

Revisiting Black's Experiments on the Latent Heats of Water

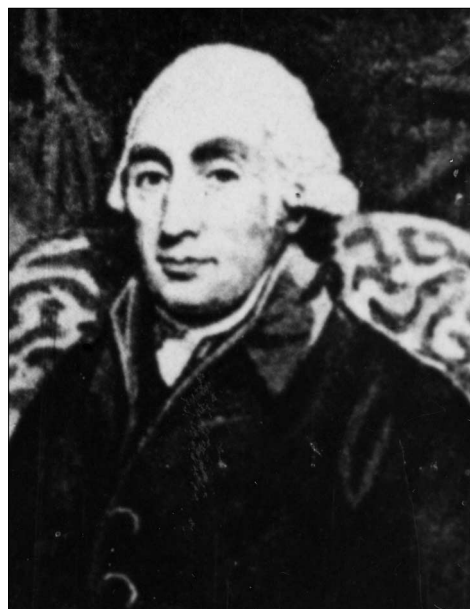
J. Güemez, Departamento de Física Aplicada, Universidad de Cantabria, E-39005 Santander, Spain; guemezj@unican.es

C. Fiolhais and M. Fiolhais, Departamento de Física and Centro de Física Computacional, Universidade de Coimbra, P-3004-516 Coimbra, Portugal; tcarlos@teor.fis.uc.pt; tmanuel@teor.fis.uc.pt

Although born in Bordeaux, France, Joseph Black was purely Scottish by blood. He began studying medicine at the University of Glasgow, where he first became interested in chemistry. After completing his medical studies in Edinburgh, Black returned to Glasgow in 1756 to become a professor of medicine. His main interest, however, remained chemistry and physics, and his lecture courses eventually grew to attract students from all over Europe and even America. Featured in his lectures were vivid descriptions of his own discoveries and experiments, and in 1766, when he accepted a chair at the University of Edinburgh, he was followed by many of his students.

As a professor at Glasgow, Black became interested in calorimetry and performed experiments on the specific heat and latent heats of water. He was the first to distinguish between temperature and heat.¹ The notion of specific heat has been attributed to him,² and the experiments to determine the specific heat (using the mixture method³), which are common in introductory physics laboratories, go back to Black. On the other hand, Black pointed out that previous ideas on melting and freezing, e.g., that the fusion of ice is instantaneous and requires almost no heat,² were wrong. He introduced the term *latent heat* to describe the energy that seems to “hide” when melting occurs, reappearing in freezing, and also to hide in evaporation, reappearing in condensation.⁴

Black's calorimetric experiments come to us in reports written by his students. One such report refers to the determination of the latent heat of melting ice:



Joseph Black
(NBS Archives, courtesy
AIP Emilio Segrè Visual Archives)

“In order to understand this absorption of heat into the melting ice and concealment of it in the water more distinctly, I made (among others) the following experiment. I put a lump of ice into an equal quantity of water heated to the temperature [80°C] and the result was that when the ice was all melted the fluid was no hotter than water just ready to freeze.”⁵

A second experiment refers to the latent heat of vaporization of water:

“I procured some cylindrical tin-plate vessels, about 4 or 5 inches diameter and flat bottomed. Putting a small quantity

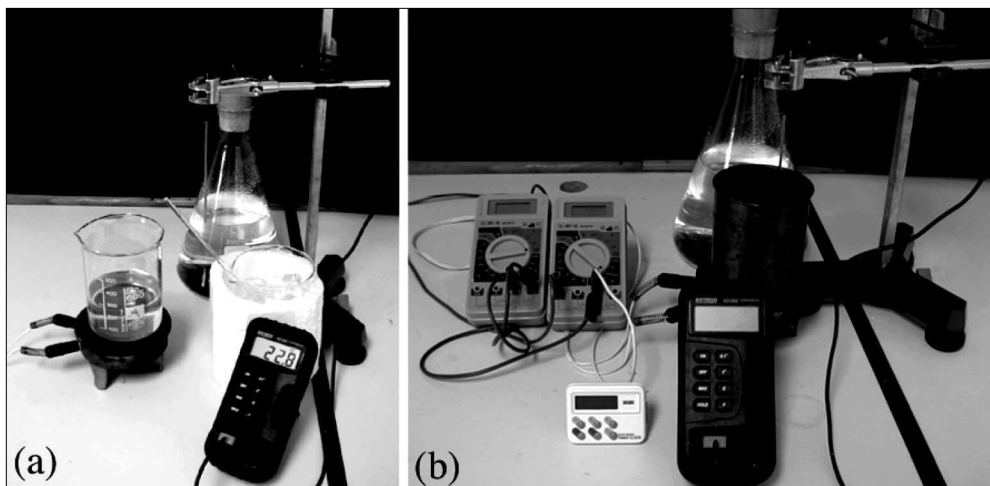


Fig. 1. Modern setups for the two experiments described by Black. (a) Setup for determining the water latent heat of fusion; (b) setup for determining the water latent heat of evaporation.

