Physics of positronium acceptor complex formation reactions

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Abstract Positronium (Ps) reaction rates (κ) with weak Acceptors (Ac) leading to the formation of Ps-Ac complexes show several interesting features non-monotonic temperature dependence of κ (departing from the usual Arrhenius behaviour), considerable variability of κ with respect to different solvents, and anomalies in response to external pressure at ambient temperature. The object of this work is to explain all these phenomena using a remarkably simple bubble model (the widely used model for the pick-off component of ortho-positronium decay in liquids), which has been revisited several times in the context and as a result smooth diffuse boundary of the bubble was suggested that yields reasonable agreement of the experimental data. The contractile force on the bubble relies much on the surface tension of the liquid, through our calculation the notion of critical surface tension emerges and enables us to explain the experimental observations satisfactorily.

Introduction

The positronium (Ps) atom, as the lightest isotope (so to say) of hydrogen, provides a simple archetype of a free radical, which moreover through its decay reveals (self analytically as it were) its state in the medium including its involvement in chemical transformations Setting aside, for the present purpose, spin-dependent interactions with paramagnetic molecules (which induce ortho-para conversion, thereby shortening the lifetime of the long-lived component and changing the shape of the two gamma angular correlation curve), we concentrate here on Ps in relationship to diamagnetic acceptors (generically denoted henceforth as Ac). In general Ps reactions with diamagnetic organic compounds follow a donor-acceptor interaction scheme with Ac possessing some low lying molecular orbital. Formation of a complex (Ps-Ac) under appropriate conditions, would lead subsequently to either electron transfer from Ps to Ac (if energetically possible, viz., when Ac is a very

strong electron acceptor) giving rise to an Ac⁻ ion and a positron which annihilates with environmental molecules, or in the event that this is not energetically allowed, positron annihilation could occur from the complex itself [1]. For this latter situation, which shall be our present concern, the process should proceed according to the scheme

$$Ps + Ac \rightleftharpoons (Ps - Ac) \rightarrow Ac + 2\gamma, \qquad (1)$$

the first step being governed by the forward and backward rate constants k_f and k_b, while the two gamma (2γ) decay from the complex occurs at the rate λ_c.

With acceptor Ac in a solvent (S) present with a concentration [Ac], the changed ortho-positronium (o-Ps) pick-off rate can be expressed as

$$\lambda_p = \lambda_p^{(0)} + \kappa[Ac], \qquad (2)$$

where $\lambda_p^{(0)}$ is the pick-off rate in the pure solvent. Pick-off is the process whereby the positron in o-Ps annihilates, with

an electron of opposite spin in the surroundings, into two gammas. k is the over all second order quenching rate constant relevant for the study of complex formation. The increase in the 'pick-off' decay rate with increasing acceptor concentration may be ascribed to the proximity of o-Ps with electrons in Ac, concommitant with the formation of the complex. The quenching rate constant (κ) is experimentally determined by plotting the observed rate λ_p against the acceptor concentration [Ac] and determining the slope. This is a measure of the strength of chemical quenching for Ps within the molecule. Following through reaction scheme (1) it is readily seen that the desired quenching rate constant is given by

$$\kappa = \frac{k_b}{k_b + \lambda_c}\, \lambda_c. \qquad (3)$$

In the circumstance that $k_b \gg \lambda_c \sim 2.5$ ns^{-1} we have [2] $\kappa \sim \left(\frac{k_f}{k_b}\right)\lambda_c$; note that under such conditions the first factor (in parentheses) is the equilibrium rate constant for Ps complex formation.

The observed rate constant (κ) for a given Acceptor depends on the solvent and for a given solvent varies in a rather remarkable manner with temperature (T), namely :

• κ increases with T at low temperatures,

• κ reaches a maximum at $T = T_0$ (the turnover temperature),

• κ decreases with increasing T above T_0.

This is shown in Figure 1 for the case of the weak Acceptor nitrobenzene in different solvents.

This unsual phenomenon [5], first observed by Goldanskii and his group [6] at Moscow, and subsequently by Hall, Madia and Ache [7], is in sharp contrast with the non trend in activated chemical processes where lnκ versus $1/T$ (the inverse temperature) yields a straight line with negative slope, as the rate is proportional to the Maxwell-Boltzmann probability factor exp$(-E^*/k_BT)$ where k_B is Boltzmann constant and E^* is the activation energy or barrier height to be overcome by thermal agitation. Possible prefactors are generally taken to be relatively mildly dependent on temperature.

One interesting thing one should notice is that the turnover temperature (T_0) varies, for a given acceptor, substantially for different solvent (Table 1). This indicates the role of the solvent on the reaction dynamcis of Ps-Ac complex formation.

Table 1. Turnover temperatures (T_0) in K for Ps-nitrobenzene reaction in different solvents.

Solvent	T_0	Solvent	T_0
n-Hexane	220	n-Heptane	256
Benzene	306	Toluene	310
Octanol	340	Water	318

Another dramatic observation [8,9] pertains to the variation of the rate constant for Ps-Ac complex formation with external pressure at ambient temperature, which again shows surprisingly strong solvent dependence. Thus, for instance, with nitrobenzene as the Acceptor and hexane as the solvent the rate constant κ was found to be enhanced by a factor of almost thirty as the pressure was increased to ~1000 kg/cm², while with benzene as the solvent the same rate manifested only small variation over the same pressure range. This feature is depicted in Figure 2.
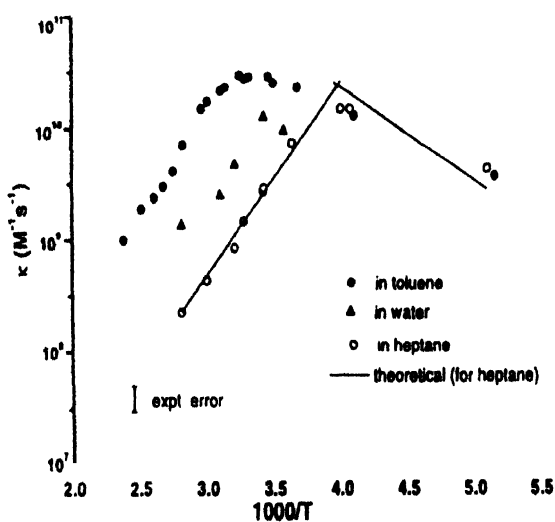

