COUPLING IN ONE ELECTRON TRANSFER PROCESSES [+]

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ABSTRACT — The correlation between the adiabatic splitting $\Delta V\ (R_c)$ and the crossing distance R_c for one electron transfer processes is analysed. This is based upon a selection of the experimental and computational data actually available, the test of several reduced variables and the correct asymptotic behaviour. A simple semi-empirical formula is proposed.

1 — INTRODUCTION

The calculation of the transition probability for electron transfer collisions of the type

$$A + B^{+n} \rightleftarrows A^{+} + B^{+(n-1)} \qquad (1)$$

requires the estimation of the coupling between the two states. This applies to many inelastic processes such as charge transfer, formation and recombination of ion pairs, chemi-ionization, an important part of chemical reactions, collisional excitation, quenching and dissociation. The adiabatic splitting $\Delta V(R_c)$ between the initial and final states is the fundamental parameter required to describe these interactions which involve curve

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crossings. The splitting is directly related to the coupling matrix element H_{12} through [1]

$$\Delta V(R_c) = 2 \, | H_{12} - S H_{11} | / (1 - S^2) \qquad (2)$$

where S is the overlap integral and $H_{ij} = < \phi_i^o | \hat{H}_{el} | \phi_j^o >$ are the matrix elements of the electronic Hamiltonian in the diabatic representation, ϕ_1^0 and ϕ_2^0. When $S \simeq 0$, then $\Delta V\ (R_c) \simeq 2\ H_{12}$.

Once one knows the coupling matrix element, the calculation of the cross section for the electron transfer process can be performed using the Landau-Zener formula

$$p_l = \exp(-v_{cr} / v_l) \quad \text{where} \quad v_{cr} = 2\pi H_{12}^2\ (R_c) / | F_{11} - F_{22} |_{R_c} . \qquad (3)$$

F_{ii} are the derivatives dH_{ii} / dR and v_l is the radial velocity for the angular momentum l, all the quantities being evaluated at the crossing point R_c.

Atomic units are used throughout this work.

2 — CORRELATION $\Delta V\ (R_c) - R_c$

Estimations of the splitting $\Delta V\ (R_c)$ or the term $H_{12}\ (R_c)$ have been obtained either from experimental or theoretical work.

Experimentally these splittings can be deduced from the behaviour of the total, as well as, from the differential cross section. However the initial and final states involved have to be inequivocally identified. The velocity where the maximum of the total cross section occurs is directly related to the coupling term [2]. The differential cross section is very sensitive to the transition probability and therefore also contains information on the coupling but the determination is not so straightforward.

From the analysis of spectroscopic data, using the Rydberg-Klein-Rees (R. K. R.) method, the adiabatic potential curves can be derived. These potentials in the neghbourhood of the diabatic crossing point allow one to estimate the splitting [3, 4].

Theoretically three methods have been used to obtain these parameters.

Calculations using variational methods have been mainly performed by Bates and associates in the fifties [5-9]. They studied several charge transfer and ion pair recombination processes. At large R_c distances, where the multipole interactions are dominant the calculations are incorrect [10].

The Heitler-London L. C. A. O. method has been also widely used. It predicts an asymptotic behaviour of the type $\Delta V_{LCAO} \sim \exp[-(\nu + \gamma) R_c]$ where $\nu = \sqrt{2\,I}$ and $\gamma = \sqrt{2\,EA}$, I and EA being respectively the ionization potential and the electron affinity or, in general, the higher and lower electron binding energy of the collision partners. At large crossing distances this method becomes also incorrect since the perturbation is as important as the zero order interaction [1].

In the Landau-Herring method, the exchange interaction $\Delta = 2\,|H_{12} - SH_{11}|$ is expressed as a surface integral of the transient particle flux in the configuration space of electronic coordinates. Several calculations have been performed using this asymptotic method [10-12]. They differ in the choice of the integration conditions and characteristics of the collisional systems. This method provides the means of obtaining the asymptotic behaviour [10] of the correlation $\Delta V - R_c$ which turned out to be $\Delta V_{LH} \sim \exp(-\nu R_c)$.

The first correlation $H_{12} - R_c$ was presented by Hasted and Chong [13]. Table I shows several theoretical and semi-empirical relations which, since then, have been forwarded. Of these, the formula of Olson, Smith and Bauer (O. S. B.) [16] is the one which has been the most extensively used although it does not have the correct asymptotic behaviour. The expression was obtained from a fit with almost one hundred theoretical and experimental points available in the literature up to 1971.

