

## Chemical effects on the Bethe-Bloch stopping formula within the statistical model

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We investigate which terms of the extended Bethe-Bloch equation do not follow Bragg's rule of simple additivity of stopping cross sections when a compound is formed. Using the statistical description of the target atom, we find the dominating contribution to these chemical effects coming from the logarithmic (Bethe) term. Only a minor contribution is due to the Barkas or  $Z_1^3$  term. Based upon scaling laws, both effects can be related to the variation of the mean ionization potential on forming the compound. [S1050-2947(98)00912-3]

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Since the pioneering experiments by Bragg at the beginning of this century, physicists aimed at a procedure to obtain stopping cross sections  $\epsilon$  of compounds from stopping cross sections of their constituents. As long as all quantities necessary to describe the stopping process stay constant when the compound is formed,  $\epsilon$  of the molecule  $A_m B_n$  has to be the weighted sum of the stopping cross sections of its atomic components [1]

$$\epsilon_{A_m B_n} = m\epsilon_A + n\epsilon_B. \quad (1)$$

Here  $\epsilon_A$  and  $\epsilon_B$  comprise all processes leading to energy transfer from projectile to target, for instance, also charge changing, i.e., electron loss from and electron capture by the projectile [2], provided the moving projectile can carry electrons.

From their measurements Bragg and Kleeman [3] deduced that the energy loss (or loss in range) of  $\alpha$  particles when penetrating metal foils divided by their areal mass density is proportional to the square root of the target atomic mass. As this quantity will not change upon forming the compound, they concluded that a relation similar to Eq. (1) has to hold. However, it turned out not to be true that "the atom has a [disk-like] form... and... that an explanation of the square-root law may be found in the hypothesis that ions can only be formed on the circumference of the atom's disk" [3]. Hence Eq. (1) is not self-evident and deviations from this relation, now called Bragg's rule, are to be expected. So it has to be decided judiciously each time whether Eq. (1) holds: For instance, for 2-MeV  $\alpha$  particles the specific energy loss in a mixture of 3 mol of  $O_2$  gas and 4 mol of solid aluminum is, within experimental accuracy ( $\approx 2\%$ ), the same [4] as in the insulating compound  $Al_2O_3$ . On the other hand, when 8-keV deuterons penetrate a mixture of the nonreacting gases  $H_2$  and He, Bragg's rule is violated [5] by more than 50%. Such a large effect is only to be expected for low-velocity projectiles in a mixture of two favorably selected gases; different capture and loss cross sections of the gases may result in an accelerated charge changing cycle [6]. As we are concerned with swift projectiles stripped of all electrons, we have to expect deviations from Bragg's rule on the order of 10% only.

Recently, Thwaites [7] suggested that one obtains reliable proton stopping cross sections of compounds the following way. One starts with Bragg's value for  $\epsilon$  determined from

measured data of the constituents and then calculates a correction term based upon the extended Bethe-Bloch equation

$$\epsilon^{(\text{theor})}(v_1) \approx \frac{Z_1^2 e^4}{4\pi\epsilon_0^2 m v_1^2} Z_2 (L_0 + Z_1 L_1 + L_2). \quad (2)$$

Here  $Z_1$  and  $Z_2$  are the charge numbers of projectile and target atom, respectively;  $m$  is the electron mass and  $v_1$  is the velocity of the projectile.  $L_0$  corresponds to the Bethe or (including  $Z_1^2$  in the first factor)  $Z_1^2$  term of the stopping number,  $L_1$  describes the  $Z_1^3$  contribution [8], causing the Barkas effect, and  $L_2$  is the Bloch correction to stopping. An expansion of  $L_2$  in powers of  $Z_1$  gives a first term proportional to  $Z_1^2$ , in total a  $Z_1^4$  contribution. This power series in  $Z_1$  is valid provided the Bohr parameter  $\kappa = 2Z_1 v_0 / v_1$  (with  $v_0$  the Bohr velocity) is smaller than 1. Therefore, we are restricted to proton energies beyond the stopping power maximum. As chemical effects dwindle away at high velocities, we have to focus on proton energies between 150 and about 500 keV. Within this range the stopping cross section of a compound may be calculated from

$$\epsilon_{\text{comp}} = \epsilon_{\text{Bragg}}^{(\text{expt})} + (\epsilon_{\text{comp}}^{(\text{theor})} - \epsilon_{\text{Bragg}}^{(\text{theor})}). \quad (3)$$

The point in the procedure proposed by Thwaites [7] is that some of the terms on the right-hand side of Eq. (2) follow Bragg's rule and therefore need not be calculated explicitly, but cancel when carrying out the difference in Eq. (3). For the rest we have to know how they change due to chemical effects.