Figure 1. Observed temperature dependence of rate constants for Ps reaction with nitrobenzene in different solvents. (Taken from [3,4]) The lines correspond to slopes in the enthalpy dominated and diffusion controlled regimes as predicted by our model.
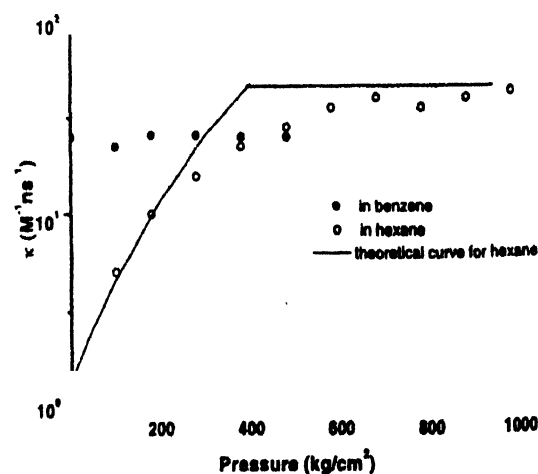

Figure 2. Observed dependence on external pressure for Ps reaction with nitrobenzene in hexane and in benzene [8]. The predicted dependence in the case of hexane is shown by the solid line.

Kobayashi [8,9] conjectured that this could indicate a in reaction mechanism in cases which do and ; which do not show marked pressure dependence, and correlation could be sought with the corresponding olvent dependence of the turnover temperature. The objective of this paper is to put forward a heuristic model captures the essence of all these puzzling aspects of sitronium reactions outlined above, through a rather simple nd reasonably accurate semi-quantitative description. The widely used bubble model, the bubble shrinkage model and the notion of critical surface tension for Ps-annihilation in liquids provides a suitable setting for the purpose at hand.

Models

The bubble model :

The bubble model was proposed by Ferrell [10] to account for the observed increase in the lifetime of o-Ps for the pick-off [11] process in liquid helium. This is a process whereby the positron in o-Ps senses electrons with opposite spin in surrounding atoms and annihilates through the two photon mode The underlying physical mechanism for the formation r the bubble around the positronium was conceived to be rough the repulsive interaction due to electron exchange etween o-Ps and atoms of the surrounding liquid leading) self-trapping. In the initial version of the model, for the ake of simplicity, the self-trapping potential confining the positronium in the bubble was taken to be an infinitely repulsive spherical well of radius say R. The resultant quantal zero point energy of the positronium of mass $2m$ (m being the electron mass) is accordingly given by $E = \dfrac{\pi^2 \hbar^2}{4mR^2}$,

which in turn exerts a pressure $-\dfrac{\partial E}{\partial R}$, to be balanced by forces of compression introduced through the rather ude notion of surface tension (σ) of the fluid. Thus the tal energy $E_{tot} = E + 4\pi r^2 \sigma$ (the second term representing the contractile surface energy) is minimised. We shall refer to this relation viz. $\dfrac{\partial E_u}{\partial R} = 0$ as the balance condition. herefore, given the surface tension of the liquid, the balance condition enables one to determine the radius R of the ubble which is thus given by $R = \left(\dfrac{\pi\hbar^2}{16m\sigma}\right)^{1/4}$. The wave-function ψ_{p_s} of the positronium inside the cavity is given by $\dfrac{1}{\sqrt{2\pi R r}}\sin\left(\dfrac{\pi r}{R}\right)$, r being the radial distance of the centre of mass of Ps from the centre of the bubble. Ferrell went on) assume that inside the bubble helium was present as a turated vapour providing the electrons for pick-off annihilation.

A variant of this scheme was put forward by Tao [12] d also by Eldrup [13] employing again the infinite spherical

well, but describing the pick-off electrons as forming a layer of thickness ΔR uniformly coating the inner surface of the bubble. These authors next assumed that the annihilation rate of o-Ps inside the electron layer is 2 ns^{-1} (the suggested mechanism being the formation of Ps or negative positronium ion inside the layer and the consequent annihilation rate when spin averaged yields 2 ns^{-1} and accordingly the pick-off rate is then obtained to be

$$\lambda_p = 2\left[\frac{\Delta R}{R} - \frac{1}{2\pi}\sin\left(2\pi\frac{\Delta R}{R}\right)\right]ns \qquad (4)$$

where the expression in braces is simply the probability for the Ps-atom to be inside the electron layer, to wit, $\int_{R-\Delta R}^{R}|\psi_{Ps}(r)|^2 d^3r$. This model has gained considerable popularity, not so much for the soundness of the underlying ideas, but rather because of the simplicity of the final expressions. Indeed algebraic relationships for lifetime and angular correlation have been found to roughly fit the general trend of mainly the lifetime data.

Roelling [14] improved upon Ferrells model (henceforth we shall call it **model I**) by emphasising that the notion of an infinitely repulsive trapping potential was physically most unsatisfactory, and that it would be far more reasonable to posit a well of finite height in its place and to ascribe the pick-off annihilation of the positron in the positronium to its quantum mechanical leakage outside the bubble and into the surrounding liquid. The Schrödinger equation is readily solved to obtain the wavefunction for the ground state centre-of-mass motion of the positronium in a spherical well of height U_0 and range R, which is of the form $\dfrac{\sin kr}{r}$ and $\dfrac{\exp(-\kappa r)}{r}$ inside and outside the well respectively. Here $k = \sqrt{\dfrac{4mE}{\hbar^2}}$ and $\kappa = \sqrt{\dfrac{4m(U_0 - E)}{\hbar^2}}$ E being the energy eigenvalue determined by the matching condition $\kappa = -k\cot(kR)$ for the wavefunction at the well boundary. This equation has to be solved numerically. The balance condition

$$\frac{\partial}{\partial R}(E + 4\pi R^2 \sigma) = 0, \qquad (5)$$

provides, given the surface tension σ of the liquid, a relationship between U_0 and R. Thus but for one independent parameter the model stands determined. Therefore, with two pieces of experimental information (lifetime and angular correlation data) the model can be tested.