The relation proposed by Hubers, Klein and Los (H. K. L.) [17] is a generalization of O. S. B. but it has been derived from experimental fits only for alkali atom-halogen molecules. It has more adjustable parameters than the O. S. B. expression, however the exponential dependence only on νR_c resulted from the best fit.

Actually the data available for electron transfer, both in atom-atom and atom-molecule, rose to more than two hundred points. Most of them are theoretically estimated. Those experimentally derived are about one fifth of the total and are confined to high ΔV i.e. large coupling and small crossing distances. The collision processes analysed are listed in Table II and plotted in

Fig. 1. The adiabatic splitting ranges for about 10 orders of magnitude when R_c ranges only less than two orders. From the theoretical data available were excluded those splittings extrapolated from formulas although some of them were taken in the

TABLE I — Proposed relations for the H_{12} or ΔV dependence on R_c (atomic units) $\nu = \sqrt{2\,I}$ $\gamma = \sqrt{2EA}$

$$H_{12} = R_c\,(\nu^2/2)\,\exp\,(-\,\nu R_c/\sqrt{2}) \qquad (\text{for } H^+ + H)$$

RAPP and FRANCIS [14]

$$H_{12} = A\left[\frac{\gamma\,\nu^2}{2}\left(\frac{4}{e}\right)^{1/\gamma}\frac{\nu^{2/\nu}\,(2\,l+1)}{\Gamma\,[\,(1/\nu)+l+1\,]\;\Gamma\,[\,(1/\nu)-l\,]}\right]^{1/2}$$

$$\cdot\; R_c^{\,1/\nu\,-\,1}\,\exp\,[\,-\,(\nu+\gamma)\,R_c/2\,]$$

SMIRNOV [12]

(A is a constant and l is the orbital angular momentum)

$$H_{12} = \frac{\nu}{\Gamma\,(1/\nu)}\,(2\,\nu)^{1/\nu\,+\,1/2}\;R_c^{\,1/\nu\,-\,1}\,\exp\,(-\,\nu R_c)$$

KOMAROV [11]

$$H_{12} = \gamma^2\,[\,8.0\,\exp\,(-\,0.91\,\gamma R_c) - 7.5\,\exp\,(-\,0.99\,\gamma R_c)\,]$$

OLSON, PETERSON and MOSELEY [15]

$$H^*_{12} = 1.0\;R^*_c\,\exp\,(-\,0.86\;R^*_c)\;,\quad H^*_{12} = H_{12}/\nu\gamma\;,\quad R^*_c = (\nu+\gamma)\,R_c/2$$

OLSON, SMITH and BAEUR [16]

$$\Delta V = \exp\,[\,(R^{o}_c - R_c)/\Delta R\,] \quad (R_c\,,\ \Delta R \text{ are parameters})$$

GRICE and HERSCHBACH [3]

$$H^{**}_{12} = 1.73\;R^{**}_c\,\exp\,(-\,0.875\;R^{**}_c)\;,\quad H^{**}_{12} = 2\,H_{12}/\nu\gamma\;,\quad R^{**}_c = \nu R_c$$

HUBERS, KLEYN and LOS [17]

TABLE II — One electron transfer processes analysed

n	$A + B^{+n} \rightleftarrows A^{+} + B^{+(n-1)}$	References
0	$M\ (n, 1) + H\ (1s) \rightleftarrows M^{+} + H^{-}$	M = H [4, 7, 10] Li [4, 8, 10] Na [4, 8, 10, 18] K [4, 8, 10, 18] Rb [4, 10] Cs [4, 10]
0	$M + X \rightleftarrows M^{+} + X^{-}$	M = Li [3, 10, 19a, 20, 21, 22] Na [3, 10, 19b, 20, 23] K [3, 10, 19c, 23, 24] Rb [3, 10, 19d, 23] Cs [3, 10, 19e, 23] X = H [3, 10, 21, 22] O [10, 23] F [3, 19a-c] Cl [3, 19a-c] Br [3, 19a-d] I [3, 19, 20, 24]
0	$M + X_2 \rightleftarrows M^{+} + (X_2)^{-}$	M = Li [3] Na [3, 17] K [3, 17, 25] Rb [3] Cs [3, 17, 25] X = Cl [3, 17] Br [3, 17] I [3, 17] O [25]
0	$M + XY \rightleftarrows M^{+} + (XY)^{-}$	M = Na [17] K [17] XY = ICl [17] IBr [17]
2	$A + B^{2+} \rightleftarrows A^{+} + B^{+}$	A = H [5, 6] He [26] Ne [13, 26] B = Li [6] Be [5] B [6] N [26] Mg [5] Al [6] Si [5] Ar [26] Kr [13]
3	$A + B^{3+} \rightleftarrows A^{+} + B^{2+}$	A = H [6] He [9, 13] Ne [13, 26, 27] B = Li [9] Be [9] Mg [9] Al [6, 9] Kr [13] Xe [27]
4	$A + B^{4+} \rightleftarrows A^{+} + B^{3+}$	A = He [13] Ne [13, 27, 28] B = Kr [13, 28] Xe [27]

