LETTER TO THE EDITOR

The yield of resonance fluorescence of Na in a flame

With good approximation the homogeneous part of a gas flame above the first combustion zone is in thermal equilibrium. This equilibrium, however, does not apply to the radiation density as the emission of radiation by the flame is not compensated by irradiation, and as at most wavelengths self-absorption is negligible. Notwithstanding this exception, the population of energy levels is adequately described by the Boltzmann formula, because mainly collision processes and not emission of radiation account for the transitions to other levels. Accordingly, the excitation temperature describing the population of an excited state is but slightly lower than the translation temperature of the colliding molecules.

The approximation which these temperatures are equal with, depends on the number of radiative transitions divided by the total number of transitions from the level concerned. This ratio may be determined by measuring the fluorescence yield. The result to be reported here has been obtained with resonance fluorescence. By combining the measured fluorescence yield with the absolute probability of radiative transition (which is known from other experiments), the absolute probability of collisional transition is found. This probability of collisions causing a transition is also interesting when the broadening of the corresponding spectral line by collisions is being considered.

Fig. 1. Scheme of experimental arrangement.

S = sodium discharge lamp.	B = colour filter.
C = chopping disk.	P = phototube.
F = flame.	A = a.c. amplifier.
	G = a.c. galvanometer.
I = arrangement for measuring the absorbed intensity.	
II = " " " " " fluorescence intensity.	

Measurements have been made with sodium vapour in a propane-air flame, into which a solution of NaCl was sprayed. The yellow light emitted by a sodium discharge lamp was focussed in a small part of the flame (fig. 1). Before entering the flame

light was periodically chopped at a frequency of 50 c/s by a rotating disk. As a result the resonance fluorescence that is caused by this primary radiation forms a periodic component in addition to the (constant) thermal radiation of the sodium atoms in the flame. The periodic component emitted in a certain direction was measured and integrated over all directions. Next the amount of primary radiation was measured that was absorbed by sodium atoms in the flame. The intensity ratio between the integrated periodic emission and the absorbed radiation is the resonance-fluorescence yield p . In our case p obviously concerns the portion of excited sodium atoms in 3P state that make a spontaneous transition to the ground state, and $1 - p$ is the portion leaving the 3P state by other means. Virtually, $1 - p$ concerns the radiationless transitions from 3P to the ground state 3S caused by collisions of the second kind ("quenching of the fluorescence").

The absorbed intensity was determined by measuring the difference in intensity of primary radiation transmitted by the flame when a blank solution and a sodium solution were sprayed respectively (see fig. 1). The fluorescence light was measured with the same phototube and a.c. amplifier, after the sensitivity had been increased by a known factor. Since the amplifier was followed by an a.c. galvanometer, which acts as a synchronous rectifier with a response frequency of 50 c/s, the (constant) thermal light-emission of the flame was not detected. The thermal lightemission exceeds the fluorescence emission by a factor 400. Only the 50 c/s component of the fluctuation in this "constant" thermal emission is visible on the reading scale, and limits, in fact, the accuracy of the fluorescence measurements.

In our (preliminary) measurements no anisotropy was found in the dependence of the fluorescence intensity on the angle φ between the direction of measuring and that of the incident beam (see fig. 1). The integrated fluorescence was therefore calculated by multiplying the measured intensity by $4\pi/\omega$; here ω = solid angle at which the diaphragm in front of the phototube is seen by the flame.

As a result p was found to be 0.040 for the 3P $\rightarrow$ 3S yellow Na doublet. According to earlier measurements, the probability of the radiative transition 3P $\rightarrow$ 3S equals $A = 0.63 \times 10^8 \text{ sec}^{-1}$. From these data the total probability of transition 3P $\rightarrow$ 3S is found to be $0.63 \times 10^8 / 0.040 = 16 \times 10^8 \text{ sec}^{-1}$, and the probability of collisional transition turns out to be $(1 - 0.040) 16 \times 10^8 = 15 \times 10^8 \text{ sec}^{-1}$; both results refer to Na atoms in the 3P state in our propane-air flame. From the latter figure the effective cross-section Q for collisions of this kind is calculated as follows:

$$Q = \frac{15 \times 10^8}{N} \left| \sqrt{\frac{8kT}{\pi} \left(\frac{1}{M_1} + \frac{1}{M_2} \right)} \right| = 24 \times 10^{-16} \text{ cm}^2;$$

here N = number of molecules/cm³ in the flame = 3.3×10^{18} , T = flame temperature = circa 2200°K, M_1 = mass of sodium atom, M_2 = mass of flame gas molecule = $28/(6 \times 10^{23})$ if the flame gas is supposed to consist of nitrogen (which in most air flames is a reasonable approximation).

It may be noted that the Q -value found by us is in fair agreement to the value $Q = 22 \times 10^{-16} \text{ cm}^2$ tabulated in Landolt-Börnstein's Tables (1) for sodium atoms in nitrogen with the same mean relative velocity as that in our flame. The tabulated value refers to measurements concerning the quenching of sodium fluorescence by nitrogen; the excited sodium was produced by light emitted from a spark (2).

The result $p = 0.040$ was obtained with low sodium concentrations in the flame. Measurements with high concentrations yielded lower values of p (see fig. 2), a considerable portion of the fluorescence radiation now being captured inside the flame because of self-absorption.

From $p = 0.040$ it can be concluded that the actual population of the 3P level is

lower than the thermal equilibrium value by 4 percent. With high sodium content this deviation is smaller because of self-absorption. Anyhow, it follows from this result that the corresponding error in temperature measured by line-reversal is at most 8° in our case.

Fig. 2. Resonance fluorescence yield p and (for comparison) thermal radiation yield q of Na in the flame, both for $5890/96 \text{ \AA}$ and as a function of the sodium content.

Abscissa: Sodium content of the sprayed NaCl solution (milligrams Na per litre solution).

Ordinate fig. 2a: Total intensity of resonance fluorescence radiation divided by absorbed intensity of primary light.

Ordinate fig. 2b: Intensity of thermal radiation divided by sodium content of solution (arbitrary units).

In the region of small self-absorption (left-hand part of the curves) the loss in yield must be proportional to the sodium content.

Checking measurements have been made with the same flame into which respectively

a) no spray,

b) a spray of distilled water,

c) a spray of KCl solution without Na

was introduced. In all three cases no absorption or scattering of the yellow discharge light in the flame was observed, and no fluorescence.

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