Since pick-off annihilation involves the positron in the positronium and the electrons in the surrounding medium, the rate for the process is governed by the product of the

probability for finding the positronium in the liquid and the density of available electrons in the surrounding liquid. This factor is given by the overlap integral

$$p = 4\pi \int_R^\infty \left| \psi_{ps}(r) \right|^2 r^2 dr, \tag{6}$$

the integration being over the region containing the liquid (*viz.* outside the bubble). The pick-off rate is thus obtained to be

$$l_{pick-off} \equiv \lambda_p = 4\pi r_0^2 c \rho_0 Z_{eff} P, \tag{7}$$

where $r_0 = \dfrac{e^2}{mc^2}$ is the classical electron radius, c is the velocity of light, ρ_0 is the number density of molecules in the liquid, Z_{eff} is the effective number of electrons available per molecule for pick-off annihilation by the positron in o-Ps.

Apart from the influence of the bubble on the annihilation rate (and hence the lifetime $\tau_p = 1/\lambda_p$), the bodily motion of the positronium confined to move in the bubble implies, by virtue of momentum conservation, a nontrivial angular correlation (*viz.* not back to back) for the two photons emitted through the annihilation of para-positronium (p-Ps) in the bubble. In order to determine the angular correlation curve $N(\theta)$ and the experimentally quoted quantity $\theta_{1/2}$ [which is the full width at half maximum (fwhm), given by, $N(\frac{1}{2}\theta_{1/2}) = \frac{1}{2}N(0)$], all one needs is the momentum distribution of the positronium inside the bubble, which given by the square modulus of the Fourier transform of the wave-function, namely

$$P(p) = 4\pi p^2 \left| \overline{\psi}_{ps}(p) \right|^2, \tag{8a}$$

with $\overline{\psi}_{ps}(p) = \left(\dfrac{1}{2\pi\hbar}\right)^{\frac{3}{2}} \int \psi_{ps}(r) \exp\left(-i\dfrac{p \cdot r}{\hbar}\right) d^3r, \tag{8b}$

and the angular distribution curve is given by

$$N(\theta) = \int_{p=mc\theta}^\infty \dfrac{1}{p'} P(p') dp', \tag{8c}$$

from which $\theta_{1/2}$ is readily calculated.

Having thus set forth the basics of the model, we go on in the next section to point out its inadequacies through a critical analysis. This is followed by a proposed modification of the model.

2.2. *Inadequacy of the sharp boundary bubble model :*

Using the formalism presented above there have been [15,16,17] extensive calculations using the finite well potential for a variety of liquids and comparison made with experimental data.

While there is reasonable agreement, at first sight, between the model and observations, nevertheless, as was pointed out [18,19] by the present authors, there exists a systematic discrepancy, in that if one determines the parameters of the model (namely R and U_0) using the balance condition [eq. (2)] and a fit to the lifetime data, and if one uses these values to calculate the fwhm $\theta_{1/2}$ of the angular correlation of the decay gammas, then $\theta_{1/2}$ is systematically underestimated as compared to experiment. Even though these deviations are at most of the order of 20%, their signs are the same in all the cases as can be seen from Table 2. The experimental data on positronium annihilation, as well as values of surface tension, density and Z_{eff} have been taken from the compilation by Jean and Nakanishi [17].

Table 2. Bubble Model parameters for different potentials

Liquid	R (Å)	E (eV)	U_0 (eV)	$\delta\theta_{1/2}$ %
Model I $\Theta(r - R)$				
n-Pentane	4.85	0.424	0.747	--17%
n-Hexane	4.66	0.456	0.790	15%
n-Heptane	4.55	0.480	0.838	15%
n-Decane	4.33	0.523	0.894	17%
Iso-octane	4.66	0.464	0.835	18%
Benzene	4.11	0.575	0.962	17%
Water	3.13	0.922	1.36	14%
Model II $\tanh^2(r/R)$				
n-Pentane	6.22	1.048	3.082	12%
n-Hexane	5.93	1.109	3.164	14%
n-Heptane	5.81	1.176	3.398	14%
n-Decane	5.50	1.256	3.506	11%
Iso-octane	6.02	1.169	3.563	11%
Benzene	5.17	1.352	3.630	11%
Water	3.75	1.911	4.118	6%
Model III $[1 - \exp(-r/R)]$				
n-Pentane	5.29	1.22	2.23	0.3%
n-Hexane	5.10	1.32	2.39	3.0%
n-Heptane	4.97	1.38	2.52	3.0%
n-Decane	4.76	1.51	2.74	0.9%
Iso-octane	5.06	1.34	2.44	-2.0%
Benzene	4.53	1.66	3.00	2.0%
Water	3.55	2.66	4.68	4.5%

To further expose the problems involving the bubble model with sharp boundaries another strategy is found to be very revealing. The model parameters are determined on the one hand by fitting the lifetime data and on the other

by fitting the angular correlation and then a comparison of the two sets is made. The result shows (not shown here, for details see [20]) that the depth of the potential U_0 obtained by using the former protocal can be as much as a factor of two smaller than that arrived at through the latter methodology, while the range parameter (R) could be 10 to 15% smaller. This inability to provide a consistent set of parameters to fit the two measurements clearly underlines the need to modify the model, more convincingly than the indications referred to in the previous paragraph. An insensitivity is discernable from the results in the energy value (E) of the positronium in the cavity as determined from the two methods of fitting, which while giving potentials with widely differing depths (U_0), yield nevertheless similar values for the energy E. This is because of the fact that as R increases the kinetic energy (due to the zero point motion dictated by the uncertainty principle) decreases. Correspondingly one sees that the potential energy in the latter case is greater. Thus the total energy in the two situations is very close to each other.