of water into them, of the temperature [10°C], I set them upon a red-hot stove taking care that the fire should be *pretty regular*. After *four minutes* the water began sensibly to boil and in *twenty minutes more* it was all boiled off.”⁶

The reproduction of historical experiments of thermodynamics, leading to the same results obtained by the pioneers of the subject, may help students to gain deeper insights on that subject. On the other hand, in doing some old experiments, one often comes to the conclusion that they are not completely appropriate to accomplish their purposes. This is especially true in thermodynamics where heat losses are always present.

One may wonder whether Black’s experiments do in fact give accurate results. In order to answer this question and since we think that modern analysis of historical experiments has pedagogical interest, we carried out these experiments with the equipment shown in Fig. 1, which can be found in any introductory physics laboratory. Black’s experiment to find the latent heat of ice leads to an accurate value (other experiments to determine the latent heat of fusion of ice have been recently reported in the literature⁷). However, Black’s experiment to determine the latent heat of steam, if naively interpreted, gives a result that differs from the accept-

ed value by 25%. In order to get more accurate values, cooling by radiation has to be considered.

Latent Heat of Fusion

A mass m_w of water, at initial temperature t_i , is mixed with a mass m_i^I of ice at 0°C in a calorimeter [a glass vessel with a Styrofoam wrapping, see Fig. 1(a)]. The temperature of the water is first raised to a few degrees above the desired initial temperature, t_i . The system then starts to cool down and, when the temperature t_i is reached, the water is rapidly poured onto the ice inside the calorimeter (kept, as the ice, at 0°C). The ice-water mixture is vigorously stirred with a glass stirring rod until its temperature stabilizes at a value t_f . It is important to keep mixing during the approximately three minutes (the frictional work is negligible) required. Finally, the remaining ice m_f^I if any, is removed and weighted. Then, $m_1 = m_i^I - m_f^I$ is the mass of the *melted* ice.

Table I shows Black’s measurements, as well as the data obtained in our own experiment for different quantities of water and ice.

For a pure substance that undergoes both a temperature change and a phase transition due to contact with a heat source, the heat absorbed is $Q = m\lambda + mc\Delta t$, with m its mass, λ the latent heat of the phase transition, c the specific heat

Table I. Data for mixtures of ice at 0°C and hot water. m_w stands for the mass of liquid water. The initial mass of ice is m_i^1 and the final mass of ice (not melted) is m_f^1 . The water initial temperature and the final mixture temperature are t_i and t_f respectively.

Run	m_w (g)	m_i^1 (g)	m_f^1 (g)	t_i (°C)	t_f (°C)
Black			0.	80.0	0.0
1	186.7±0.2	188.1±0.2	0.5±0.2	80.0±0.1	0.0±0.1
2	179.8±0.2	178.2±0.2	0.4±0.2	80.0±0.1	0.0±0.1
3	172.0±0.2	218.6±0.2	44.4±0.2	80.0±0.1	-0.2±0.1
4	172.1±0.2	263.3±0.2	89.3±0.2	80.0±0.1	-0.2±0.1
5	173.9±0.2	148.5±0.2	0.0±0.2	80.0±0.1	5.4±0.1
6	170.6±0.2	128.1±0.2	0.0±0.2	80.0±0.1	9.6±0.1

(at constant pressure), assumed to be constant, and $\Delta t = t_f - t_i$ the temperature variation. For the liquid water, $Q_w = m_w c_w (t_f - t_i)$ (the specific heat of water, c_w , is considered to be constant between 0°C and 80°C) and, for the melted ice, $Q_i = m_i \lambda_f + m_i c_w (t_f - 0)$, where λ_f is the latent heat of fusion of ice. When the final temperature is $t_f = 0^\circ\text{C}$, the calorimeter does not gain or lose heat and $Q_i = -Q_w$. Thus,

$$\lambda_f = c_w t_i \frac{m_w}{m_i} \quad (1)$$

In the original experiment by Black, $m_w = m_i$, $t_i = 80^\circ\text{C}$ (and $t_f \approx 0^\circ\text{C}$), leading to $\lambda_f = 80c_w$. Using $c_w = 4.18 \text{ Jg}^{-1}\text{C}^{-1}$ (a value later found by Joule), one finds $\lambda_f = 334 \text{ Jg}^{-1}$, which is close to the current value 333.9 Jg^{-1} .⁸

