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Failure of Bragg's rule for a mixture of nonreacting gases

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We show by calculation that for a mixture of nonreacting gases the electronic stopping cross section at low projectile velocities may deviate from the weighted mean of the single-component values (Bragg's rule). This departure is significant if the individual cross sections for electron capture and electron loss differ considerably. In this case, mixing not only changes the mean charge state in a nonlinear way, but also speeds up the charge-changing cycle. For stopping of 4-keV hydrogen projectiles in a mixture of helium and hydrogen gas, we find that energy losses due to charge-changing processes differ by a factor of 2 from simple additivity. The stopping cross section will be about 50% larger than the result obtained from Bragg's rule.

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Bragg's rule [1] predicts the electronic stopping cross section ϵ^{AB} of a two-component target AB—either a compound $(A+B)$ or a mixture (A,B)—to be the weighted mean of the stopping cross sections ϵ^A and ϵ^B of its constituents A and B,

$$\epsilon^{AB}=a\epsilon^{A}+b\epsilon^{B}\,, \tag{1}$$

where a and b are the respective fractions of A and B within AB (we shall consider atomic concentrations, so $a+b=1$).

There is a huge amount of literature dealing with departures from Bragg's rule for *compounds* (for a recent review, see Refs. [2,3], and references therein). Deviations of measured values from Bragg's rule are usually found to be smaller than 20% at the stopping power maximum. They are explained by the change of the electron orbital structure due to binding. No such argument applies to a *mixture* and no deviation is usually expected. But even in this case, there might be a departure if charge-changing collisions (electron capture and stripping) contribute significantly to stopping. In the following we present a calculation for a particularly striking example: 4-keV protons stopped in a mixture of helium and hydrogen gas. The individual stopping cross sections have recently been measured by us [4,5].

To calculate the stopping of a mixture, we use a concept introduced by Allison, Cuevas, and Garcia-Munoz [6]: all possible collision events that give rise to an energy loss T with cross section σ (which by definition add up to the stopping cross section $\epsilon=\int T\,d\sigma$), are separated into two groups. The first (I) comprises interactions that keep the projectile's charge unchanged (weighted by their respective charge-state fraction), the second (II) includes those that do change the charge state. To keep notation and calculation as simple as possible, we consider the equilibrium fractions of protons and hydrogen atoms only (the population of the negative charge state in H_2 and in He is always below 1% above 4 keV),

$$\epsilon=\{F_0\epsilon_0+F_1\epsilon_1\}^{\mathrm{I}}+\{F_0\sigma_{01}T_{01}+F_1\sigma_{10}T_{10}\}^{\mathrm{II}}\,. \tag{2}$$

Here we denote the fraction of neutral projectiles by $F_0=\sigma_{10}/(\sigma_{01}+\sigma_{10})$ and the fraction of protons by $F_1=\sigma_{01}/(\sigma_{01}+\sigma_{10})$, where σ_{01} is the stripping cross section and σ_{10} is the cross section for electron capture, respectively; ϵ_0 and ϵ_1 within the first bracket $\{\}^{\mathrm{I}}$ are the so-called *partial stopping cross sections,* which include only those energy losses where the atom or the proton *keeps* its respective charge state; the second bracket $\{\}^{\mathrm{II}}$, which describes stopping associated with charge-changing collisions, will be named ϵ_{CC}. T_{01} and T_{10} are the mean energy losses due to stripping and capture, respectively. Only two charge states are considered, so $F_0\sigma_{01}=F_1\sigma_{10}=\sigma_{01}\sigma_{10}/(\sigma_{10}+\sigma_{10})=\sigma_{CC}$ and $\epsilon_{CC}=\sigma_{CC}(T_{01}+T_{10})$. This partition of collision events may be incorrect when multiple processes, e.g., stripping of the projectile electron and target excitation at the same time, become highly probable. Those occurrences might be included, but they have no influence on the fundamentals of the effect considered here.

The failure of Bragg's rule in a mixture can be understood already at this point: to obtain the *partial* stopping cross sections of the mixture it is correct to add the weighted *partial* stopping cross sections of the components; this is in general no longer true, however, for the charge-state fractions since here the underlying cross sections must be combined linearly. Additivity has to fail in general for ϵ_{CC}^{AB}, since it depends on the *product* of the respective cross sections.

This mixing effect will be marked if cross sections are as different as those for electron capture by 4-keV protons in helium and in hydrogen gas, respectively. The extreme difference is due to the large mismatch or close matching of target (He, 24.6 eV; H_2, 15.4 eV) and projectile (H^0, 13.6 eV) ionization energies; the following cross sections in units of 10^{-16} cm^2 per atom are taken from Ref. [7]: $\sigma_{01}^{\mathrm{He}}=1.1$, $\sigma_{10}^{\mathrm{He}}=0.20$; $\sigma_{01}^{\mathrm{H_2}}=0.43$, $\sigma_{10}^{\mathrm{H_2}}=4.7$.

