



## The First Calculation to the Proton ( $H^+$ ) Absolute Hardness

Robson Fernandes de Farias

Universidade Federal do Rio Grande do Norte. Cx. Postal 1664, 59078-970, Natal-RN, Brasil

**Abstract** In the present work, for the first time, the absolute hardness for  $H^+$  is calculated. Employing empirical equations derived from five different approach, values for  $\eta^+$  ranging from 87.90eV to 103.72 eV are calculated, with a mean value of 95.23 eV. The value of 93.00 eV, obtained from the up to date experimental proton nuclear radius [18], is considered the most reliable one.

**Keywords** Proton,  $H^+$ , absolute hardness, empirical equation

### Introduction

The molecular hardness  $\eta$  and electronegativity  $\chi$  are defined from formal density functional theory [1-5]. Electronegativity is formally defined as  $(\partial E/\partial N)_V$  and hardness as  $\frac{1}{2}(\partial^2 E/\partial N^2)_V$  where E is the energy, N is the number of particles, and V is the potential due to the nuclei [6-10]. The  $\chi$  of a molecule can be defined as the average of its (first) ionization potential (IP) and its electron affinity (EA), i.e.  $\chi = (IP + EA)/2$ . By using a DFT variation for Koopmans' theorem (KT), we can obtain  $\chi = -(\epsilon_{HOMO} + \epsilon_{LUMO})/2$ .  $\eta$  for a molecule is defined as  $\eta = IP - EA$  and we can use KT to obtain  $\eta = (\epsilon_{LUMO} - \epsilon_{HOMO})/2$ .

So far the author is concerned there is not, in the literature, a calculated value for the absolute hardness for proton,  $H^+$ .

Absolute hardness ( $\eta$ , eV) is a key property/parameter able to rationalize and predict, for example, the acid-base behaviour (including the energetics) of a given chemical specie [11,12].

Taking into account the paramount presence of  $H^+$  in so many inorganic, organic and biochemical systems, to have a complete set of properties for such cation is a relevant goal.

In order to calculate the absolute hardness of a given monocation (e.g.  $Na^+$ ), we need to know/use the first and second ionization energies of the neutral atom.

Of course, hydrogen has not a second electron to be removed and so, such approach is not applicable to  $H^+$ .

In the present work, employing five different approach, the proton ( $H^+$ ) absolute hardness is calculated, for the first time.

All employed auxiliary data are summarized in Table 1.

**Table 1:** Employed auxiliary data (Refs. 13-16).

Specie/parameter	$\eta/eV^d$	$\eta^+/eV$	$\Delta_f H^0_{(g)}/eV$	$-\Delta_{hyd} H^0_{(g)}/eV$	$1^{st}IE/eV$	$2^{nd}IE/eV$	Nuclear radius/ $10^{-15} m$
H	6.43	—	—	—	13.60	—	—
$H^+$	—	—	15.92	11.34 <sup>a</sup> 11.92 <sup>b</sup>	—	—	0.8335 <sup>c</sup>
Li	2.39	—	—	—	5.39	75.64	2.39



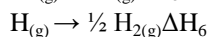
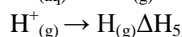
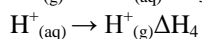
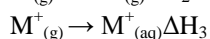
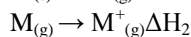
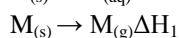
Na	2.30	–			5.14	47.29	3.55
K	1.92	–			4.34	31.63	4.24
Rb	1.85	–			4.18	27.29	5.52
Cs	1.71	–			3.89	23.16	6.38
Li <sup>+</sup>	–	35.12	7.11	5.99	–	–	–
Na <sup>+</sup>	–	21.08	6.32	4.80	–	–	–
K <sup>+</sup>	–	13.64	5.33	3.94	–	–	–
Rb <sup>+</sup>	–	11.56	5.08	3.68	–	–	–
Cs <sup>+</sup>	–	9.61	4.75	3.43	–	–	–

<sup>a</sup>This work, using tabulated data (Ref. 15); <sup>b</sup>After Jenkins (Ref. 13); <sup>c</sup>Experimental value, Ref. 18; <sup>d</sup>(Ref. 2).