However, when the final temperature of water differs from 0°C, heating of the calorimeter has to be taken into account in the heat balance and Eq. (1) does not apply. A calorimeter is an adiabatic system (there is no heat exchange with its surroundings). For water mixed with ice in the calorimeter, we have

$$\begin{aligned} Q_i + Q_w + Q_C &= \\ m_i \lambda_f + m_i c_w (t_f - 0) + m_w c_w (t_f - t_i) + m_c c_w (t_f - 0) &= \\ &= 0. \end{aligned} \quad (2)$$

The calorimeter has been modeled by an (equivalent) amount of water, m_c , which absorbs the same heat, Q_C , as the calorimeter when the mixture takes place.³ From Eq. (2), we have

$$\lambda_f = c_w \left(t_i \frac{m_w}{m_i} - t_f \frac{m_w + m_i + m_c}{m_i} \right). \quad (3)$$

The equivalent in water of the calorimeter depends on the thermodynamical process, but we performed a single experiment to estimate m_c (note that all runs in Table I were done in similar conditions). We mixed equal masses of hot and cold water (approximately 170 g each, as in Table I), at 92.7°C and 2.7°C, respectively (as in the experiments of Table I). After stirring during three minutes, the temperature 41.9°C was reached. From an equation like Eq. (2), but applied to hot water, cold water, and the calorimeter, we found $m_c \approx 57 \pm 4 \text{ g}$.

Using the m_c in Eq. (3) we obtain values for λ_f which are given in the third column of Table IV. These values are all pretty close to the current value.

Latent Heat of Vaporization

We placed water in a copper vessel with a flat bottom [see Fig. 1(b)]. The temperature was raised to the boiling point, $\approx 100^\circ\text{C}$ at a pressure of 1.010 bar (atmospheric pressure), and then the water was totally converted to steam. An electric hotplate served as the heat source. Let P be the constant power supplied during the process, τ_1 be the time for water to reach the boiling point starting from the temperature t_i (room temperature), and τ_2 be the time for the water to evaporate completely.

One should consider that the container is always *radiating* to the environment since its temperature is higher than that of the air. Thus, in the heating and evaporation processes,

$$\begin{aligned} P\tau_1 &= m_w c_w (100 - t_i) + Q^{\text{heating}}, \\ P\tau_2 &= m_w \lambda_v + Q^{\text{boiling}} \end{aligned} \quad (4)$$

where m_w is the mass of water, λ_v the latent heat of vaporization, and Q^{heating} and Q^{boiling} are energy exchanges with the environment (heat losses) in the heating and boiling processes, respectively.

Following Ref. 9, not taking into account heat losses (i.e., $Q^{\text{heating}} = Q^{\text{boiling}} = 0$), with $t_i = 10^\circ\text{C}$, $\tau_1 = 4$ min, and $\tau_2 = 20$ min, as in Black's work,

$$\lambda_v = \frac{\tau_2}{\tau_1} c_w (100 - t_i), \quad (5)$$

one obtains $\lambda_v = 450c_w = 1881.0 \text{ Jg}^{-1}$, very different from the current value, 2261.1 Jg^{-1} .

In Table II we show Black's measurements and our own data collected in six runs of the same experiment, using different quantities of water. The fourth column of Table IV shows our own results for the latent heat of evaporation using Eq. (5). Since the values are too high, we have to take into account heat losses.

The effect of radiation can be dealt with using Newton's law of cooling.¹⁰ To estimate the energy loss of the water in the cooling process, we carried out the following experiment. We heated a mass of water in the copper vessel up to the boiling point. Then we let it cool down to room temperature, t_R , in order to measure the cooling rate of water. We performed this cooling experiment twice with $m_w = 100$ g and $m_w = 300$ g. In Table III we report the elapsed times, τ , and temperatures, t .

The power lost to the environment is

$$\frac{\delta Q}{d\tau} = m_w c_w \frac{dt}{d\tau}. \quad (6)$$

Using Newton's law of cooling¹⁰ in its differential form,

$$\frac{dt}{d\tau} = -k_m (t - t_R), \quad (7)$$

where k_m is the cooling parameter (the index m stresses that k depends on the mass of water). Eq. (6) becomes

Table II. Data obtained in water vaporization experiments. m_w is the mass of water, t_i its initial temperature, τ_1 the elapsed time for water to start boiling, and τ_2 the elapsed time for water to evaporate completely.

