William Esson

Ton Yeh

Who was he?

For a man who could claim to be a Savilian Professor and the co-founder of an entire area of theoretical chemistry, William Esson left very little that is worth saying about his life. The biographical source I am using is an obituary published by the Royal Astronomical Society in February 1917, the year after his death [5], as well as an obituary from the Journal of the Chemical Society in the same year [6]. From these, I gleaned the following: Born at Carnoustie in the erstwhile county of Forfarshire (now in Angus, Scotland) on 17 May 1838, he received his secondary education from the Inverness Royal Academy and Cheltenham Grammar School. He entered Oxford University just before his 17th birthday, having been elected to a Bible Clerkship at St John's College. His undergraduate career was marked by academic brilliance – he won a First Class in one of his two Classical Honours Examinations, and a Second Class in the other; more importantly, he won all the Mathematics Honours available then. Merely 5 years after matriculation, he obtained a Fellowship at Merton College. Together with Dr A. Vernon Harcourt from Christ Church College (then a Demonstrator of Chemistry), who was in need of someone with some mathematical expertise, Esson undertook research on the rather recent subject of chemical kinetics. They published two papers in the 1860s [1, 2], a third in 1895 [3] and one in 1913 for which Esson provided the appendix [4]. Recognition came for him in the form of Fellowship of the Royal Society in 1869, and his election as a Visitor to the University Observatory in 1875, and as a Secretary to the same body. Curiously, says the obituary, his other research publications 'were neither numerous nor of great importance'. Few academics today, let alone the holder of a Savilian chair, would get away with publishing so little. That is not to say that his time was idly spent: *au contraire*, he devoted much energy to teaching, lecturing and administration, which proved increasingly important not only for Merton College, but the University in general.

Before we turn our attention to the papers which he wrote, let us pause to look at a caricature drawn by George Martin, who matriculated in 1980 to read Chemistry at Merton. His depiction of Esson reminds one of the style of Max Beerbohm, the great Mertonian caricaturist who studied at the same time as Martin. The limerick beside the drawing of him reads,

There once said a tutor called Esson,
With a beard that seemed never to lessen,
'It is quite Essontial [sic]
To use differential
To prosper in any profession'

Courtesy of the Warden and Fellows of Merton College Oxford

What did he study?

Chemical kinetics is interested in the course of a chemical reaction and the relevance of surrounding conditions to it. In particular, what change is there in the reaction rate over time? As Esson and Harcourt astutely noted, this topic diverged sharply from the previous focus on the results of chemical reactions – the inputs and outputs, as it were – as though what happened in between were just ‘a means to an end’. Without getting bogged down in the details of the specific reactions chosen by Harcourt, we can summarise the mathematical approach of Esson in these three papers as follows:

1) Common sense and context lead him to believe that the rate of a chemical reaction is determined by certain ordinary differential equations, which he proceeds to solve.
2) He then finds most of the experimental data to match his suspicions.

We see this procedure at work, when Esson derives a particular case of the law of mass action (here involving just one reagent), in the first of his three papers.

1) What, he asks, might influence the rate of the reaction at any given time? That, of course, depends on the experiment in question. He explicitly makes the sensible assumption that a certain

reagent R is being converted by this reaction, or equivalently, that R is taking away chemical energy – and that the quantity of other reagents S, T, ... is so large that its changes can be neglected. (Compare this to a fire outdoors: there is enough oxygen in the atmosphere to let it burn as long as the fuel demands.) Now, he observes that if R were replenished as it is destroyed, so as to keep the quantity of R constant too, then of course the reaction rate would never change. The rate of chemical change would be proportional to the fixed quantity of R. But what if we do not replenish R? He argues that the reaction rate should still be proportional to the amount of R, since in a small unit of time, the amount of R can be modelled as constant. If we now represent the rate of loss of R – which is basically the reaction rate, given no replenishing of R – as a function of time, $x(t)$, then we have the ordinary differential equation

$$\frac{\mathrm{d}x}{\mathrm{d}t} = -kx, \tag{1}$$

where k is some positive constant. We might want to impose an initial condition, $x(0) = a > 0$, just to represent the amount of R used in the experiment. Equation (1) is well within the reach of A-level mathematics. We have

$$\int \frac{\mathrm{d}x}{x} = -k \int \mathrm{d}t, \qquad \text{which implies} \qquad \ln(x) = -kt + C,$$

or equivalently $x = \exp[-kt + C]$ for some real constant C. The initial condition forces $x(0) = e^C = a$, which means $x(t) = a\exp[-kt]$.