## Methodology, Results and Discussion

### Approach 1. Hydration enthalpies

Hydration enthalpy ( $\Delta_{\text{hyd}}H^{\circ}$ ) values can be calculated using tabulated data and a thermochemical cycle to the reaction  $M_{(s)} + H^{+}_{(aq)} \rightarrow M^{+}_{(aq)} + \frac{1}{2} H_{2(g)}$ . The enthalpy of such reaction is the formation enthalpy of the  $M^{+}_{(aq)}$  ion.



Hence,  $\Delta H_3 = \Delta_{\text{hyd}}H^{\circ} = \Delta H_f M^{+}_{(aq)} - \Delta H_1 - \Delta H_2 - \Delta H_4 - \Delta H_5 - \Delta H_6$ . In such cycle,  $\Delta H_1 = \Delta H_f M_{(g)} - \Delta H_f M_{(s)}$ ;  $\Delta H_2$  = the first ionization energy of M;  $\Delta H_4$  = the negative of the hydration enthalpy of  $H^{+}$ ;  $\Delta H_5$  = the negative of the first ionization energy of hydrogen = -13.60 eV, and  $\Delta H_6$  is the negative of half the dissociation energy of  $H_2$  = -2.26 eV. Recently [13], was shown that the standard hydration enthalpy for  $H^{+}$  correlates very, very well ( $r = 0.9999$ ) with the hydration enthalpies for group 1 cations (from  $Li^{+}$  to  $Cs^{+}$ ).

I have found that the hydration enthalpies for group 1 cations correlate very well ( $r = 0.9962$ ) with their absolute hardness, as shown in Figure 1, providing the following equation:

$$\eta^{+} = (\Delta_{\text{hyd}}H^{\circ} - 2.550)/0.100$$

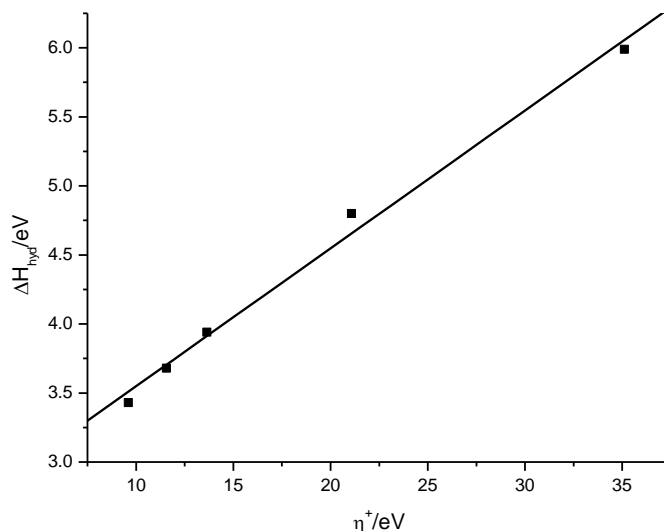


Figure 1: Hydration enthalpies as a function of absolute hardness for group 1 cations (from  $Li^{+}$  to  $Cs^{+}$ )



Hence, using the hydration enthalpy for  $H^+$  as 11.34 eV (previously, Smith [14] have used a value of 11.31 eV), obtained employing tabulated values [15], in Eq. (1), the absolute hardness for proton can be calculated as 87.90 eV. If we apply, in the same equation, a value of 11.92 eV to the  $H^+$  hydration enthalpy, after Jenkins [15],  $\eta^+ = 93.70$  eV.

#### Approach 2. Formation enthalpies

Formation enthalpies for +1 cations were taken from literature [15,16].

Using the formation enthalpies data for  $M^+$  cations (from  $Na^+$  to  $Cs^+$ ), Eq. (2) ( $r = 0.9991$ ) was obtained.

$$\eta^+ = (\Delta_f H_{(g)}^0 - 3.487) / 0.135 \quad (2)$$

Using Eq. (2), and the  $\Delta_f H_{(g)}^0$  for  $H^+$  as 15.92 eV [16] the absolute hardness for proton can be calculated as 92.09 eV. It is worth noting that the  $\eta^+$  value calculated from formation enthalpies is very close to the value calculated by using hydration enthalpies.