Run	m_w (g)	t_i ($^\circ\text{C}$)	τ_1 (s)	$\tau_1 + \tau_2$ (s)
Black		10.	240	1440
1	100.3 ± 0.2	19.5 ± 0.1	115 ± 5	1066 ± 8
2	100.4 ± 0.2	19.9 ± 0.1	118 ± 5	1069 ± 8
3	150.4 ± 0.2	20.4 ± 0.1	164 ± 5	1506 ± 8
4	200.3 ± 0.2	20.5 ± 0.1	195 ± 5	1977 ± 8
5	250.2 ± 0.2	20.4 ± 0.1	271 ± 5	2625 ± 8
6	300.2 ± 0.2	20.7 ± 0.2	320 ± 5	3085 ± 8

$$\frac{\delta Q}{d\tau} = -k_m m_w c_w (t - t_R). \quad (8)$$

In the heating process, we observed that the temperature varies linearly with time,

$$t = t_R + \frac{100 - t_R}{\tau_1} \tau. \quad \text{The power lost in the}$$

heating process is then

$$\frac{\delta Q^{\text{heating}}}{d\tau} = -k_m m_w c_w \frac{100 - t_R}{\tau_1} \tau. \quad (9)$$

During boiling, the temperature of the recip-

Table III. Times and temperatures for (a) cooling 100 g of water in an environment at $t_R = 19.7^\circ\text{C}$ and (b) cooling 300 g of water at $t_R = 21.0^\circ\text{C}$. In both cases, cooling occurred in a copper vessel with 155 g.

(a)		(b)	
τ (s)	t ($^\circ\text{C}$)	τ (s)	t ($^\circ\text{C}$)
0	100.2 ± 0.1	0	100.1 ± 0.1
10	98.8 ± 0.1	10	99.6 ± 0.1
20	96.1 ± 0.1	20	98.7 ± 0.1
30	93.7 ± 0.1	30	97.5 ± 0.1
40	90.5 ± 0.1	40	96.5 ± 0.1
50	88.6 ± 0.1	50	95.4 ± 0.1
60	86.4 ± 0.1	60	94.4 ± 0.1

Table IV. Latent heat of fusion of ice, whose standard value is $\lambda_f = 333.9 \text{ Jg}^{-1}$, and latent heat of water evaporation, whose standard value is $\lambda_v = 2261.1 \text{ Jg}^{-1}$.⁸ We note that Eq. (1) only applies when $t_f = 0^\circ\text{C}$, which is not the case for runs 5 and 6 of the fusion experiment.

Run	$\lambda_f \text{ (Jg}^{-1}\text{)}$ [Eq. (1)]	$\lambda_f \text{ (Jg}^{-1}\text{)}$ [Eq. (3)]	$\lambda_v \text{ (Jg}^{-1}\text{)}$ [Eq. (5)]	$\lambda_v \text{ (Jg}^{-1}\text{)}$ [Eq. (15)]
Black	334		1881	
1	333	333 ± 6	2710	2540 ± 180
2	338	338 ± 6	2700	2440 ± 170
3	332	332 ± 6	2700	2350 ± 130
4	331	332 ± 6	3000	2650 ± 150
5	(343)	334 ± 6	2890	2410 ± 180
6	(351)	334 ± 6	2860	2370 ± 190

ient remains at $t = 100^\circ\text{C}$. Hence, the power lost during boiling is

$$\frac{\delta Q^{\text{heating}}}{d\tau} = -k_m m_w c_w (100 - t_R). \quad (10)$$

Integrating, we find

$$Q^{\text{heating}} = -k_m m_w c_w (100 - t_R) \frac{\tau_1}{2},$$

$$Q^{\text{boiling}} = -k_m m_w c_w (100 - t_R) \tau_2. \quad (11)$$

Using the data from Table III in the integral form of Newton's law of cooling [integral of Eq. (7)],

