Diffusion PowerPoint presentation

The following comments accompany the Diffusion PowerPoint presentation:

May 20, 2012 (included Petropoulos and coworker experiments) expanded July 4, 2012 with Thomas and Windle experiments at the last.

1. The figure is the cover of the second edition of Hansen Solubility Parameters: A User's Handbook, CRC Press, Boca Raton FL, 2007. Reference is frequently made to this as a source of further information and many of the slides and references can be found in Chapter 16.
2. The outline of the talk is given.
3. Fick's First and Second Laws (the diffusion equation) are given.
4. The usual dimensionless quantities are introduced.
5. The equation for steady state permeation with a constant diffusion coefficient.
6. A preferred method to measure diffusion coefficients by absorption or desorption is to find the time at which half of the equilibrium amount of mass has been transferred. This half-time can be used with the equation given. Comparisons of solutions to the diffusion equation that also include concentration dependence and/or a significant surface condition have been generated to establish factors to correct the apparent (constant diffusion coefficient interpretation) to the true values. This is an interative process, that with the advent of the software in the HSPiP, can be replaced by simple curve matching having assumed the appropriate parameter values.
7. The differences between the constant diffusion coefficient solutions and those with concentration dependence are used to give the correction factors in the slide. In the following it is shown that the much larger corrections required for desorption give the same diffusion coefficients as the relatively small corrections for absorption. In many older articles this lack of correction can be seen when a series of absorption experiments from zero to increasingly higher equilibrium concentrations do not give the straight line of log diffusion coefficient versus volume fraction solvent.
8. The surface condition is usually assumed to be that of an immediate change in the surface concentration to the equilibrium value. That this is not always the case, and the consequences of this, are the main points of this presentation. The external factors that can cause a delay in the attainment of the equilibrium concentration are diffusion in a stagnant gas phase, transfer of mass to or from the surface over longer distances, such as in pressure regulating, and what is almost always neglected heat transfer to or from the surface. The heat of condensation must be removed from a system during absorption, and when the absorption is rapid, this factor can be important. It is known to be important as well in evaporation (desorption) from films. Note that the units of the surface mass transfer coefficient include time.

9. The corrections to the apparent diffusion coefficient measured by the half-time method are given.
10. The equation for correcting for resistances in permeation cups and at surfaces is given. An example is given in the next slide. This procedure has been used many times. A similar relation exists for diffusion coefficients.
11. This figure appeared in Hulden and Hansen 1985, and see also page 302 of the second edition of the CRC handbook in Chapter 16.
    Huldén, M. and Hansen, C.M., Water Permeation in Coatings, Prog. Org. Coatings, 13, No. 3/4, 171-194 (1985).
    Units for the permeation coefficient are kg Pa^{-1} s^{-1} m^{-1}. Ref. 10 in this same chapter studies the permeation cup in depth.
    Nilsson, E. and Hansen, C.M., Evaporation and Vapor Diffusion Resistance in Permeation Measurements by the Cup Method, J. Coatings Techn., 53, No. 680, 61-64 (1981).
12. Before proceeding there is a warning in this slide about side effects. The usual assumption of mass transport in one direction only is in error to the extent given by the equations. (See again Chapter 16 of the CRC handbook for further discussion). The use of tensile bars for absorption measurements must be done with care. The use of small disks should also be subjected to these considerations.
13. The significance of the absorption, desorption, and film drying data for the system chlorobenzene in poly(vinyl acetate) is presented. These data are presented and used in the following slides. They took years to accumulate. The next slide shows diffusion coefficients over the entire concentration range of zero solvent in the polymer with a uniform extrapolation to the self diffusion coefficient.
14. The decrease in the apparent diffusion above volume fraction 0.2 is caused by increasing surface resistance in the absorption measurements used in this region. A series of experiments going from one equilibrium concentration to a higher one requires more and more solvent be transferred as the concentration increases and this heat of condensation must also be removed. One of these experiments is reported for the first time in detail in a following slide to show the S-curvature is a clear indication of a surface condition of significance.
15. Written information related to the content of the following slides.
16. The absorption experiments are reported in blue while the desorption experiments are given in red. These yield the same values when the proper corrections are applied as discussed earlier. Above 0.2 volume fraction chlorobenzene in poly(vinyl acetate), the surface condition becomes increasingly important. Note that the corrections are quite different in all cases, but the end result is a smooth diffusion coefficient curve.
17. This is a detailed report of the absorption experiment from 0.22 to 0.27 volume fraction. The total correction for this experiment is “only” 1.63 compared with the correction of 1.2x250 = 300 applied for the surface condition at higher concentrations as seen in the previous slide. This experiment was reported in detail in: Hansen, C.M., Diffusion Coefficient Measurements by Solvent Absorption in Concentrated Polymer Solutions, J. Appl. Poly. Sci., 26, No. , 3311-3315 (1981).