2) Like any good scientist, he compares his hypothesis with the data collected. (For too much faith in theory is dangerous, when it veers away from reality.) Reproduced below is the table in which one such comparison is made.

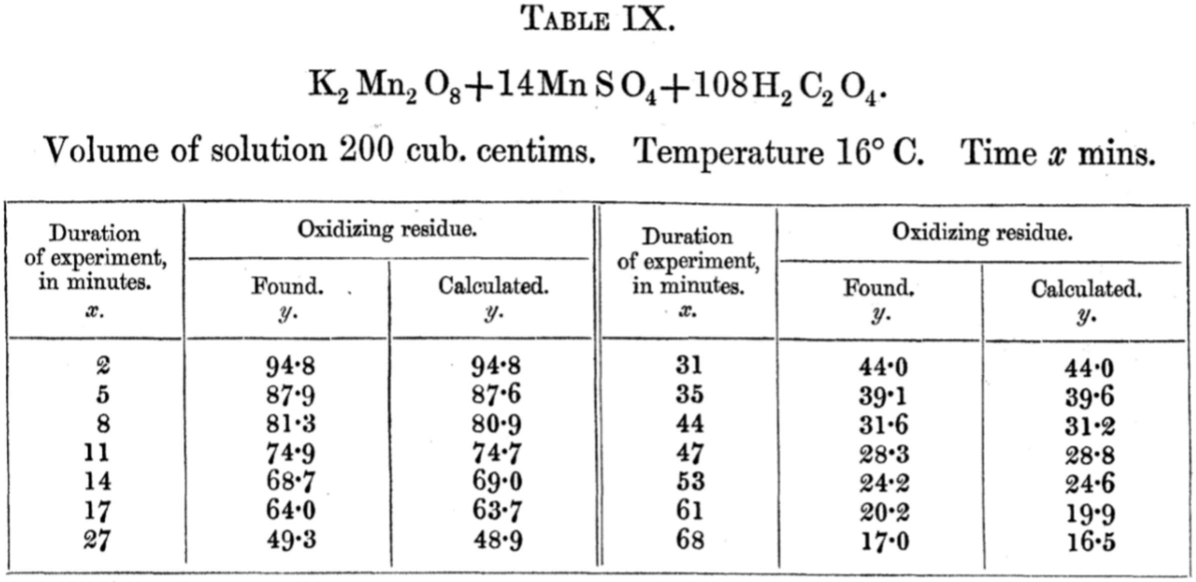


TABLE IX.

$K_2Mn_2O_8+14MnSO_4+108H_2C_2O_4$.

Volume of solution 200 cub. centims. Temperature 16° C. Time x mins.

Duration of experiment, in minutes. x.	Oxidizing residue.		Duration of experiment, in minutes. x.	Oxidizing residue.	
	Found. y.	Calculated. y.		Found. y.	Calculated. y.
2	94·8	94·8	31	44·0	44·0
5	87·9	87·6	35	39·1	39·6
8	81·3	80·9	44	31·6	31·2
11	74·9	74·7	47	28·3	28·8
14	68·7	69·0	53	24·2	24·6
17	64·0	63·7	61	20·2	19·9
27	49·3	48·9	68	17·0	16·5