A further indication of the inadequacy of the bubble model with sharp boundaries is revealed when one examines the data pertaining to pick-off annihilation in ordinary water H_2O and heavy water (D_2O). The best fits to the angular correlation data in the two cases are given by potential depths (U_0) which differ from each other by about 20% [20]. This, however, should not be the case as the depth of the potential is essentially provided by the exchange interaction between the electron in the positronium and the electrons in the surrounding molecules of the liquid. But the wavefunctions of electrons in the molecules of H_2O and D_2O must be essentially identical. Therefore, one expects that the values of U_0 in the two cases must be almost the same or close (within experimental errors). Thus when looked upon critically the bubble model with sharp boundaries appears to be sorely in need of modification.

3 Revised bubble model :

Despite the popularity of the bubble model, however, the picture of a sharp boundary is at variance with the general notion of liquid-vapour interfaces, and even more so in the context of such microscopic dimensions. Indeed remarks to that effect may be found in the literature [14] : "the agreement between the calculated values and the experimental data is surprising, for the bubble may not possess a definite radius, and there may very well be a transition region between the cavity which has...a density of zero and the bulk density of the liquid". To quote from a paper written by Tao [12] : "Which type of more complicated potential well is the best or better one in the calculation of the pick-off rate of o-Ps

in liquids"? It is, therefore, rather strange that despite the recognition of this important aspect of the problem there has been no attempt, so far as we are aware, except for a recent attempt by the present authors [18,19], to go beyond this patently unphysical concept of a sharp boundary.

Taking cognizance of the fact that the density profile of the molecules of the liquid around the Ps atom should be one changing gradually from zero at the center of the positronium, and should with increasing distance tend to density (ρ_0) of the bulk fluid, we shall choose functional forms that admit analytical solutions, so as to avoid cumbersome numerical work where the underlying physics may be lost. The density profile will contain a parameter R characterizing the "size" of the cavity. Futhermore, since the repulsive exchange interaction between the Ps atom and the host molecules is short ranged it is not too unresonable to take the self-trapping potential (which confines the positronium) to have the same radial dependence as that of the density. As before the Schrödinger equation for the center-of-mass motion of positronium will have to be solved and the corresponding wave function ψ_{ps} found. We shall take two functional forms for the density profile (with the corresponding potentials), and shall label these as models II and III. The pick-off annihilation rate is easily calculable in each of the models using eq. (7), however, the range of integration for the overlap (p) shall be now from zero to infinity as the bubble in the modified versions of the model does not have a sharp boundary. Our strategy to compare the different models with the experimental data will be to fix the value of the overlap p to fit the measured pick-off lifetime and to use the parameters so determined to obtain the prediction of the model for the angular correlation ($\theta_{1/2}$) which can then be compared with the observed values.

Model 2 : In this version we take the density profile of the cavity to be [18]

$$\rho(r) = \rho_0 \tanh^2(r/R) \tag{9}$$

Thus the density of the surrounding fluid is zero at the center-of-mass of the Ps atom and with increasing distance tends to density (ρ_0) of the bulk liquid. The parameter R is the radius parameter and characterizes the size of the bubble. Furthermore, as already stated the exchange interaction between the Ps atom and the host molecules being short ranged, the self-trapping potential which confines the positronium is taken to be of the same form, namely

$$U(r) = U_0 \tanh^2(r/R) \tag{10}$$

where U_0 is the depth parameter of the potential. The s-wave ground-state wave function can be easily solved for (in

terms of a hypergeometric function), which when normalized reads as

$$\psi_{ps} = \frac{1}{2\pi R} \frac{\Gamma(s+\frac{1}{2})}{\Gamma(3/2)\Gamma(s-1)}$$

$$\times \frac{1}{r} \mathrm{sech}^s(r/R)\sinh(r/R) \qquad (11a)$$

where $\quad s = \frac{1}{2}\left| -1 + \sqrt{\dfrac{1+16mU_0R^2}{\hbar^2}} \right| \qquad (11b)$

and $\quad E = U_0 - \dfrac{\hbar^2}{16mR^2}\left[-3 + \sqrt{\dfrac{1+16mU_0R^2}{\hbar^2}} \right] \qquad (11c)$

The pick-off rate is now easily calculated using eq. (7) and the overlap integral may be done analytically in this case to yield $p = 3/(2s + 1)$. Having fixed the parameters of the potential to give the experimental value of the pick-off rate (*vide p*), the measured angular correlation parameter $\theta_{1/2}$ is readily calculated from the Fourier transform of the wavefunction (eq. 11a) and using eq. (8). It may be observed that though model II is conceptually more attractive than model I since the sharp bubble boundary has been disposed off, neverthless the agreement is only marginally better (Table 2). However, what is more important is to remark that while model I consistently underpredicts $\theta_{1/2}$, model II systematically overpredicts these values. Hence it is clearly indicated that a density profile be chosen which lies in between the two shapes considered.

This brings us to model III, in which we make the choice [19]

$$\rho(r) = \rho_0[1 - \exp(-r/R)] \qquad (12a)$$

and, accordingly

$$U(r) = U_0[1 - \exp(r/R)] \qquad (12b)$$

The normalized ground-state wave function is easily found to be

$$\left(\frac{k}{2\pi S}\right)^{1/2}\left(\frac{1}{r}\right)J_{2kR}\left(2b\,Re^{-r/2R}\right) \qquad (13a)$$

where $k = \sqrt{(4m/\hbar^2)(U_0 - E)}$, $b = \sqrt{(4m/\hbar^2)U_0}$

and $\quad s = \sum_{n=0}^{\infty}\left\{ \left[J_{2kR+1+n}(2bR)\right]^2 + \left[J_{2kR+n}(2bR)\right]^2 \right\} \qquad (13b)$

$J_v(z)$ being the Bessel function of order v and argument z. The ground-state energy is obtained from the eigenvalue condition

$$J_{2kR}(2bR) = 0. \qquad (13c)$$

The overlap integral is readily evaluated to yield

$$P = 1 - \frac{2kR}{s}\left[J_{2kR+1}(2bR)\right]^2 \qquad (14)$$

The Fourier transform necessary for the calculation of the angular correlation is also analytically available in the form of a rapidly convergent series. The predicted result shows (Table 2) that the agreement is 5% or better for all the cases except water.