work of Olson et al. Although an exponential decrease is in general observed, one notes a divergence with increasing R_c that depends mainly on the electron affinity. This divergence is not clear in the experimental data plot and therefore it is probably related to the method of calculation (Fig. 1).

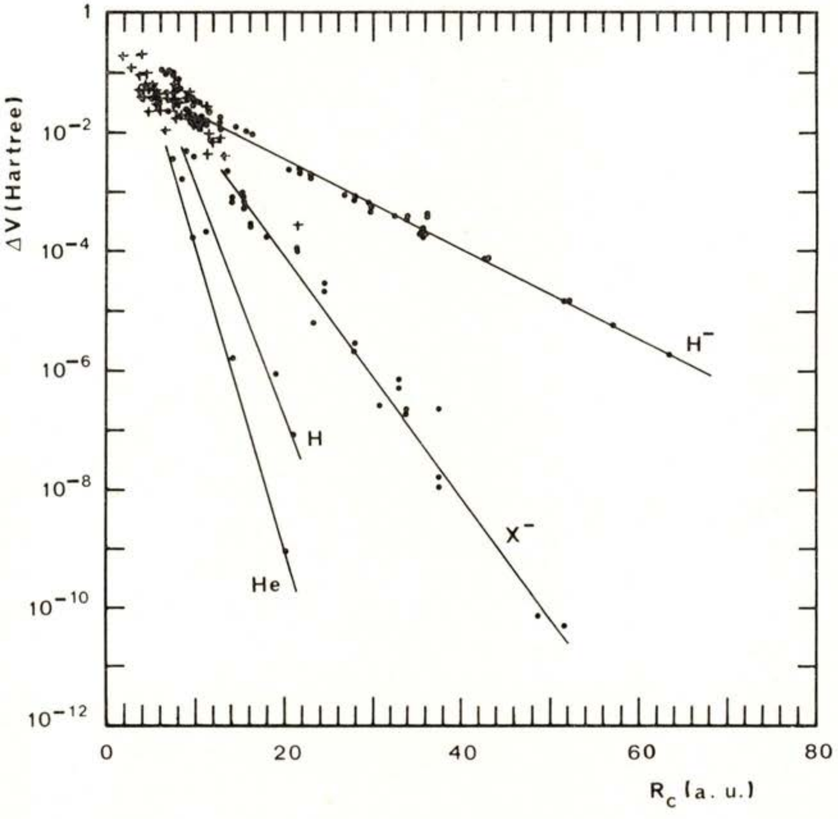

Fig. 1 — Experimental (+) and theoretical (•) splittings, ΔV, as function of the crossing distance R_c.

In order to get a simple relationship, several reduced variables (X, Y) have been tested. This was done assuming always an exponential relation

$$Y = a \exp(-b X) \tag{4}$$

TABLE III — Correlation $\Delta V - R_c$ with reduced variables

$Y = a \exp(-bX)$ σ – standard deviation (atomic units)