For nonrelativistic projectiles  $L_0$  can be written

$$L_0 = \ln\left(\frac{2mv_1^2}{I}\right) - \frac{C(v_1^2)}{Z_2}. \quad (4)$$

$C(v_1^2)/Z_2$  is the shell correction term originating from non-negligible target-electron velocities. Evidently, it applies first of all to inner shells that will rarely be affected by chemical reactions. Hence the only quantity in  $L_0$  that may be subject to changes in the chemical environment is the mean ionization potential  $I$ . Within the statistical model of the atom,  $I$  can be written [9] as  $I = K_B(Z_2) Z_2$ , called the Bloch relation, with the Bloch factor  $K_B$  depending weakly on  $Z_2$  and approaching the value  $\approx 10$  eV in the limit of large  $Z_2$ . The

fact that  $I$  is roughly proportional to  $Z_2$  is a result of the scaling properties of the statistical model: The characteristic frequency  $\omega$  of the statistical atom scales with  $Z_2$ . Now the energy  $\hbar\omega \propto Z_2$  can be taken as an estimate for the mean excitation energy or mean ionization potential  $I$  of the real atom.

We deal with chemical effects on stopping. For simplicity, we now will consider a homonuclear molecule, e.g.,  $\text{Cl}_2$ . Because of symmetry, the bond can be divided between the two atoms. So the number of electrons per Cl atom is the same in the atom and in the molecule. However, the energy and to a smaller degree the velocity distribution of the target electrons may change upon forming the compound. However, within the statistical model all properties of the atom are plugged into the single quantity  $Z_2$ . To allow for flexibility we have to distinguish between the number of electrons  $Z_2$  and the scaling parameter  $Z_2^*$ . Equation (4) now reads

$$L_0 = \ln\left(\frac{2mv_1^2}{K_B Z_2^*}\right) - \frac{C(v_1^2)}{Z_2}. \quad (4')$$

$L_2$  bridges the gap to Bohr's classical result when  $\kappa$  is getting large compared to 1:

$$L_2 = \psi(1) - \text{Re} \psi\left(1 + \frac{iZ_1 e^2}{4\pi\epsilon_0 \hbar v_1}\right) = \psi(1) - \text{Re} \psi\left(1 + \frac{i\kappa}{2}\right). \quad (5)$$

The  $\psi$  function is the logarithmic derivative of the  $\Gamma$  function. An expansion of the  $\psi$  function in powers of  $i\kappa/2$  results in a leading real term proportional to  $Z_1^2$  and hence in a dependence on  $Z_1^4$ . Apparently, Eq. (5) depends only on the properties of the projectile and should therefore follow Bragg's rule. However, as both the Bethe logarithm and the Bohr logarithm need shell corrections, these have to be applied to  $L_2$  too [8,10]. However, one could follow the same reasoning as for the  $L_0$  term. In addition, the Bloch correction modifies the contribution to stopping arising from small impact parameters, as shown by Lindhard and Sørensen [11]. These close collisions should be less sensitive to changes in the binding energy of the target electron. So we can safely consider the Bloch term to follow Bragg's rule.

In the nonrelativistic regime, we can neglect any contribution to the  $Z_1^3$  term arising from Mott scattering [12]. According to Ashley, Ritchie, and Brandt [13]  $L_1$  can then be written

$$L_1 = \frac{1}{Z_2^{*1/2}} \frac{F\left(\frac{\lambda Z_2^{*1/6}}{x^{1/2}}\right)}{x^{3/2}}, \quad (6)$$

where  $x = v_1^2/Z_2^* v_0^2$  is except for a factor 4, the argument of the Bethe logarithm (with  $K_B \approx 1 \text{ Ry} = mv_0^2/2$ ). The function  $F$  is displayed in Ref. [14]. The constant  $\lambda$  is  $\approx \sqrt{2}$ . Equation (6) is based upon a classical calculation of the response of a harmonically bound electron to a swift projectile. The binding force is characterized by the frequency  $\omega_0$ . This result is generalized using the statistical model for the target atom in the Lenz-Jensen approximation [15]. The oscillator strength

density  $g(\omega)$  has been taken in the simplest approximation [16]. To learn about the dependence of  $L_1$  on  $Z_2^*$ , we rewrite Eq. (6) as

$$L_1 = \frac{Z_2^* v_0^3}{v_1^3} F\left(\frac{\lambda Z_2^* Z_2^{*-1/3} v_0}{v_1}\right). \quad (6')$$

The factors  $Z_2^*$  are due to the scaling of frequencies (as in the Bethe logarithm) and the factor  $Z_2^{*-1/3}$  is the scaling parameter of the radius; it enters the argument of  $F$  via the minimum impact parameter taken to be approximately the same size as the radius  $r$  of the shell of electron density  $4\pi r^2 n(r) dr$  associated with the local plasma frequency  $\omega_0[n(r)]$ . In Ref. [14]  $\lambda Z_2^{*1/6}$  has been combined to give the "constant"  $b \approx 1.8$ . By this the  $Z_1^3$  term is made to depend on  $x$  only [17]. There are a number of alternative approaches to the  $Z_1^3$  term [17–19], but a modified version of Eq. (6) turns out to describe measured stopping cross sections of protons and He projectiles satisfactorily [20]. The modification concerns the consideration of close collisions [21,18] either by reducing the minimum impact parameter (the optimum choice would be  $b \approx 1.36$ ) or by applying some sort of equipartition rule (taking the  $Z_1^3$  contribution twice); we have made use of the latter modification.