To calculate the mean energy loss due to stripping, we take into account only the H^0 ground state (according to conditions in a stripping cross-section measurement) and assume a mean kinetic energy of 5 eV and an isotropic emission of the stripped electron in the projectile's frame of reference ($T_{01}^{\mathrm{He}}=T_{01}^{\mathrm{H_2}}=18.6$ eV). Our estimate of the kinetic energy is in reasonable agreement with the value

4.4 eV used by Phelps [8] for ionization of H_2 by 4-keV protons and with approximate values 6 and 7 eV derived from measurements by Rudd for ionization of H_2 [9] and of He [10] by 5-keV protons, respectively. It should be mentioned that at low velocities ionization by a neutral particle (stripping is considered here as ionization of the projectile by the neutral target) may lead to an increased electron kinetic energy compared to ionization by a charged particle [11]. For the mean energy loss due to electron capture ($T_{10}^{He}=13.2$ eV, $T_{10}^{H_2}=4.0$ eV), we take a lower limit by assuming capture from target ground state into projectile ground state only. For both the He and the H_2 targets, an energy of 2.2 eV is required for an electron to change over to the moving 4-keV proton, and this value has been added to the difference of ionization energies. At first, the amount of energy needed to accelerate the electron reduces the *velocity* of the projectile, but it becomes apparent as an energy loss after the subsequent stripping process. Within this model the stopping cross sections of 4-keV hydrogen projectiles in He and in H_2 are

$$\epsilon^{He}=0.72\times10^{-15}\,\mathrm{eV\,cm^2}=\{0.15\epsilon_0^{He}+0.85\epsilon_1^{He}\}^{I}+\{0.017\times10^{-15}\,\mathrm{cm^2}[(18.6+13.2)\,\mathrm{eV}]\}^{II};$$

$$\epsilon^{H_2}=2.7\times10^{-15}\,\mathrm{eV\,cm^2}=\{0.92\epsilon_0^{H_2}+0.08\epsilon_1^{H_2}\}^{I}+\{0.039\times10^{-15}\,\mathrm{cm^2}[(18.6+4.0)\,\mathrm{eV}]\}^{II}.$$

ϵ^{He} and ϵ^{H_2} are taken from our measurements [4,5]. It might be interesting to note that charge-changing collisions in helium gas contribute almost 75% to electronic stopping, although electron capture is quite inefficient ($\epsilon_{CC}^{He}=0.54\times10^{-15}$ eV cm^2, $\epsilon_{CC}^{H_2}=0.89\times10^{-15}$ eV cm^2).

The stopping cross section of the He-H_2 mixture is given by

$$\epsilon^{He,H_2}=\{F_0^{He,H_2}(a\epsilon_0^{He}+b\epsilon_0^{H_2})+F_1^{He,H_2}(a\epsilon_1^{He}+b\epsilon_1^{H_2})\}^{I}+\{\epsilon_{CC}^{He,H_2}\}^{II}, \quad (3)$$

where the charge-state fractions follow from the charge-changing cross sections $\sigma_{01}^{He,H_2}=(a\sigma_{01}^{He}+b\sigma_{01}^{H_2})$, $\sigma_{10}^{He,H_2}=(a\sigma_{10}^{He}+b\sigma_{10}^{H_2})$:

$$F_0^{He,H_2}=\sigma_{10}^{He,H_2}/(\sigma_{01}^{He,H_2}+\sigma_{10}^{He,H_2})=(1-F_1^{He,H_2}), \quad (4)$$

and the energy loss due to charge-changing collisions is

$$\epsilon_{CC}^{He,H_2}=F_0^{He,H_2}(a\sigma_{01}^{He}T_{01}^{He}+b\sigma_{01}^{H_2}T_{01}^{H_2})+F_1^{He,H_2}(a\sigma_{10}^{He}T_{10}^{He}+b\sigma_{10}^{H_2}T_{10}^{H_2}). \quad (5)$$

The small fraction of neutral projectiles in He at 4 keV, $F_0^{He}=0.15$, changes significantly when hydrogen gas is added. As an example, we shall consider an atomic concentration of 20% hydrogen ($a=0.8$, $b=0.2$, corresponding to a mixture of He atoms and H_2 molecules in the ratio 8:1); here

$$F_0^{He,H_2}=\frac{(0.8\times0.20+0.2\times4.7)\times10^{-16}\,\mathrm{cm^2}}{(0.8\times1.3+0.2\times5.13)\times10^{-16}\,\mathrm{cm^2}}=0.53$$

follows from Eq. (4), whereas the weighted mean of the individual neutral fractions is 0.30.

