated by Chase [30], who reported an upper limit of  $4 \text{ km s}^{-1}$  on any æther-drift velocity, compared with the earth's orbital velocity of  $30 \text{ km s}^{-1}$ . More recently, Hayden [31] designed an experiment that is  $10^5$  times more sensitive than the original Trouton–Noble experiment and that also yielded a null result.

The Trouton–Noble experiment is generally regarded as the electrostatic equivalent of the Michelson–Morley optical experiment, it looked for an effect to be caused by the absolute motion of the Earth through the æther due to the orbital velocity  $u = 3 \times 10^6 \text{ cm s}^{-1}$  of the Earth about the Sun.

In spite of the failure of the first experiments, Trouton kept interested in the question of relative motion between the Earth and the neighboring æther. In 1908 he and Rankine performed another series of experiments where they determined the ratio of the resistance of a wire traveling parallel to its axis to that when it travels perpendicular the velocity vector [32]. Trouton and Rankine assumed that if the FitzGerald–Lorentz shrinkage applied, then the resistance of the wire traveling at a velocity,  $v$ , parallel to the major axis would be  $(1 + \beta^2)$  times larger than the resistance when traveling in the normal direction. Here  $\beta = v/c$  where  $c$  is the speed of light.

Once again, the results showed a null effect in spite of extreme care in their performance and avoidance of the mechanical shaking of the galvanometer, "a disturbance that is never absent in London, except in the early hours of the morning!"

The negative results of the Trouton–Noble experiments have been explained on the basis of (a) a need for a better understanding of the constraint forces holding the capacitor in equilibrium (There are forces that keep the two plates at a fixed distance apart and forces that maintain the static charge distribution on the plates despite the electrostatic repulsion within the planes of the plates.) and (b) on relativistic

arguments (If the capacitor is in equilibrium for an inert observer at rest with respect to the capacitor, then it cannot appear to be rotating in a uniformly moving frame, for otherwise this effect could be used to single out the preferred frame that has no rotation.).

### Damping of Hertzian Waves and Communication

FitzGerald and Trouton were troubled by another theoretical predicament: the damping of Hertzian waves. In December 1891, Trouton concluded in a public lecture that "no doubt [electric waves] will be turned by man to serve useful purposes," but that insufficient power caused by the high damping of spark-generated waves was a barrier that needed overcome. The only way to avoid damping was to create a continuous wave, and for this purpose, Trouton suggested the use of a 50 hp (horsepower) engine. Only with such a powerful beam, he continued, would communication by means of Hertzian waves between a lighthouse and ships in foggy days be possible. Trouton's emphasis on diminishing damping was based on FitzGerald's previous research on multiple resonance. FitzGerald had recognized that radiation energy created from spark discharge was sent off nearly instantaneously or in one-hundredth to one-thousandth portion of the interval between consecutive sparks. Trouton had something like ship-to-lighthouse communication in mind for which Hertzian waves might substitute for ordinary light.

### Conclusion

Trouton made significant contributions in several areas. His results concerning the constancy of the entropy of vaporization and in the field of rheology are everlasting. They will continue to be mentioned and discussed in textbooks.

### References and Notes

1. *Proc. Roy. Soc. (London)* **1926**, *A110*, iv–ix.
2. *Am. J. Phys.* **1963**, *31*, 85–86.
3. *Nature* **1922**, *110*, 490–491.
4. Trouton, F. T. *Nature* **1883**, *27*, 292.
5. Trouton, F. T. *Phil. Mag.* **1884**, *18*, 54–57.
6. Pictet, R. *Ann. Chim. Phys.* [6] **1876**, *9*, 180–193.
7. Hildebrand, J. H. *J. Am. Chem. Soc.* **1915**, *37*, 970–978.
8. Everett, D. H. *J. Chem. Soc.* **1960**, 2566–2573.
9. Levine, I. N. *Physical Chemistry*, 4th Ed.; McGraw-Hill: New York, 1997.
10. Shinoda, K. *J. Chem. Phys.* **1983**, *78*, 4784.
11. Kistiakowsky, V. A. *Z. Physik. Khim.* **1923**, *107*, 65–73.
12. Héberger, K.; Kowalska, T. *J. Chromatogr. A* **1999**, *845*, 13–20.
13. Eyring, H.; Hirschfelder, J. *J. Phys. Chem.* **1937**, *41*, 249–257.
14. Lennard-Jones, J. E. *Proc. Royal Soc.* **1938**, *165A*, 1–11.
15. Wilson, G. M. *Equations of State*, ACS Symposium Series 300; American Chemical Society: Washington, DC, 1986; pp 520–536.
16. Rackett, H. G. *J. Chem. Eng. Data* **1970**, *15*, 514–517.
17. Zhao, L.; Li, P.; Yalkowsky, S. *J. Chem. Inf. Comput. Sci.* **1999**, *39*, 1112–1116.
18. Riedel, L. *Chem. Ing. Tech.* **1954**, *26*, 679–683.
19. Watson, K. M. *Ind. Eng. Chem.* **1943**, *35*, 398–406.
20. Basarová, P.; Svodova, V. *Fluid Phase Equilibria* **1995**, *105*, 27–47.

21. Trouton, F. T. *Proc. Royal Soc.* **1912**, 86A, 149–154.
22. Trouton, F. T.; Pool, B. *Proc. Royal Soc.* **1906**, 77A, 292–314.
23. Trouton, F. T.; Searle, J. H. C. *Philos. Mag.* **1906**, 12, 336–347.
24. Macosko, C. W. *Rheology—Principles, Measurements, and Applications*; Wiley-VCH: New York, 1994.
25. Trouton, F. T. *Phil. Mag.* **1904**, 19, 347–355.
26. Trouton, F. T. *Proc. Royal Soc.* **1906**, 77A, 426–440.
27. Trouton, F. T. *Trans. Royal Dublin Soc.* **1902**, 7, 379–384.
28. Trouton, F. T.; Noble, H. R. *Phil. Trans. Royal Soc.* **1903**, 77A, 132–133.
29. Trouton, F. T.; Noble, H. R. *Phil. Trans. Royal Soc.* **1904**, 202A, 165–181.
30. Chase, C. T. *Phys. Rev.* **1926**, 28, 378–383.
31. Hayden, H. C. *Rev. Scientific Instruments* **1994**, 65, 788–793.
32. Trouton, F. T., Rankine, A. O. *Proc. Royal Soc.* **1908**, 80A, 420–435.