Furthermore, the bubble model in its rudimentary form has also received criticism on another count. With the bubble radius turning out to be between 3 and 6 Å it has been emphasised [21,22] that it would only be proper to consider the effect of the radius of curvature, which in turn leads to the notion of the effective (σ_{eff}) rather than the bulk (σ) value for the surface tension. However, this finite size effect necessitates, for the underlying theory, the introduction of, not only the radius R of the surface of tension, but also the distance a characterising the diffusivity of the surface (which is related to the difference between the surface of tension and the equimolecular dividing surface). Nakanishi, Wang and Jean [22] using the Gibbs-Tolman [23]'-Koenig [24] relationship between (σ_{eff}) and σ, and also Byakov and Grafutin [21], using an approximate expression due to Tolman [23],

$$\sigma_{eff}(R) = \sigma\frac{R}{R+a}, \qquad (15)$$

discuss the situation *vis a vis* positronium pick-off annihilation using the bubble model, particularly in high surface tension liquids, with σ_{eff} used in place of σ. It was argued [21] that though doubts had been expressed [16] as to the applicability of the bubble model to liquids with large values of σ, the use of σ_{eff} in its place removes these misgivings. However, these authors left the form of the density profile and the potential unaltered (that is they retained the sharp boundary) but only put into the balance equation (5) the work for bubble formation (with r the radial distance from the centre of the bubble), given by

$$\int_0^R \frac{2\sigma_{eff}(r)}{r}4\pi r^2 dr, \qquad (16)$$

in place of $4\pi\sigma R^2$, which would have been appropriate only if the dependence of surface tension on the bubble size was ignored. However, they treated a (introduced only in the formula for σ_{eff}) as a free parameter tailored to fit the data. Indeed while these authors did capture an important aspect of the underlying physics, their work left a lot to be desired and this bring us to model IV to bridge this lacuna.

As indicated earlier the density profile should contain a parameter R characterizing the 'size' of the cavity, and also

another quantity '*a*' parametrizing the diffuseness of the transition layer. To motivate the choice of the density profile we go back to a paper [25] which, employing intermolecular interactions given by the Lenard-Jones potential, uses numerical simulation to study density profiles for small liquid droplets. It turns out that the resultant density profiles are well described by a form which when modified to account for the fact that we are here dealing with a cavity in the liquid, reads

$$\rho = \rho_0 \left[1 - \frac{1 + e^{-(R/a)}}{1 + e^{(r-R)/a}} \right].$$ (17)

The same form had in fact been suggested by several authors [26] and is indeed the generalization to a curved surface of the form obtained for a flat surface [27]. It may also be remarked that this expression is the same as the celebrated Woods-Saxon potential popular among nuclear physicists. In accordance to the arguments given earlier, the potential well in which the positronium finds itself shall also be taken to be of the same form, to wit

$$U(r) = U_0 \left[1 - \frac{1 + e^{-(R/a)}}{1 + e^{(r-R)/a}} \right].$$ (18)

The Schrödinger equation for the center-of-mass motion of the positronium trapped in such a potential will have to be solved for the lowest and only relevant state, which has the orbital angular momentum $l = 0$ (*s*-wave), and the corresponding wave-function can be found analytically in terms of the hypergeometric function $_2F_1(\mu + \nu, \mu + \nu + 1, 2\nu + 1; y)$ [28].

The rate constant for the pick-off component of the decay can now readily be found using the wafefunction [28] and the density profile as discussed earlier, and one arrives at the result

$$\lambda_p = 4\pi r_0^2 c Z_{\text{eff}} \rho_0 \left[1 + \frac{C_2}{C_1}(1 + \exp(-R/a)) \right]$$ (19a)

where $C_1 = \int_0^\xi |y^\nu(1-y)^\nu \,{}_2F_1| \frac{dy}{y(1-y)},$ (19b)

$$C_2 = \int_0^\xi |y^\nu(1-y)^\nu \,{}_2F_1|^{\xi} \frac{y\,dy}{y(1-y)}.$$ (19c)

and $\frac{1}{1 + e^{(r-R)/a}} \equiv y,$

$$\mu = i \left[\frac{4ma^2}{\hbar^2}(E + U_0 e^{-R/a}) \right]^{\frac{1}{2}},$$

$$\nu = \left[\frac{4ma^2}{\hbar^2}(U_0 - E) \right]^{\frac{1}{2}}.$$

Having solved the Schrödinger equation in terms of well-known standard functions we now need to impose the condition for stability of the positronium bubble system. This condition [given by eq. (5)] will not have to be modified on two counts. Firstly, with size dependence of surface tension, described through eqs. (15), the surface energy will have to be incorporated through the replacement of $4\pi R^2 \sigma$ by the work for bubble formation, and accordingly the total energy of the Ps-bubble system is now given by