#### Approach 3. Absolute hardness for the neutral atom

Using the values of absolute hardness for the neutral atoms, from Li to Cs [2], the following empirical equation was derived ( $r = 0.9974$ ):

$$\eta^+ = (\eta - 1.244) / 0.050 \quad (3)$$

Using 6.43 eV as the value of the absolute hardness for H [2],  $\eta^+$  to  $H^+$  is calculated as 103.72 eV.

#### Approach 4. First ionization energy

The absolute hardness for the monocation is related with the first ionization energy for the neutral atom by the equation (from Na to Cs;  $r = 0.9979$ ):

$$\eta^+ = (IE - 2.900) / 0.106 \quad (4)$$

Using the first ionization energy for hydrogen as 13.60 eV [15], we obtain, to  $H^+$ ,  $\eta^+ = 100.94$  eV.

#### Approach 5. Nuclear radius

The nuclear radius for group 1 elements (from Li to Cs) listed in Table 1, were calculated by using the equation  $R = r_0 A^{1/3}$  [17] were  $r_0 = 1.25$  fm and  $A$  = the mass number (that is, number of protons + number of neutrons) for the considered nucleus. From Li to Cs, the most abundant isotope (e.g.  ${}^7\text{Li}$  for lithium) was taken for calculation. The  $\eta^+$  was then plotted as function of the nuclear radius, and the curve shown in Figure 2 was obtained.

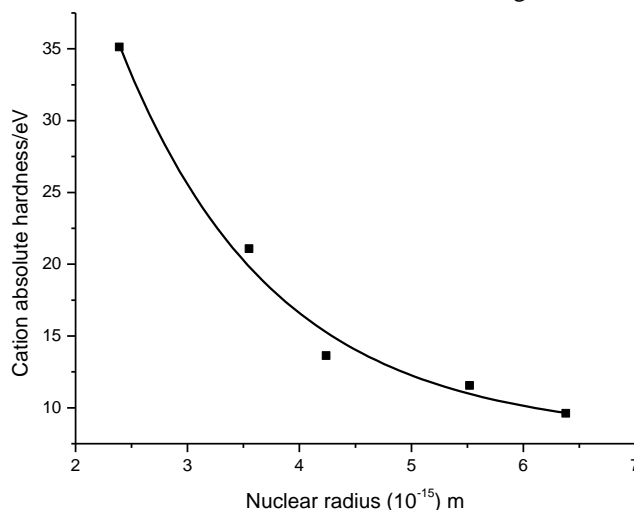


Figure 2: Absolute hardness for the cation ( $\eta^+$ ) as function of the nuclear radius, from Li to Cs.

The obtained curve provides the equation:

$$\eta^+ = -14.096 + 155.871 e^{-(R/1.352)} + 23.054 e^{-(R/206.811)} \quad (5)$$



Applying, in Eq. (5), the experimental proton radius (R) of 0.8335 fm [18],  $\eta^+ = 93.00$ . All obtained values for  $H^+$  absolute hardness are summarized in Table 2.

**Table 2:** Calculated proton ( $H^+$ ) absolute hardness, by using five different approach

Approach/method	$\eta^+/\text{eV}$
Hydration enthalpy	87.90 <sup>a</sup>
	93.70 <sup>b</sup>
Formation enthalpy	92.09
Neutral atom absolute hardness	103.72
First ionization energy for the neutral atom	100.94
Nuclear radius	93.00

<sup>a</sup>Using the  $H^+$  hydration enthalpy as 11.34 eV; <sup>b</sup>Using, after Jenkins [13], the  $H^+$  hydration enthalpy as 11.92 eV.

Is worth noting that the values calculated by using formation and hydration enthalpies agrees very well with the value obtained based on the proton nuclear radius.

The fact that Eq.(5) provides a value of  $\eta^+$  based on the most up to date experimental value for proton radius [18] and that such value in very good agreement with the values obtained by another approach, and specially with the value obtained by using up to date hydration enthalpy data [13], proves that such agreement between all values shown in Table 2 is not a simple coincidence.

Since 93.00 eV is the value calculated by using the “naked” proton radius, it is considered here the most reliable one.