Now we have to know how  $Z_2^*$  changes when the compound is formed. Using the Bloch relation  $I = K_B Z_2^*$ , with

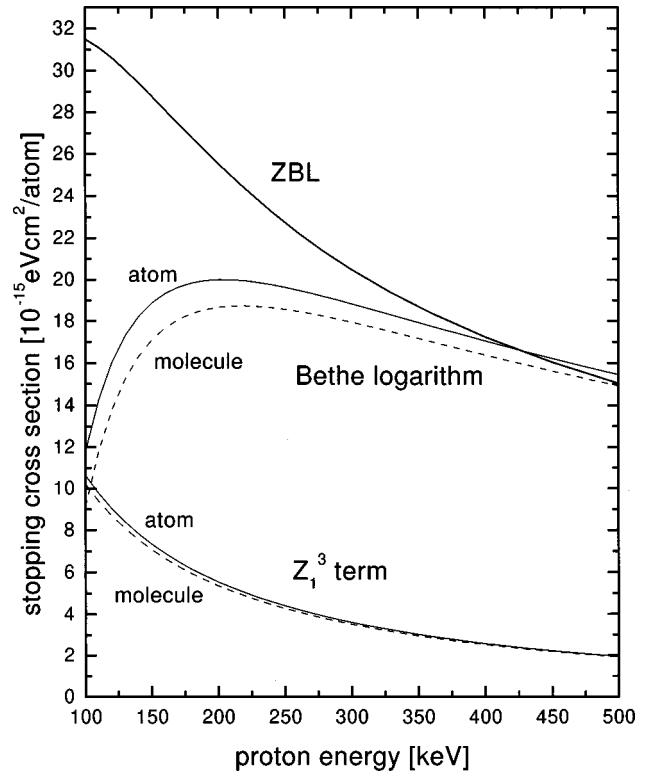


FIG. 1. Contribution of the Bethe logarithm and the  $Z_1^3$  term to the stopping cross section of atomic Cl (solid lines) and half of the  $\text{Cl}_2$  molecule (dashed lines) for swift protons as a function of the proton energy. Also shown is the total stopping cross section of half of the  $\text{Cl}_2$  molecule according to Ziegler, Biersack, and Littmark [22].

$K_B$  being a true constant within a small  $Z_2^*$  range, and writing  $Z_2^*$  instead of  $Z_2^{*(\text{atom})}$ , we can define

$$Z_2^{*(\text{comp})} = Z_2^* \frac{I^{(\text{comp})}}{I^{(\text{atom})}}. \quad (7)$$

In our model, above the stopping power maximum any deviation from Bragg's rule can be reduced to a variation of  $I$ . In Fig. 1 we show the Bethe logarithm and the  $Z_1^3$  term for both the Cl atom and half of the  $\text{Cl}_2$  molecule. For comparison, the stopping cross section per atom of  $\text{Cl}_2$  according to Ziegler, Biersack, and Littmark [22] is also displayed. The mean ionization potential of Cl (162.9 eV) has been calculated by Dehmer, Inokuti, and Saxon [23,24], whereas  $I$  for  $\text{Cl}_2$  (174 eV) is taken from Ref. [25]. At our lowest energy of 150 keV we find a maximum change of the  $Z_1^3$  term of 0.9% of the total stopping cross section (3.5% of the  $Z_1^3$  term), which is negligible in comparison to a more than 6% change of the Bethe logarithm (9.4% with respect to the logarithm). With increasing energy the  $Z_1^3$  term becomes more and more insensitive to the chemical environment. For  $x = 2$ , i.e., in the case of  $\text{Cl}_2$  for 850-keV protons, the Barkas terms for the atom and for half the molecule intersect and the  $Z_1^3$  term does not change at all when the compound is formed; for still larger energies the sign of the chemical effect is inverted. Formally, this is due to the fact that  $F(b/x^{1/2})$  as a function of  $x$  is almost proportional to  $x$ . So the ratio that describes the change of the  $Z_1^3$  term with  $Z_2^*$ ,  $F(x)/x$ , is a flat curve with a maximum at  $x = 2$ .

