# Research Notes

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## Further Studies of Cr I Emission from the Shock Tube

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WE report here some results of shock-tube spectroscopic work previously introduced on these pages.[1] Whereas we had apparently found anomalies in the excitation temperature of Cr I behind reflected shock waves, it is now clear that the anomalies do not exist, and that our spectral line intensity measurements define a new scale of $gf$ values (transition probabilities) for Cr I. The old relative scale of Hill and King[2] contained systematic errors which confused not only our initial work but also other observations of Cr I in arcs[3] and the solar atmosphere.[4,5] This note is intended both to affirm the attainability of electronic excitation equilibria in conventional shock tubes, and to suggest that the chromium spectrum may now reliably be used for the measurement of temperature in experimental gas dynamics. Of course, nonequilibrium regimes of operation can be found for any spectroscopic source, whence the usual interpretations of spectral line intensity become doubtful.

Space does not permit a complete description of our measurements here. We have determined atomic $gf$ values by combining (1) measured spectral line intensities and (2) calculated atomic abundances and level populations. The methods employed have been outlined in the literature[1,6]; detailed accounts have been prepared[7-9] and will be published in the near future. Much of the work has dealt with item (2) above, or more exactly, the reliability of calculating the gaseous state behind the reflected shock wave from the initial gas composition and the observed primary shock speed. The correspondence with Rankine–Hugoniot theory has been checked by measurements of pressures[6,8,9] and Balmer line intensity.[7] Absolute $gf$ values have been found for many lines of Ne I, Ar I, C I, O I, N I, Cr I and Cr II, with a random error $\sim 10\%$ arising from the photographic procedures of item (1) above.

In addition, the work on Cr I and Cr II has been substantiated by line-reversal measurements of excitation temperature.[9] In each such experiment, reversal temperatures are found for many individual lines and then compared with each other and with the thermodynamically predicted value. The agreement is better than 3% for both comparisons, even when the amount of spectroscopic additive (chromium carbonyl[1,6]) is made so high as to induce large temperature drops (1000°–2000°K) in the neon carrier gas.

The comparison of our Cr I results ($gf$) with the previous work of Hill and King (relative values $gf_r$) may be made in various ways. The essential point is shown by considering the ratio $gf_r/gf$. If both sets of data were correct, this ratio would be a constant for *all* lines, namely just the scale factor required for transforming Hill and King's relative scale into an absolute one. Instead we find that (1) $gf_r/gf$ is constant only within *groups* of lines, (2) each of these groups is characterized by the energy $E_j$ of the lower levels, and (3) $gf_r/gf$ increases strongly with $E_j$ as shown in Table I. This table covers the

TABLE I. Correction of previous work on Cr I $gf$ values.

| $E_j$(eV) | 0.9–1.1 | 2.5–2.7 | 3.1–3.2 |
|---|---|---|---|
| Measured ratio of $gf_r^2$ to $gf^{3,9}$ | 1100 ± 100 | 4800 ± 600 | 8000 ± 2000[a] |
| Range of absolute $gf^{3,9}$ | 0.20–0.60 | 0.28–20. | 3.2–7.2 |
| Standard multiplet numbers[10] | 21. | 31, 33, 38, 67. | 143, 145, 186. |

[a] Absolute $gf$ measured with 10–15% precision, but Hill and King's $gf_r$ uncertainty 20–25% for many lines of high excitation.

data analyzed most thoroughly so far, namely 35 lines belonging to 8 multiplets and lying between 3980 and 4930 Å. Since our results are supported by several independent checks of the shock-tube conditions, we can only conclude that the earlier work on Cr I suffers from a systematic error which increases with increasing excitation potential. This contention is supported by analyses of Cr I spectra in other light sources.[3-5] In addition, the new $gf$ values yield, for the first time, a consistent picture of Cr I intensities in the Fraunhofer spectrum.[11] In the manner described in our previous Note,[1] we have applied the corrected $gf$-value system to measurements of excitation temperature in individual shock-tube experiments. The anomaly we then reported is thereby removed; i.e., we obtain agreement (again uniformly better than 3%) between predicted and observed temperature over the range 6600°–9600°K.

In the following discussion, we do not mean to imply that the absorption furnace method used by Hill and King is basically unreliable. Quite to the

contrary, furnace measurements on various metals (e.g., Fe I[12,13] and Co I[14]) have given reliable and useful results. The $gf$-value corrections required for Cr I, however, are consistent with a furnace-temperature error, and our remaining discussion assumes this point of view.

The important point for gas dynamics experiments is that a set of erroneous $gf$ values can give very deceptive results when used for excitation temperature measurements. If the $gf$ values contain a hidden temperature error, they will affect the interpretation of line intensities to give not just a meaningless scatter of energy level populations but, rather, an apparently *bona fide* Boltzmann distribution appropriate to some temperature other than the true temperature of the gas under study. This is precisely the form in which the Cr I hiatus appeared in our initial work.[1] In effect, we computed too low a relative population for the higher excited states of Cr I because the appropriate $gf$ values of Hill and King were relatively too large. Quantitatively, our earlier spurious temperatures (e.g., 5200°K at 9200°K true temperature) can be ascribed, via the $gf$-value corrections given in Table I, to a much smaller *underestimate* of furnace temperature in the original work. According to Hill and King, the range 1100°–2800°C was used to bring out various multiplets under conditions of small optical depth. Assuming the median value ($\sim$2220°K), the $gf$-value corrections imply an actual furnace temperature of 2700 $\pm$ 50°K. An error of this order of magnitude is hard to understand in itself, but has also been suggested previously.[3,5] It is particularly noteworthy that small or moderate temperature errors made in low temperature experiments can cause serious percentage errors at high temperature. Thus, the accurate measurement of $gf$ values should continue to be of importance in studies of high-temperature gases.

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# Comments

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## Stability of Electrically Charged Conducting Droplets

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RECENTLY Ailam and Gallily[1] have investigated the stability of a charged spherical drop by comparing its energy with that of ellipsoids of revolution at the same volume and charge. Expressing their results in terms of the dimensionless ratio $\alpha$ of twice the electrostatic to surface energies, they found, as did Rayleigh,[2] that the sphere becomes unstable with respect to infinitesimal distortion at $\alpha = 4$. In addition, they found that between $\alpha = 3.5$ and $\alpha = 4$, the sphere is only metastable because a prolate spheroid of axial ratio near 2.3 is of lower energy.

Because Ailam and Gallily limited their investigation to spheroids they correctly expressed the possibility that shapes of still lower energy exist and that the sphere may become metastable at lower values of $\alpha$. A straightforward calculation of the surface tractions due to the electric field and surface tension[3] shows that they are different functions of position on the surface of a spheroid and therefore cannot be in balance over the entire surface except for the sphere. Thus no spheroid except the sphere can be an equilibrium shape. The question then arises, what are the equilibrium shapes? It is the purpose of this note to point out that a sphere becomes metastable at a value of $\alpha$ in excess of 1.41 with respect to separation of the drop into a number of equal smaller spheres and that such a configuration probably gives the lowest energy for the system.