Pair (X, Y)	X	Y	Set 1			Set 2			Set 3			Obs.
			a	b	σ	a	b	σ	a	b	σ	
I	νR_c	$\Delta V/\nu$	5.95	0.86	0.521	0.69	0.52	0.366	0.14	0.26	0.308	
II	νR_c	$\Delta V/\nu^2$	9.16	0.85	0.509	1.48	0.59	0.345	0.25	0.32	0.265	Simple expression
III	νR_c	$\Delta V/\nu X$	1.54	0.94	0.479	0.25	0.64	0.363	0.054	0.39	0.311	
IV	νR_c	$\Delta V/\nu^2 X$	2.37	0.93	0.463	0.54	0.71	0.341	0.093	0.45	0.271	
V	νR_c	$\Delta V/(\nu^2 R_c^{1/\nu-1})$	2.26	0.96	0.981	0.18	0.45	0.563	0.045	0.17	0.510	Komarov type
VI	νR_c	$\Delta V/\gamma$	12.0	0.89	0.492	1.93	0.60	0.369	0.34	0.32	0.315	
VII	νR_c	$\Delta V/\gamma^2$	37.3	0.91	0.504	11.7	0.75	0.425	1.36	0.45	0.400	
VIII	νR_c	$\Delta V/\gamma X$	3.10	0.97	0.458	0.70	0.72	0.370	0.13	0.45	0.321	
IX	νR_c	$\Delta V/\nu^2 X$	9.64	0.99	0.478	4.22	0.87	0.428	0.51	0.58	0.409	
X	νR_c	$\Delta V/\nu \gamma$	18.5	0.88	0.497	4.16	0.67	0.375	0.58	0.39	0.322	
XI	νR_c	$\Delta V/\nu \gamma X$	4.77	0.96	0.460	1.50	0.79	0.375	0.22	0.52	0.330	H. K. L. revised
XII	γR_c	$\Delta V/\gamma^2$	4.18	0.89	0.433	1.71	0.67	0.336	0.59	0.45	0.316	
XIII	$\frac{\nu + \gamma}{2} R_c$	$\Delta V/\nu \gamma$	6.43	0.87	0.458	1.70	0.64	0.337	0.41	0.39	0.290	
XIV	$\frac{\nu + \gamma}{2} R_c$	$\Delta V/\nu \gamma X$	2.00	0.96	0.412	0.76	0.78	0.342	0.18	0.54	0.311	O. S. B. revised

Set 1 — Computational and experimentally derived data;
Set 2 — Partial set (see text); Set 3 — Experimental derived data.

the constants being derived by least square fits (Table III). The standard deviations, σ, were used to compare the different fits. The exponential dependence of ΔV upon R_c is suggested by the exponential tails of the orbitals.

Although the experimental points (set 3) are not numerous and are confined to splittings larger than 10^{-4} Hartree and R_c smaller than 20 a.u., they show a general exponential decrease expressed by