$$k_m = -\frac{1}{\tau} \ln \frac{t(\tau) - t_R}{t(0) - t_R}, \quad (12)$$

one obtains the (mass dependent) cooling parameter: $k_{100} = 3.59 \times 10^{-3} \text{ s}^{-1}$ and $k_{300} = 1.36 \times 10^{-3} \text{ s}^{-1}$ for $m_w = 100 \text{ g}$ and $m_w = 300 \text{ g}$, respectively. For the (mass independent) quantity $m_w c_w k_m$, one obtains $100 c_w k_{100} = 1.72 \text{ W}^\circ\text{C}^{-1}$ and $300 c_w k_{300} = 1.79 \text{ W}^\circ\text{C}^{-1}$. Inserting the average value, $1.75 \text{ W}^\circ\text{C}^{-1}$, back into Eq. (11) we obtain the following heat losses during heating and boiling:

$$|Q^{\text{heating}}| = 1.75(100 - t_R) \frac{\tau_1}{2} \approx 71.6\tau_1,$$

$$|Q^{\text{boiling}}| = 1.75(100 - t_R) \tau_2 \approx 143.2\tau_2. \quad (13)$$

Taking into account these heat losses in Eq. (4), the energy balance equations are

$$P\tau_1 = m_w c_w (100 - t_i) + 71.6\tau_1,$$

$$P\tau_2 = m_w \lambda_v + 143.2\tau_2. \quad (14)$$

Eliminating P in these equations, we obtain

$$\lambda_v = \frac{\tau_2}{\tau_1} \left[c_w (100 - t_i) - \frac{71.6}{m_w} \tau_1 \right]. \quad (15)$$

Taking $c_w = 4.18 \text{ Jg}^{-1}\text{C}^{-1}$ and inserting data given in Table II in this equation, one obtains the results displayed in the last column of Table IV. They improved with respect to the results arising from Eq. (5) (the average deviation is less than 10% now). However, one should notice the large uncertainty estimates. In these experiments to determine the latent heat of vaporization, uncertainties are mainly associated with difficulties in measuring exact times when water starts to boil and when water evaporates completely. The heat absorbed by the metallic vessel and the water losses during heating and steam condensation in the recipient walls are other sources of uncertainty.⁹

Comments

In summary, we have carried out Black's experiments on the latent heats of water, which may be done nowadays for teaching thermodynamics. The first one is usually performed in introductory physics laboratories, either at high school or college level, in order to obtain the latent heat of fusion of ice, but we pointed out the need for using the water equivalent of the calorimeter when the final temperature is different from 0°C . On the other hand, the determination of the latent heat of vaporization using Black's experiment requires a model for heat losses. We used Newton's law of cooling, but nevertheless it turned out to be difficult to obtain the accepted value with a precision much better than 10%. The uncertainties are simply too large to make this method of great practical value. The most common method to determine the latent heat of water evaporation is the so-

called Berthelot's method.^{3,11}

We would like to stress that mastering the scientific method also requires understanding why, sometimes, some experiments *do not work well*. Failed experiments, suitably presented and discussed, may be of pedagogical value.

References

1. S.C. Brown, "The caloric theory of heat," *Am. J. Phys.* **18**, 367 (Sept. 1950).
2. L.W. Taylor, *Physics: The Pioneer Science. Volume I. Mechanics Heat, Sound* (Dover Publications, New York), Ch. 20, p. 267. This reproduces the original *Lectures on Elements of Chemistry*, given by Black at the University of Edinburgh, published from his manuscripts by John Robinson (Longman & Rees, London, 1803).
3. H.S. Allen and H. Moore, *A Textbook of Practical Physics* (MacMillan, London, 1965), p. 296.
4. P.H. Bligh and R. Haywood, "Latent heat — Its meaning and measurement," *Eur. J. Phys.* **7**, 245 (1986).
5. See Ref. 2. Note that Black's thermometers were graduated in Fahrenheit degrees, but temperatures have been converted here to Celsius.
6. See Ref. 2. Italics added to call attention to the fact that both times have to be measured in "regular" heating conditions.
7. S.Y. Mak and C.K.W. Chun, "The measurement of the specific latent heat of fusion of ice: two improved methods," *Phys. Educ.* **35**, 181 (May 2000).
8. H.U. Fuchs, *The Dynamics of Heat* (Springer, New York, 1996), p. 659.
9. C.D. Galles, "Revival of Black's experiment," *Am. J. Phys.* **47**, 1008 (Nov. 1979).
10. J.W. Dewdney, "Newton's law of cooling as a laboratory introduction to exponential decay functions," *Am. J. Phys.* **27**, 668 (Dec. 1959).
11. H. Lindeman and A. Lavie, "Instrument for the measurement of the heat of vaporization of water," *Am. J. Phys.* **29**, 705 (Oct. 1961).