#### Final considerations

The calculated  $\eta^+$  value for  $H^+$ , such as the  $\eta^+$  values for other cations can, of course, be useful from a practical point of view, allowing the calculation, for example, of hydration enthalpies [19].

However, since  $H^+$  is only a “naked” proton (no electrons, no neutrons, of course) one needs to think about the physical meaning of the calculated  $\eta^+$  value.

The absolute hardness is defined as  $\eta = (IE - EA)/2$  and by using a DFT variation for Koopmans' theorem we obtain  $\eta = (\epsilon_{\text{LUMO}} - \epsilon_{\text{HOMO}})/2$ [1-10].

In  $H^+$  the lumo orbital is the 1s orbital. What is the homo orbital? In fact, there are not electrons, at all. Because this, exactly, was necessary to found another approach to calculate the absolute hardness of  $H^+$ .

We know that, at the most probable distance from the nucleus (52.92 pm,  $a_0$ ), the electron has a potential energy of 13.6 eV. In the hydrogen atom, the energy of the quantum level can be calculated by:  $E_n = (Z^2/n^2) \cdot 13.6$ .

To obtain a  $\eta^+$  value of 93.0 eV, is necessary an energy level with an energy of 199.6 eV:  $(199.6 - 13.6)/2 = 93.0$ . Using such energy value (199.6 eV),  $n = 0.26a_0$ , where  $a_0$  is the Bohr radius.

Hence, the calculated  $\eta^+$  value is half the energy difference between  $0.26a_0$  and  $a_0$ . Hence,  $\eta^+$  is related with the probability of to find the 1s electron of a hydrogen atom closer to the nucleus.

#### References

- [1]. P. Geerlings, F. De Proft, W. Langenaeker, Chem, Rev. 103 (2003) 1793.
- [2]. R.G. Pearson, *Inorg. Chem.* 27 (1988) 734.
- [3]. R.G. Pearson, *Hard and soft acids and bases*, Dowden, Hurchison and Ross, Stroudsburg, 1973.
- [4]. R.G. Pearson, J. Am. Chem. Soc., 85(1963) 3533.
- [5]. R.G. Pearson, *Coord. Chem. Rev.*, 100 (1990) 403.
- [6]. R.G. Parr, R. G. Pearson, J. Am. Chem. Soc., 105(1983) 7512.
- [7]. Y.G. Zhang, *Inorg. Chem.*, 21(1982) 3886.
- [8]. R.G. Parr, W. Yang, *Density-functional theory of atoms and molecules*, Oxford University Press, Oxford, 1994.
- [9]. R.G. Pearson, *Hard and soft acids and bases*, J. Am. Chem. Soc., 85(1963) 3533.



- [10]. C-G. Zhan, J.A. Nichols, D.A. Dixon, *J. Phys. Chem. A*, 107(2003)4184.
- [11]. B.W. Pfennig, *Principles of inorganic chemistry*, Wiley, New Jersey, 2015.
- [12]. M.V. Putz, *Absolute and chemical electronegativity and hardness*, Nova Science Publishers, New York, 2009.
- [13]. C.E. Housecroft, H.D.B. Jenkins, *RSC Adv.*, 7 (2017)27881.
- [14]. D.W. Smith, *J. Chem. Ed.*, 54 (9) (1977) 540.
- [15]. *CRC Handbook of chemistry and physics*, 96<sup>th</sup> Ed., Taylor and Francis, Boca Raton, 2016.
- [16]. D.D. Wagman, W.H. Evans, V.B. Parker, R.H. Schumm, I. Halow, S.M. Bailey, K.L. Churney, R.L. Nuttall, The NBS tables of chemical thermodynamic properties., *J. Chem. Ref. Data*, 11 (1982) (supplement n° 2).
- [17]. K.S. Krane, (1987). *Introductory Nuclear Physics*. 3<sup>rd</sup> Ed. Wiley, New York, 1987.
- [18]. A. Beyer, L. Maisenbacher, A. Matveev, R. Pohl, K. Khabarova, A. Grinin, T. Lamour, D.C. Yost, T.W. Hänsch, N. Kolachevsky, T. Udem, *Science*, 358 (2017) 79.
- [19]. S. Kaya, R.F. de Farias, *Chem. Phys. Lett.*, 691 (2018) 169.