The main deviation from Bragg's rule is due to the contribution of charge-changing processes: whereas the linear combination gives

$$(0.8\times0.54+0.2\times0.89)\times10^{-15}\,\mathrm{eV\,cm^2}=0.61\times10^{-15}\,\mathrm{eV\,cm^2},$$

the actual value [Eq. (5)] will be twice as large:

$$\epsilon_{CC}^{He,H_2}=0.53(0.8\times1.1\times10^{-16}\,\mathrm{cm^2}\times18.6\,\mathrm{eV}+0.2\times0.43\times10^{-16}\,\mathrm{cm^2}\times18.6\,\mathrm{eV})+(1-0.53)(0.8\times0.20\times10^{-16}\,\mathrm{cm^2}\times13.2\,\mathrm{eV}+0.2\times4.7\times10^{-16}\,\mathrm{cm^2}\times4.0\,\mathrm{eV})=1.23\times10^{-15}\,\mathrm{eV\,cm^2}.$$

This is a consequence of efficient neutralization by H_2 and efficient stripping by He.

To actually calculate the stopping of a He-H_2 mixture, we have to know the ratios of the partial stopping cross sections $R^{He}=\epsilon_0^{He}/\epsilon_1^{He}$ and $R^{H_2}=\epsilon_0^{H_2}/\epsilon_1^{H_2}$. If we assume $R^{He}=R^{H_2}=1$, the contributions from energy-loss processes at fixed projectile charge state behave exactly according to simple additivity and any deviation from Bragg's rule is only due to ϵ_{CC}^{He,H_2}, which has been calculated fairly accurately. Since $(F_0+F_1)=1$, we have

$$\epsilon_0^{He}=\epsilon_1^{He}=(\epsilon^{He}-\epsilon_{CC}^{He})=0.18\times10^{-15}\,\mathrm{eV\,cm^2}$$

and

$$\epsilon_0^{H_2}=\epsilon_1^{H_2}=1.81\times10^{-15}\,\mathrm{eV\,cm^2},$$

and we obtain

$$\epsilon^{He,H_2}=1(0.2\times0.18+0.8\times1.81)\times10^{-15}\,\mathrm{eV\,cm^2}+1.23\times10^{-15}\,\mathrm{eV\,cm^2}=1.74\times10^{-15}\,\mathrm{eV\,cm^2},$$

whereas the result from Bragg's rule [Eq. (1)] is $\epsilon_{Bragg}^{He,H_2}=1.12\times10^{-15}$ eV cm^2.

The solid curve in Fig. 1 shows the stopping cross section of the He-H_2 mixture for varying atomic concentrations, b, of hydrogen in helium ($a=1-b$). Bragg's rule is plotted as a dashed line; our calculation of ϵ^{He,H_2} exceeds $\epsilon_{Bragg}^{He,H_2}$ by about 55% at $b=0.2$, where the maximum relative deviation occurs. The choice of $R^{He}=R^{H_2}=1$ introduces some arbitrariness, but a variation over a broad range has only minor influence on the result: ϵ_{CC}^{He,H_2} is unaffected and the sum of the partial stopping contributions (plotted as the dash-dotted line for $R^{He}=R^{H_2}=1$) changes the deviation at $b=0.2$ from about 45% (for

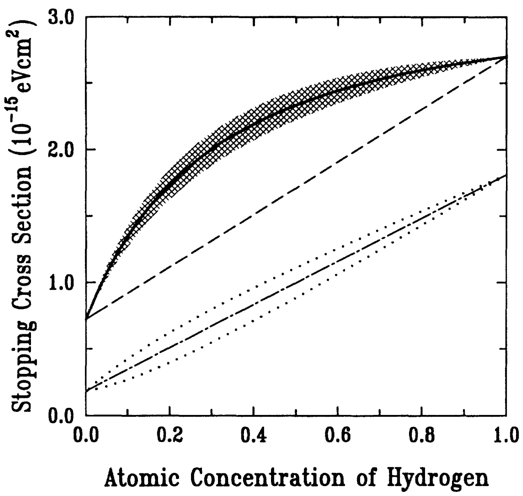

FIG. 1. Stopping cross section ϵ^{He,H_2} of a He-H_2 mixture for hydrogen projectiles at 4 keV as a function of the atomic concentration of hydrogen gas. Solid line, this calculation; dashed line, prediction from Bragg's rule; dash-dotted line, stopping from collisions with projectile's charge state fixed; the difference to the solid line is the contribution of charge-changing processes; dotted lines, two particular ratios of partial stopping cross sections (see text); cross-hatched area, the influence on ϵ^{He,H_2}.

$R^{He}=1$, $R^{H_2}=4$) to about 65% for ($R^{He}=4$, $R^{H_2}=1$); both choices are shown by dotted lines, and the influence on ϵ^{He,H_2} is indicated by the cross-hatched area. In fact, we expect both ratios to be larger than one, since projectile excitation contributes only to ϵ_0 and target excitation and target ionization might be enhanced by neutral projectiles at low velocities [7,11].

In summary, a failure of Bragg's rule for a gas mixture (A, B) occurs if the stopping by component A is modified by the influence of component B on the projectile's charge state and *vice versa.* If A and B differ strongly with respect to their charge-changing cross sections, this leads to a departure from simple additivity, since both the population of the different charge states and stopping due to charge-changing collisions will be affected. We wish to add that the considerations presented here for a gas mixture should also be taken into account for compounds, and the discrepancy may be especially severe if Bragg's rule is applied to targets in a physical state different from that in which the components have been measured.

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