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This Week's Citation Classic

Carter G. Thermal resolution of desorption energy spectra.
Vacuum **12**:245-54, 1962.
[Department of Electrical Engineering, University of Liverpool, Liverpool, England]

Rate equations for desorption of gases possessing a distribution of desorption activation energies during prescribed heating (tempering) are developed. The analogy of optical line spectra and desorption from discrete sites is shown to be useful in defining the 'activation energy resolution' of the tempering method. [The *SCI*® indicates that this paper has been cited over 115 times since 1962.]

George Carter
Department of Electrical Engineering
University of Salford
Salford, Lancashire M5 4WT
England

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"From 1956 to 1960 I was working, as a graduate student, with Harry Leek in the department of electrical engineering at the University of Liverpool on the processes of ion pumping into the glass envelopes of Bayard-Alpert vacuum ionization gauges. The quantity of gas which had been trapped was subsequently determined by heating the gauge and monitoring the rate of gas evolution as a function of temperature. The results were interesting in that gas was evolved continuously and indicated a peak evolution rate at about 500K. In attempting to understand this phenomenon, first order kinetic rate reaction theory was employed and as a result the plot of gas evolution rate as a function of reciprocal temperature was made in order to deduce an activation energy for the process. Rather disturbingly the plot was nonlinear and if quasi-linearity was assumed, a ridiculously low value of activation energy was deduced. In searching for an explanation for such anomalies, I remembered my undergraduate physics courses which taught that processes were just as likely to be distributed as single valued and the concept of a continuous distribution of activation energies lor gas evolution emerged. Following discussions with Ron Bloomer, initial population distributions of trapped atoms in sites with different discrete activation energies were assumed, and from first order reaction theory the form of the evolution rate transient as a function of increasing temperature for each activation energy was evaluated. These transients were summed for each population distribution until an optimum match with experimental data was achieved. We were thus synthesising theoretically predicted transients to match experimental measurements.[1]

"These experiments led me to become more seriously interested in the mathematical theory of thermal evolution spectroscopy. Having researched the literature, I wrote a review on the theory and experimental study of thermal evolution spectroscopy from trapping sites of both discrete and continuously distributed evolution activation energy and dispatched it to one of the most prestigious British research journals. After a delay of more than a year, rejection was announced. I then submitted the paper to *Vacuum,* the most relevant journal for these studies. The editor soon advised me that a similar manuscript with about 50 percent of the same content had been received from Paul Redhead of the National Research Council, Ottawa, and was accepted for publication.[2] Hurried revision, deletion of overlap, and highlighting of different concepts resulted in publication of a much condensed version of the paper in 1962 which complemented Redhead's paper and explored in detail novel ideas of deconvolution of distributed activation energy spectra and the ability to resolve, experimentally and theoretically, sites of small activation energy separation. The idea of the 'resolution' of the technique was born.

"Thus, my paper and Redhead's are highly complementary and are often cited jointly in the literature Redhead apparently suffered a rejection/acceptance experience similar to mine. The probable major reason for the frequency of citation of these papers is that they provide a fundamental starting point for the many investigators of thermally activated phenomena to interpret their data. The field is not dead and a new paper of a more advanced nature is soon to be published."[3]

1. **Carter G & Leck JH.** A study of the mechanism of ion pumping for the noble gases. *Proc. Roy. Soc. A* **261**:303-15, 1961.
2. **Redhead P A.** Thermal desorption of gases. *Vacuum* **12**:203-11, 1962.
[Citation Classic. *Current Contents/Engineering. Technology & Applied Sciences* **11**(36):16, 8 September 1980.]
3. **Carter G, Bailey P, Armour D G & Collins R.** The deduction of continuously distributed activation energy site populations from tempering schedules. *Vacuum.* To be published, 1982.