$$\Delta V = 0.21 \ \exp \ (-0.29 \ R_c) \tag{5}$$

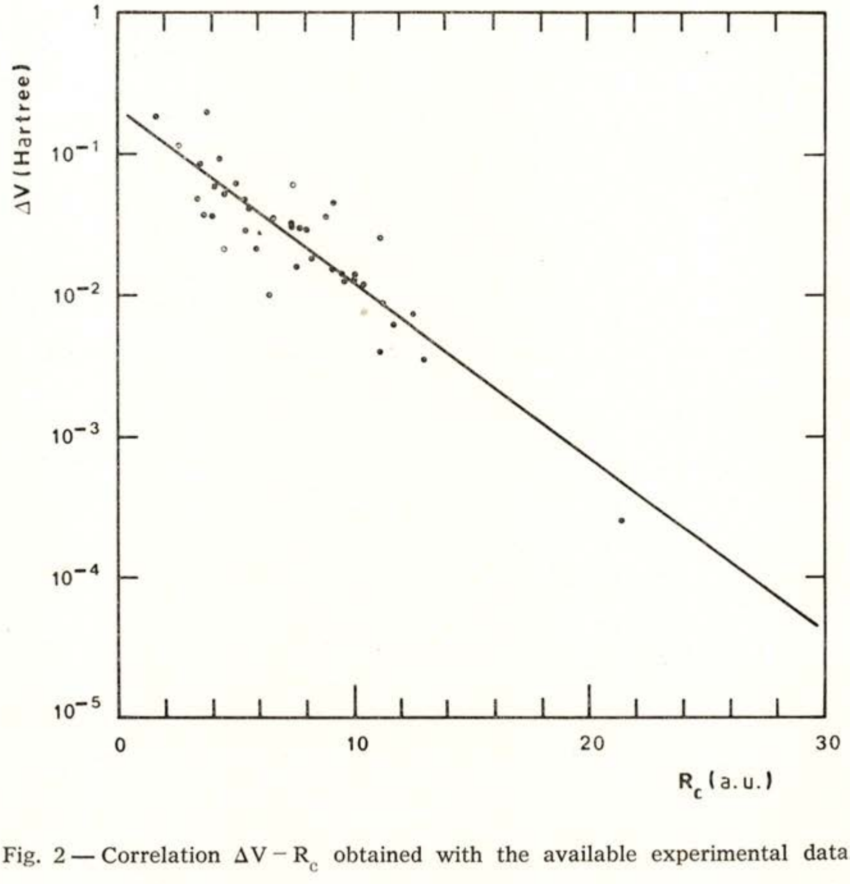

Fig. 2 — Correlation $\Delta V - R_c$ obtained with the available experimental data.

The fit (Fig. 2) has a standard deviation of 0.222. It is smaller than the other ones obtained with reduced variables for the set of experimental derived data. Almost all the points lie within a factor of three to the average line.

Most of our effort was focused on relations with the correct asymptotic behaviour because, to our knowledge, general fits of this type have not yet been obtained. Also with that in mind a selection of theoretical data has been tried. In fact, at very large distances either the L. C. A. O. or the old variational data seem to be incorrect. Therefore, fits have been obtained with a partial set of experimental and theoretical data (set 2) which excluded those points computed by the referred methods and corresponding to crossings larger than 8 Å. This limit was arbitrarily chosen but it is reasonable since at larger distances the relative errors increase [1].

The so much used O. S. B. relation has been also revised, although it misrepresents the asymptotic behaviour as was already referred. Indeed it is interesting to include all the data, which doubled after that work. One can see that, both the total set and the partial one give clearly good fits but the exponential constant has to be somewhat changed. With the total set the expression is now

$$\frac{\Delta V}{\nu \gamma X} = 2.0 \exp(-0.96\, X) \text{ with } X = \frac{\nu + \gamma}{2} R_c \tag{6}$$

and is represented in Fig. 3. About 90 % of the data lie within a factor of three, as in the early fit.

Fits with small deviation were obtained with ($X = \gamma R_c$, $Y = \Delta V / \nu^2 X$) or ($X = \gamma R_c$, $Y = \Delta V / \nu \gamma$) but they have the drawback of a wrong asymptotic behaviour.

The H. K. L. relation [17] has been derived only for the systems $M + X_2$ and $M + XY$ (13 points) and gives an excellent fit. Moreover it has the advantage of having the correct behaviour at large R_c. However, when tested with the complete and partial sets of data, the constants have to be changed and the deviations become larger.

For the selected set of data. the other fits with $X = \nu R_c$ show deviations almost of the same order (except for the Komarov type expression) being slightly smaller for the reduced variables $Y_{IV} = \Delta V / \nu^2 X$ and $Y_{II} = \Delta V / \nu^2$. These pairs of reduced variables have also the advantage of avoiding the use of electron affinity which is of particular importance for molecular systems with near zero or negative electron affinity. The second pair has