$$E_{\text{total}} = E + 4\pi R^2 \sigma \left[1 - 2\frac{a}{R} + 2\frac{a^2}{R^2} \ln \right]$$ (20)
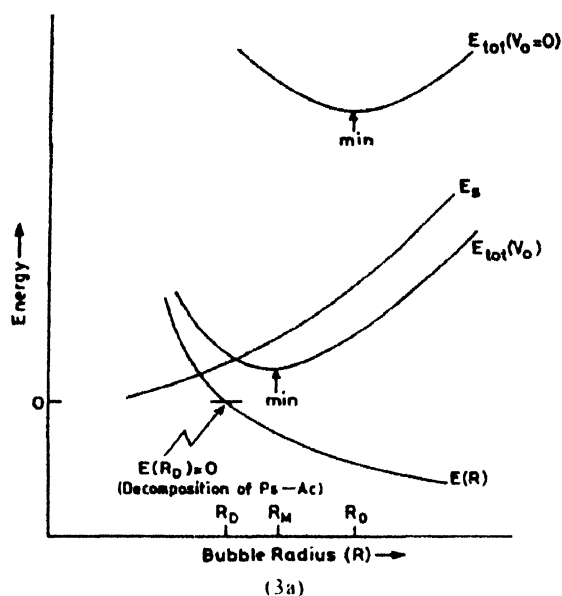
which of course reduces to the case of the sharp bubble boundary without curvature corrections as the diffusivity *a* goes to zero. Secondly, in contrast with what one had earlier, E_{tot} has now to be minimised both with respect to the size and diffusivity paramenters R and *a*; thus unlike what was the case in the attempt by Byakov and Petuchov [29], here even though we have introduced a diffuseness parameter it is not free, as there is an additional energy minimisation constraint. The detailed results are described in [28].
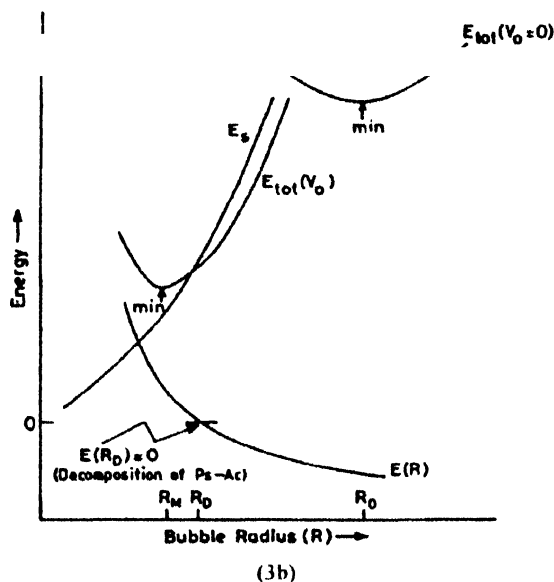
3. Bubble Shrinkage model

One of the attempts towards understanding some aspects of Ps-Ac complex formation in liquids has been through the Bubble Shrinkage Model proposed [1,30] by workers at the Institute of Chemical Physics at Moscow. This was in turn subjected to a critical assessment by Kobayashi and Ujihira [31], and further developed by Ryzkov and Shantarovich [30].

It is assumed that the penetration of the acceptor into the bubble induces the formation of the complex, with the Ps now experiencing, not only the confining potential $U(r)$ due to the surrounding solvent, but also the attractive potential $V(r)$ caused by the interaction of Ps with the active centre of the acceptor Ac. Modelling both $U(r)$ and $V(r)$ by square well potentials of height U_0 and range R for the former, and depth V_0 and range *a*, for the latter the net potential felt by Ps now is $W(r) = U(r) + V(r)$. In this potential the positronium is in a state of energy E say. However, the capture of Ps by the acceptor results in a reduction of the outward pressure exerted by it on the bubble wall due to the uncertainty motion. the surface tension takes over as the balance condition is disturbed, inducing thereby a shrinkage of the bubble. This in turn brings the repulsive potential due to the solvent in closer proximity to the positronium and as a consequence the binding energy $|E|$ decreases and when $E(R)$ becomes greater than zero, the complex dissociates. Solution of the Schrödinger equation for $E(R)$ is readily found and one examines $E(R)$ and also the total energy

$E_{tot} = E(R) + 4\pi R^2 \sigma$ as a function of R. Two typical possible scenarios are depicted schematically in Figure 3(a) and 3(b).

Figure 3. Schematic representation of the energy of the positronium acceptor bubble system as a function of the bubble radius showing contributions of different components in the case of stable complex [Figure 3a] and unstable complex [Figure 3b]

In each case the curve labelled E_{tot} ($V_0 = 0$) shows the energy of the Ps-bubble system in the pure solvent (no Ac) and its minimum of course gives the equilibrium bubble radius R; also the curve for $4\pi\sigma R^2$ gives the surface energy. The curve labelled E shows the energy eigenvalue of Ps in the presence of the acceptor while E_{tot} depicts the total energy $E + 4\pi R^2 \sigma$.

In the situation shown through Figure 3(a) the minimum of E_{tot} is at R_M which is then the equilibrium radius of the bubble in the presence of the acceptor. Note here that

$E(R_M) < 0$ implying that Ps-Ac complex is stable at equilibrium. Indeed the dissociation radius R_D [$E(R_D) = 0$] occurs at a value $R_D < R_M$. This then describes the case of the table complex. On the contrary Figure 3(b) shows the circumstance where $R_D > R_M$. In other words the complex would have dissociated before equilibrium is arrived at. It is the unstable complex case.

4. Ps-Ac complex formation and its stability in the bubble

To raise the status of this contention [32] to at least a semi-quantitative level let us consider the positronium to be subjected to an attractive potential $V(r)$ due to the Acceptor, while it also feels the infinite repulsion due to the solvent located at the bubble wall at a distance R. Taking the potential $V(r)$ to be a spherical well [33] of depth V_0 and range a viz. $-V_0\Theta(a-r)$ where Θ is the step function, the relevant Schrödinger equation for the centre-of-mass motion of Ps is

$$\frac{\hbar^2}{4m}\frac{d^2}{dr^2} - V_0 \bigg| u = -Bu \quad \text{for } r < a \tag{21a}$$

$$\frac{\hbar^2}{4m}\frac{d^2}{dr^2} u = -Bu \quad \text{for } r > a \tag{21b}$$

with $\psi = u/r$. The appropriate boundary conditions are $u(r = 0) = 0$ and $u(r = R) = 0$, while u and its derivative must be continuous at $r = a$, yielding the eigenvalue condition

$$k \tan \kappa a = -k \tanh k (R - a) \tag{22}$$

where $k = \sqrt{\frac{4mB}{\hbar^2}}$ and $\kappa = \sqrt{\bar{g}^2 - k^2}$ with $\frac{4mV_0}{\hbar^2} = \bar{g}^2$.