The close fit of the exponential estimate is quite remarkable. The error in the percentage of oxidised residue is never more than 0.5 percent, despite this being a chemical experiment. However, Esson and Harcourt found that some set-ups which are supposed to improve the accuracy of the estimate, e.g. an even greater excess of background reagents S, T, ... as if infinitely supplied, turn out to worsen the accuracy, which the co-authors attributed to the complexity of the permanganic-oxalic reactions studied in [1]. This means that theory is not an acceptable fit when conditions exacerbate the effects of complex intermediary reactions. In their second paper, they opt for hydriodic acid and hydrogen peroxide, which involves fewer complexities and makes it possible to vindicate Esson's theory. Esson extends his insight on the law of mass action to two reagents,

say P and Q. Suppose that the other reagents are again present in near-infinite amounts. Then, holding Q fixed, the reaction rate is proportional to the quantity of P – and vice versa. So the reaction rate is proportional to the product of the amount of Q and that of P. If we scale up or down the units for P or Q, so that 1 unit of P reacts with exactly 1 unit of Q, and if we make the simplifying assumption that the products do not interfere with the reaction, then given an initial A units of P and B units of Q, the rate of chemical change, which is the rate at which P and Q disappear, is proportional to the product of the quantities of P and Q remaining, so if z denotes the amount of each that has been destroyed,

$$\frac{\mathrm{d}z}{\mathrm{d}t} = k(A-z)(B-z).$$

Again,

$$\int \frac{\mathrm{d}z}{(A-z)(B-z)} = k\int dt.$$

Esson distinguishes between two cases:

(i)$A \neq B$. Now $\dfrac{1}{(A-z)(B-z)} = \dfrac{1}{B-A}\left(\dfrac{1}{A-z} - \dfrac{1}{B-z}\right)$,

which implies

$$kt + C = \frac{1}{B-A}\big(\ln(B-z) - \ln(A-z)\big),$$

and since $z(0) = 0$, we have

$$C = \frac{\ln(B) - \ln(A)}{B-A} \qquad \text{and} \qquad z = AB\,\frac{\exp[(B-A)kt] - 1}{B\exp[(B-A)kt] - A}.$$

(ii)$A = B$. Then $kt + C = \dfrac{1}{A-z}$, which implies $z = A - \dfrac{1}{kt+C}$,

now with $C = 1/A$, so that

$$z = \frac{A^2kt}{Akt+1}.$$

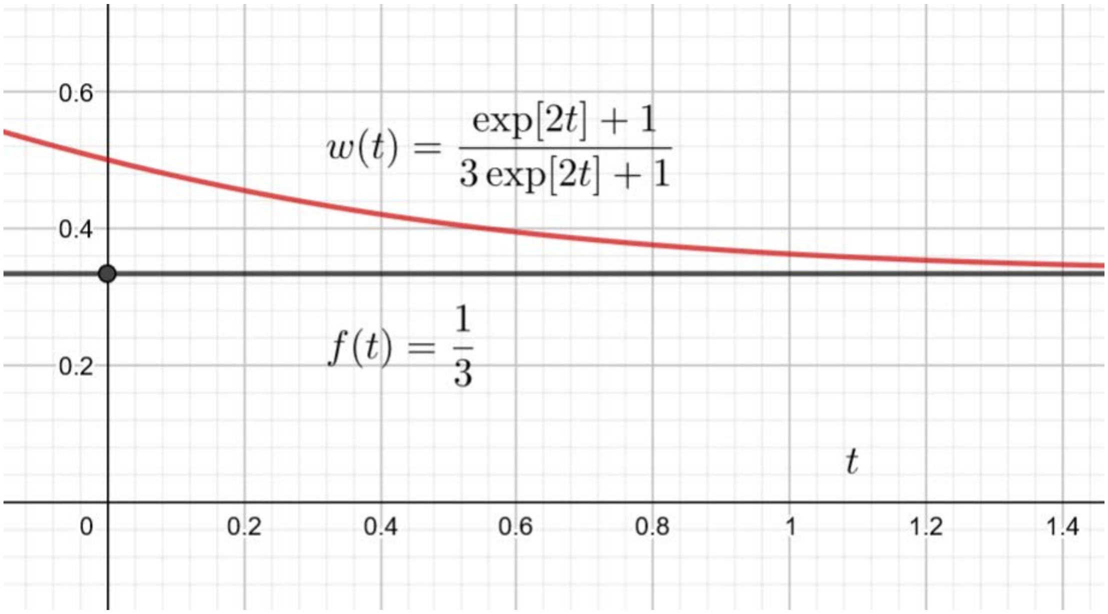
It is a little exercise to show that the former tends to the latter as B tends to A. The first paper by Esson and Harcourt [1] failed to establish the Law of Mass Action conclusively; the second succeeded [2]. The third paper [3] establishes that the reaction rate is proportional also to the amount of constituents of the medium, or the 'background reagents'. It also considers the effect of temperature. Other things being equal, the reaction rate is proportional to the m-th power of the temperature measured in Kelvin, for some positive m. They compute the value of m under different conditions, and show the model to agree with the sensible belief that at 0 K, no chemical change can take place. There follows, in the appendix, an interesting discussion of chemical equilibrium, i.e. when a net reaction does not take place and the quantity of different substances becomes constant. Normally reactions tend (at infinite time) towards equilibrium, because a system normally loses chemical energy in the process. Esson now considers a reversible reaction in a homogeneous medium, where a substance comprised of $AB + CD$ forms a substance comprised of $AC + BD$, and vice versa. Denoting the amount of AB, BC, AC, BD by w, x, y, z, and scaling the units, we still have the relations governed by the law of mass action