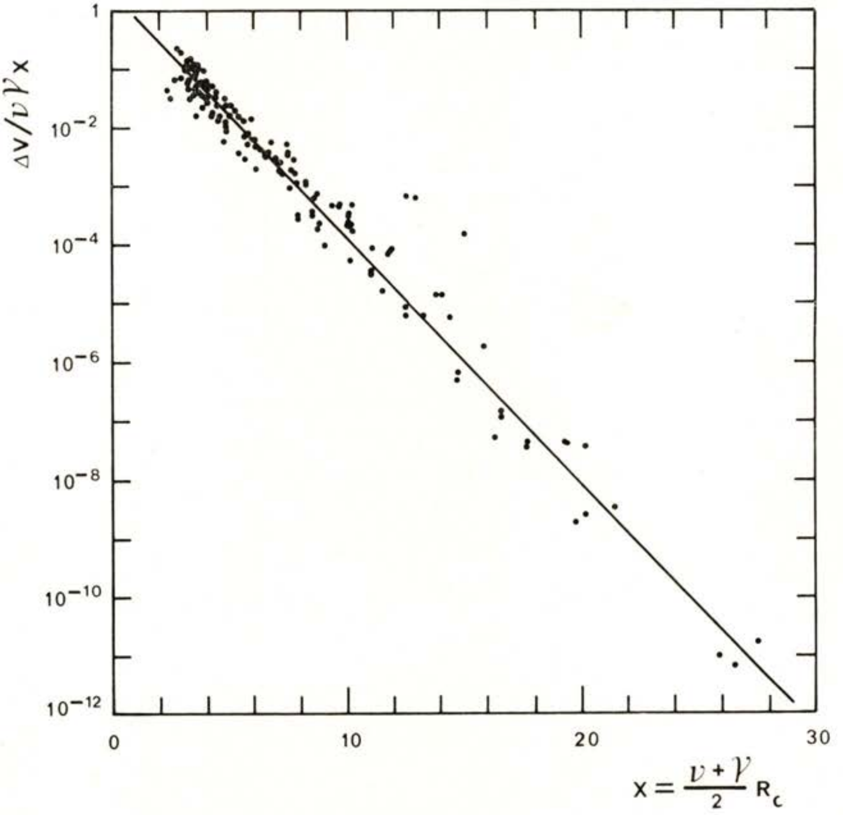

Fig. 3 — Fit with Olson, Smith and Bauer (O. S. B.) reduced variables, using the total set of data.

the advantage of being quite simple and also has a small deviation when tested with the experimental set. With the partial set of data it corresponds to the relation

$$\Delta V = 1.48\, \nu^2 \exp(-0.59\, \nu R_c) \qquad (7)$$

The simple relation (7) is shown in Fig. 4 together with the selected set of data. One notes that it is a reasonable one and, like the O. S. B. expression, most of the data are within a factor of three.

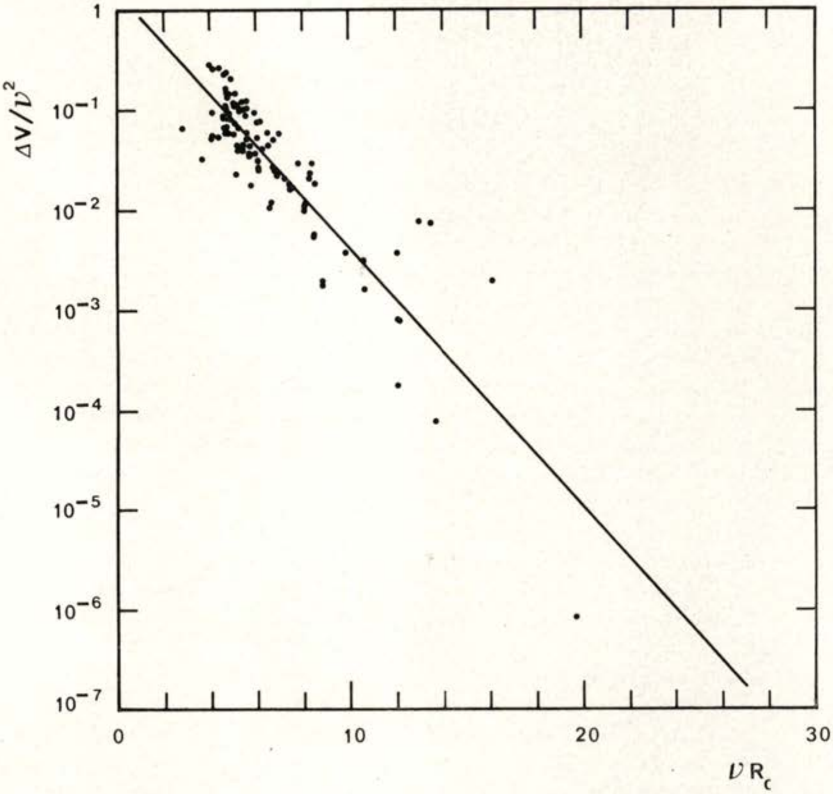

Fig. 4 — Plot with the reduced variables (νR_c , $\Delta V/\nu^2$) for the selected set of data.

3 — CONCLUDING REMARKS

Exponential relations involving reduced variables are particularly suitable to represent the correlations $\Delta V - R_c$. The experimental derived data show a general exponential decay which is acceptable within errors. From several variables tested, one concludes that, within the errors, they do not differ so much. From those with the correct asymptotic behaviour the set $(\nu R_c, \Delta V / \nu^2)$ is favoured because it is the simplest.

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