The basic requirement for the occurrence of a  $Z_1^3$  term is the binding force on the target electron. For that reason, binary encounter approximations [26] had to result in stopping cross sections strictly proportional to  $Z_1^2$ . There the bound state of the electron is taken into account only by the electron distribution in momentum space and by a minimum excitation energy; the energy transfer itself takes place in an encounter of free particles. The amazing result is that in spite of the importance of the bound state for the Barkas effect, the  $Z_1^3$  term seems to be rather insensitive to changes in the binding energy, at least within the local plasma approximation [27]. Only if the Barkas term would strictly follow Bragg's rule may the formulas for compound targets given by Ashley, Ritchie, and Brandt [14] for the  $Z_1^3$  term be used.

In conclusion, there are only two terms in the extended Bethe-Bloch equation that are subject to changes in the chemical state of an element: the dominating Bethe logarithm and the  $Z_1^3$  term. Within the statistical atomic model the chemical state effect on the stopping cross section above the stopping maximum is fully determined by the variation of the mean ionization potential and mainly effects the Bethe logarithm.

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- [1] W. Whaling, in *Korpuskeln und Strahlung in Materie II*, edited by S. Flüge, Handbuch der Physik Vol. XXXIV (Springer-Verlag, Berlin, 1958), p. 13.
- [2] A. Schieffermüller, R. Golser, R. Stohl, and D. Semrad, Phys. Rev. A **48**, 4467 (1993).
- [3] W. H. Bragg and R. Kleeman, Philos. Mag. **10**, 318 (1905).
- [4] J. E. E. Baglin and J. F. Ziegler, J. Appl. Phys. **45**, 1413 (1974).
- [5] R. Golser, D. Semrad, and F. Aumayr, Phys. Rev. Lett. **76**, 3104 (1996).
- [6] R. Golser and D. Semrad, Phys. Rev. A **45**, R4222 (1992).
- [7] D. I. Thwaites, Nucl. Instrum. Methods Phys. Res. B **69**, 53 (1992).
- [8] P. Sigmund, Nucl. Instrum. Methods Phys. Res. B **85**, 541 (1994).
- [9] U. Fano, *Studies in Penetration of Charged Particles in Matter*, Nuclear Science Series No. 39 (National Academy of Sciences-National Research Council, Washington, DC, 1964).
- [10] D. Semrad, Ch. Eppacher, and R. Tober, Nucl. Instrum. Methods Phys. Res. B **48**, 79 (1990).
- [11] J. Lindhard and A. H. Sørensen, Phys. Rev. A **53**, 2443 (1996).
- [12] N. F. Mott, Proc. R. Soc. London, Ser. A **124**, 425 (1929).
- [13] J. C. Ashley, R. H. Ritchie, and W. Brandt, Phys. Rev. B **5**, 2393 (1972).
- [14] J. C. Ashley, R. H. Ritchie, and W. Brandt, Phys. Rev. A **8**, 2402 (1973).
- [15] H. Jensen, Z. Phys. **77**, 722 (1932).
- [16] W. Brandt and S. Lundquist, Phys. Rev. **139**, A612 (1965).
- [17] J. D. Jackson and R. L. McCarthy, Phys. Rev. B **6**, 4131 (1972).
- [18] P. B. Eby and S. H. Morgan, Phys. Rev. A **5**, 2536 (1972); K. W. Hill and E. Merzbacher, *ibid.* **9**, 156 (1974); S. H. Morgan and C. C. Sung, *ibid.* **20**, 818 (1979).
- [19] H. H. Mikkelsen and P. Sigmund, Phys. Rev. A **40**, 101 (1989).
- [20] L. E. Porter, Phys. Rev. A **50**, 2397 (1994).
- [21] J. Lindhard, Nucl. Instrum. Methods **132**, 1 (1976).
- [22] J. F. Ziegler, J. P. Biersack, and U. Littmark, *The Stopping and Ranges of Ions in Matter* (Plenum, New York, 1985), Vol. 1. Stopping cross-section data updated in 1995 and contained in TRIM95.
- [23] J. L. Dehmer, M. Inokuti, and R. P. Saxon, Phys. Rev. A **12**, 102 (1975).
- [24] More recent calculations are provided by M. Inokuti (unpublished).
- [25] International Commission on Radiation Units and Measurements, ICRU Report No. 37 (unpublished), p. 17.
- [26] A. F. Burenkov, F. F. Komarov, and M. M. Temkin, Radiat. Eff. **46**, 99 (1980); E. Kührt, R. Wedell, D. Semrad, and P. Bauer, Phys. Status Solidi B **127**, 633 (1985).
- [27] R. E. Johnson and M. Inokuti, Comments At. Mol. Phys. **14**, 19 (1983).