$$\frac{\mathrm{d}w}{\mathrm{d}t} = \frac{\mathrm{d}x}{\mathrm{d}t} = ayz - bwx,$$
$$\frac{\mathrm{d}y}{\mathrm{d}t} = \frac{\mathrm{d}z}{\mathrm{d}t} = bwx - ayz,$$

where a and b are positive constants. It follows that $w + y$, $w + z$, $x + y$, $x + z$ are all constant (and so are $w - x$, $z - y$). This allows a conversion into $\frac{dw}{dt} = a(k_1 - w)(k_2 - w) - bw(k_3 + w)$ which is then a separable ODE. The values of k_1 , k_2, k_3 are of course determined by the initial conditions. For instance, $a = 4$, $b = 1$, $k_1 = k_2 = 0.5, k_3 = 0$, $w(0) = 0.5$ gives

$$w = \frac{\exp[2t] + 1}{3\exp[2t] + 1}.$$

As suspected, w converges to some equilibrium value, i.e. 1/3. The relation between w and t is represented in the graph below by $w(t)$, and the asymptotic value by $f(t)$. The interested reader may investigate x, y, z for himself or herself.



These two insights – that the law of mass action tells us how fast a reaction goes, and that it tells us about the equilibrium result of the reaction – lay the foundation for further research in chemical kinetics, and therefore Esson, despite what may appear at first to be mathematically unsophisticated work, should be counted among the most important applied mathematicians of the 19th century.

References

[1] A. V. Harcourt and W. Esson, "On the Laws of Connexion between the Conditions of a Chemical Change and Its Amount", *Philosophical Transactions of the Royal Society of London* **156**, pp. 193-221 (1866)

[2] A. V. Harcourt and W. Esson, "On the Laws of Connexion between the Conditions of a Chemical Change and Its Amount", *Philosophical Transactions of the Royal Society of London* **157**, pp. 117-137 (1867)

[3] A. V. Harcourt and W. Esson, "Bakerian Lecture: On the Laws of Connexion between the Conditions of a Chemical Change and Its Amount. III. Further Researches on the Reaction of Hydrogen Dioxide and Hydrogen Iodide", *Philosophical Transactions of the Royal Society of London* **186**, pp. 817-895 (1895)

[4] A. V. Harcourt (with an appendix by W. Esson), "On the Variation with Temperature of the Rate of a Chemical Change", *Philosophical Transactions of the Royal Society of London* **212**, pp. 484-496 (1913)

[5] H. T. Gerrans, "William Esson", *Monthly Notices of the Royal Astronomical Society* **77(4)**, p. 299 (1917)

[6] A. V. Harcourt, "William Esson", *Journal of the Chemical Society* **111**, p. 332 (1917)