The bond breaking (dissociation) radius R_D, viz where $k = 0$, is thus given by

$$R_D = a\bigg[1 - \frac{\tan \bar{g}a}{\bar{g}a}\bigg]. \tag{23}$$

Since in the leading approximation (adopted by us) the effect of the solvent is represented by an infinite repulsion (tantamount to a boundary condition forcing ψ to vanish at R), the radius R_D depends only on the characteristics of the Acceptor *vis a vis* its affinity for the positronium, and is. to that extent, same for all solvents. However, we must also consider the fact that the Ps-Ac-bubble system would equilibrate at some radius R_M at which the total energy is a minimum, namely,

$$\frac{\partial}{\partial R}\big[-B + 4\pi R^2 \sigma\big] = 0. \tag{24}$$

5. The notion of critical surface tension

A big step forward is made possible by our recognition that in leading approximation R_D is essentially solvent

independent, while solvent dependence enters through R_M and that too only through σ. As the surface tension of the solvent is a function of temperature, the equilibrium radius of the bubble (with Ps-Ac inside) depends on temperature only through σ viz. $R_M(T) = R_M[\sigma(T)]$. As T is decreased, σ increases, R_M decreases. When R_M becomes less than R_D the Ps-Ac-bubble system is no longer stable. Clearly there is a critical value of σ, σ_{cr}, at which $R_M[\sigma_{cr}] = R_D$, marking the watershed beyond which the Ps-Ac-bubble system destabilises. The value of T at which σ attains the value σ_{cr} depends on the particular solvent, but σ_{cr} does not, but is, in the leading order, a property of the Acceptor under consideration. We argue that the turnover temperature T_0 is the temperature at which, for the solvent at hand, $\sigma(T_0) = \sigma_{cr}$. Indeed at sufficiently high temperature where $\sigma(T) < \sigma_{cr}$, a large negative change in enthalpy occurs as the reactants

[Ps in a bubble of radius $R = \left(\dfrac{\pi\hbar^2}{16m\sigma}\right)^{1/4}$ and the Acceptor]

react to form the product [Ps-Ac Complex in bubble] with the radius having shrunk to R_M. This makes it a down-hill reaction, since for weak Acceptors the activation energy is expected to play a sub-dominant role and also the effect of solvent viscosity is negligible (because the complex is protected by the bubble from the buffetting by the solvent molecules). It is thus basically the negative activation volume that is responsible for the anti-Arrhenius behaviour for $T > T_0$ On the other hand for $T < T_0$ when $\sigma(T) > \sigma_{cr}$ the Ps-Ac-bubble system is unstable, the Ac is squeezed out of the bubble and the formation of the Complex must of necessity take place in the milieu of the solvent accompanied by the continual impact of the solvent molecules. As such, following Kramers [34] the role of the medium would be said to belong to the Smolochowski regime, with the dependence of the rate constant on the viscosity (η) varying as $\dfrac{1}{\eta} \sim D$ where D is the diffusion coefficient of the liquid, the last tep being a consequence of the Einstein-Stokes relation). In view of the smallness of the activation energy for weak acceptors, we would therefore expect that $\kappa \sim \exp[-E_\eta/k_B T]$, where E_η is the activation energy associated with the process of diffusion. The reaction in this region would be diffusion controlled and would exhibit a normal Arrhenius behaviour. This enables us to make the important prediction that $\kappa(T_0) = \sigma_{cr}$ and that it is approximately solvent independent. In order to confront this with experiment, we have plotted in Figure 4, $\sigma(T)$ against $T - T_0$ for various solvents (for which data is available with nitrobenzene as the Acceptor).

It is indeed highly gratifying to note that while T_0 differs widely from solvent to solvent, and also the values of the surface tension σ at a given temperature for different solvents

have a substantial spread, nevertheless $\sigma(T_0) = \sigma_{cr}$ for the solvents under consideration lie in a rather narrow range, namely, $\sigma_{cr} = 26 \pm 2$ dynes/cm.
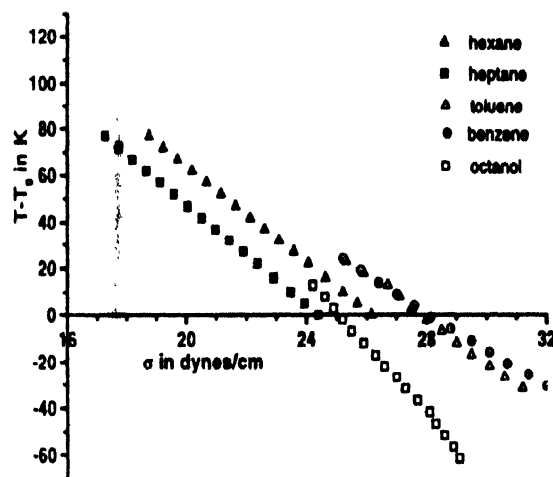

Figure 4. Surface tension $\sigma(T)$ for different solvents as a function of $T - T_0$ exposing the concept of the critical surface tension (σ_{cr}).

This model gives (from eq. 24)

$$\sigma_{cr} = \left(\frac{1}{8\pi\sigma}\right)\left(\frac{\hbar^2}{4m}\right)\left(\frac{1}{a^4}\right)$$

$$\times \frac{6\zeta^4}{(\zeta - \tan\zeta)(3\zeta - 3\tan\zeta + 3\zeta\tan^2\zeta - 2\tan^3\zeta)} \quad (25)$$

where $\zeta = \bar{g}a$. Whether the Ps-Ac-bubble system will be stable or not will depend on whether R_M is greater than or lesser than the bond-breaking radius R_D.

6. Discussion

Armed with this value of σ_{cr} we are now in a position to access the Ps-Ac interaction parameters which, as we shall discuss below, are unfortunately not available from any other source. Being led by the estimates of other authors let us fix the range of the interaction to be $a = 1.5$ Å, and determine $\bar{g}$ by putting, in accordance to our discussions above, $\sigma = \sigma_{cr}$ and $R_M = R_D$ [refer eq. (23)]. This immediately yields the value $\bar{g} = 1.25$ Å^{-1} which corresponds to the Ps-Ac binding energy (the Acceptor being nitrobenzene) $B_0 = 0.18$ eV. Note that B_0 signifies the basic binding in the absence of the solvent, namely, $B_0 = \text{Lim}_{R\to\infty}B$, which implies vide eq. (22), the well-known result : $-\kappa\cot\kappa a = k$ the eigenvalue condition for a spherical well. Unfortunately there is no direct measurement of this binding energy B_0, and the approaches based on first principles [35] are beset with huge theoretical uncertainties. However, using our methodology we have now completely tied down the model and shall proceed to show how this explains all the main observed features.

In order to find the slope of the ln κ *versus* $1/T$ plot in the higher temperature anti-Arrhenius region we recognise that this is nothing but the activation free energy, the major contribution to which come from the change in enthalpy arising from the shrinkage of the bubble from its value given by R to the size determined by R_M, *viz.* $4\pi R_m^2 \sigma - 4\pi R^2 \sigma$ where, of course the radii are functions of temperature through the surface tension. To this must be added the change in the Ps-Ac binding due to the approach of the bubble wall from R to R_M. The resulting behaviour (appropriately normalized as described below) is depicted in Figure 1 for the case of Ps nitrobenzene reaction in heptane, for instance, as a solvent. The slope obtained through our model corresponds to ≈ 0.15 eV which agrees very well with the experimental value. While the change in enthalpy does provide an understanding of the slope of the ln κ *vs* $1/T$ line at higher temperatures, this thermodynamic argument is, however, not sufficient to predict the actual rate as the pre-factors of the exponential term remain unknown. None the less, arguing that the reaction rate should be a continuous function of temperature, we should match it with that below the turnover temperature (namely in the Arrhenius region). Here as we stated earlier the reaction occurs outside the cavity and the reactants (Ps and Ac) are no longer protected by the bubble from the impact of the solvent molecules (S). The processis diffusion controlled (being as it is in the Smolochowski region) and accordingly the reaction rate is given by

$$\kappa = \frac{4\pi DRN}{1000} \qquad (26)$$

where D is the sum of the diffusion coefficients of the two reactant in the solvent, R is the sum of the reactant radii (*viz.* $R = R_{Ps} + R_{Ac}$ which may be taken as $R_{Ps} \sim 0.053$ nm and for nitro-benzene $R_{Ac} \sim 0.3$ nm) and N is the Avagadro number. The diffusion coefficients may be estimated through the use of the Einstein-Stokes relation, and we arrive at

$$D = \frac{k_B T}{6\pi\eta}\left[\frac{1}{R_{Ps}} + \frac{1}{R_{Ac}}\right]. \qquad (27)$$

Using the values for the activation energy (E_η) for diffusion through heptane and the measured value of η, the magnitude and slope of the Arrhenius plot is reproduced in good agreement with experiment. Figure 1 demonstrates that the main aspects of the temperature dependence of the rate has been captured in an extremely satisfactory manner.

Apart from providing an interpretation of the temperature dependence of the reaction as set forth above, this simple model is also able to furnish an explanation of the observed variation with the external pressure (P). In view of the small compressibility of liquids one would hardly expect any appreciable activation volume when $T < T_0$ as the reaction occurs in the solvent itself. However, for $T > T_0$ due to the involvement of the bubble a large ΔV^* (activation volume) becomes possible and hence a significant pressure dependence can occur, in view of the basic Polyani relationship :

$$\left(\frac{\partial \ln\kappa}{\partial P}\right)_T = -\frac{\Delta V^*}{k_B T} \qquad (28)$$

between the effect of external pressure on the rate of a chemical reaction and the activation volume of the reaction (namely, the difference between the volume of the activated complex and the volume of the reactants). To obtain quantitative estimates it is to be noted that the initial volume *viz.* Ps in the bubble without the Ac must be found now by minimizing the total energy, namely $E_{tot} = \frac{\hbar^2}{4mR^2} + 4\pi R^2 \sigma$ $+ \frac{4\pi}{3} R^2 P$ with respect to R and thereby obtain $R(P)$. Here P is measured in kgwt/cm^2 ($= 0.613 \times 10^{-6}$ eV/Å^3). Similarly the equation determining the equilibrium radius $[R_M(P)]$ with Ps-Ac inside the bubble must be appropriately modified, so that in place of eq. (24), we now have

$$\frac{\partial}{\partial R}\left(-B + 4\pi R^2 \sigma + \frac{4\pi}{3} R^3 P\right) = 0 \qquad (29)$$

Equipped with $R(P)$, $R_M(P)$ and $B[R(P)]$ the variation of the rate constant with pressure can be readily calculated.

Consider the two typical cases depicted in Figure 2 out of the many taken from the experimental studies of Kobayashi [8,9]. All these experiments were performed at ambient temperature ($T_{expt} = 19 \pm 1°C$). With nitrobenzene as the Acceptor and benzene as the solvent we note that there is no significant effect of pressure on the reaction rate. This is quite consistent with the model in view of the fact that the turnover temperature in this case [36] is considerably above T_{expt} and hence one is working in the Arrhenius region where the pressure effect is expected to be small. On the other hand when the solvent is hexane, the experiment was performed in the regime where the Ps-Ac-bubble system is stable (as the turnover temperature here is $-53°C$), and accordingly the reaction rate responds appreciably to external pressure. Indeed the enhancement of the rate by a factor of about thirty in our model is even in quantitative agreement with the experimental results of Kobayashi. Using the experimental value of the surface tension of hexane at T_{exp} ($\sigma \approx 19$ dynes/cm), the model indicates the behaviour shown in Figure 2.

Above a critical pressure the Ps-Ac-bubble system destabilizes and the rate *versus* pressure curve levels off. Except for the fact that there is a somewhat precocious

...set of the Arrhenius regime the general experimental trend is captured very well indeed considering the approximations involved.

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