18. There are numerous examples of a significant surface condition given in Chapter 16 of the CRC handbook as well as elsewhere including: Nielsen, T.B., and Hansen, C. M., "Significance of Surface Resistance in Absorption by Polymers", Industrial & Engineering Chemistry Research, Vol. 44, No. 11, 3959-3965 (2005).
    The curvature at the start of the absorption experiments is a clear sign of a surface condition effect. The reason for this has been called an entry resistance, since the liquid contact precludes those types of surface effects found otherwise. The size and shape of the molecules determines how easily they can adsorb/absorb after finding suitable "holes" for entry. In the present case for the COC polymer it was found that solvents with aromatic rings could simply not enter at all, in spite of solubility parameter considerations indicating that they should. This entry resistance will vary from system to system, but all polymers will delay entry of solvents of some larger size. This is a general situation and the cause of many of the so-called "anomalies" observed in the past.
19. Additional examples of surface condition significance.
20. The following slides are from Hansen (1980): Hansen, C.M., Diffusion in Polymers, Poly. Eng. Sci., 20, No. 4, 252-258 (1980).
    This one shows linear uptake as a function of time (Case II) as well as uptake faster than with linear time (Super Case II).
21. The concentration gradients accompanying Case II and Super Case II show the surface concentration only slowly rises to the assumed equilibrium value.
22. Film formation by solvent evaporation can be modeled as a desorption experiment starting from the solution concentration and letting the diffusion equation then describe the first stage with solvent at the air surface and the second stage controlled totally by diffusion. The significant surface condition in the first stage cannot be denied, but yet many deny that absorption to similar concentrations from a bone dry start does not involve a significant surface condition.
23. My doctoral thesis showed that solvent retention was a matter of solvent size and shape. The same solvents were retained most in different polymers. The order is that shown in the figure with a cyclohexyl ring delaying the diffusion process more than an aromatic ring, etc. The belief at the time was that solvent retention was caused by hydrogen bonding, which is clearly not the case, with smaller solvents such as methanol escaping more rapidly than the others shown. Since diffusion coefficients were extensively measured for several of these in poly(vinyl acetate), the diffusion coefficients for the others can be estimated by interpolation. Those for which there are more data are cyclohexanone, ethylene glycol monomethyl ether, and methanol. See my doctoral dissertation that can be downloaded from the website.
24. The diffusion coefficients at low concentrations in PVC are used to show that size is an important factor is diffusion. The diffusion coefficient for iodine is expected to be about 50 times lower than that of methanol at low concentrations in polymers, also the PMMA studied by Thomas and Windle. The consequences are discussed at the last of the

presentation. See also the separate document "Reinterpreting Case II Absorption in Polymers – An Examination of the Thomas and Windle Data

25. The appearance of an article that assumed absorption of water into bone dry poly(vinyl alcohol) to very high concentrations could be explained on the basis of stress relaxation in the film only caused me to respond. The software in the HSPiP had become available and with a few simple assumptions a perfect match of the experimental data could confirm that the expected significant surface concentration could fully explain the data with parameters that were reasonable:
    Hansen, C. M., "The significance of the surface condition in solutions to the diffusion equation: explaining "anomalous" sigmoidal, Case II, and Super Case II absorption behavior", European Polymer Journal, Vol. 46, 651-662 (2010).
26. The S-shaped absorption curve is typical of a significant surface condition, in this case for the absorption of water from bone dry to 0.748 volume fraction in poly(vinyl alcohol). Diffusion resistance is significant only for the first few percent of the absorption as can be seen from the concentration gradients at the lower left.
27. The phenomena called Case II are modeled here using the diffusion coefficients for chlorobenzene in poly(vinyl acetate) and an assumed surface mass transfer coefficient. It has been possible to produce absorption curves similar to those called "Case II" in the literature. The initial slope may be greater than that at longer times. If it is lower, then one has what is called Super Case II, with the uptake being faster than linear with time. Such a situation is modeled in the next slide. The tail at the longest times is an effect from the surface resistance. Whether or not such surface resistance changes with concentration can be discussed. I have not seen data examining this possible effect.
28. Super Case II is here modeled with an improved figure over that in the article mentioned earlier. This was because of a comment to the effect that the "advancing front" was not sharp enough in earlier figures. If one decreases the mass transfer coefficient still more, the rate of uptake changes still more at longer times. If one increases the mass transfer coefficient Case II kinetics are found.
29. The article cited in the slide appeared in the European Polymer Journal as a response to the article by myself that has just been touched upon. I responded to this with a manuscript that is described in more detail in an Appendix here, but this was rejected by the European Polymer Journal after a considerable delay. The Title and Abstract of this unpublished manuscript are:

Does Stress Relaxation or a Significant Surface Condition Control "Anomalous" Absorption in Polymers?

Similar equations have been used to model absorption in polymers by Petropoulos, his coworkers, and Hansen, respectively. Curve fitting of absorption experimental results will therefore be similar and satisfactory to all of these. There are quite different interpretations for the parameters used, however. The "kinetic" stress relaxation modulus of Petropoulos and coworkers includes a rate parameter called β, which, in the relevant equations, is the counterpart of the surface mass transfer coefficient, h, used by Hansen. Both enter respective dimensionless quantities in models for absorption based on (numerical) solutions to the diffusion equation. A stress relaxation interpretation seems improbable for absorption of vapors to high solvent concentrations. The diffusion coefficient is high enough to assure an essentially uniform concentration gradient and very mobile polymer chains. A significant surface mass transfer coefficient in vapor absorption reflects transfer of the latent heat of condensation away from the film, diffusion in air above the film, etc. A kinetic stress relaxation model for desorption or steady state permeation is not possible. All of these have been modeled satisfactorily using verifiable and consistent parameters by Hansen. This latter approach includes exponential diffusion coefficients as predicted by free volume theory. A surface entry mass transfer coefficient that can approach zero may also prevail when larger and/or more bulky molecules have difficulty entering and passing through the polymer surface, even though they may be there in abundance. It is such cases that clearly yield what are called Case II and Super Case II absorption curves and concentration gradients have advancing fronts. A very special case of dichloromethane absorption into simultaneously restrained and stretched cellulose acetate is modeled perfectly here in the direction across that of stretching using concentration dependent diffusion coefficients with no significant mass transfer coefficient. A different physical model is thought necessary for diffusion in the direction of orientation. This is based on the slow “freeing” of the highly associated, long, stiff polymer molecules allowing very rapid diffusion behind the front and very slow diffusion in its precursor. This physical model is supported by calculations using relevant parameters, with stress relaxation considerations not being required.

30. The Petropoulos challenge. The data in the slide are for uptake of methylene chloride into cellulose acetate sandwiched between glass slides. The sample had been stretched to study the entry of the methylene chloride from the not oriented and well as oriented directions. The following slides show results closely duplicating these two situations without the need to consider stress relaxation.
31. Calculated absorption curve and concentration gradients for entry perpendicular to the direction of stretch are perfectly matched by the assumed parameters. No diffusion coefficient is reported by Petropoulos et.al.
32. Calculated absorption curve for absorption in the direction of orientation is matched perfectly but the advancing front is not as sharp as the experimental data. It is thought that the stretched, oriented cellulose acetate molecules may not maintain the initial conditions as the experiment progresses. Additional solvent in the film in excess of that “expected” would make a sharper front. Adhesion to the glass slides must be maintained as the film swells into the liquid, and one can question whether the restrained equilibrium concentration 0.28 volume fraction is maintained in the whole experiment while the unrestrained concentration would otherwise be 0.73 volume fraction. Any bulging of the exposed, swollen film would tend to increase the solvent content over that expected by the assumptions. It is concluded that the calculated data match very well the experimental data and this could only have been attempted since Petropoulos et.al. do report sufficient

experimental data. They do not report a diffusion coefficient, however. The lack of sufficient data has prevented such recalculation of experiments in most of the older literature.

33. Data from Thomas and Windle for uptake of methanol into PMMA at 30°C. The straight line uptake with linear time is characteristic for Case II absorption.
34. Data from Thomas and Windle for presumed concentration gradients for methanol in PMMA at 30°C as indicated by the unsuitable tracer iodine. The step-like concentration gradients have been considered an inherent part of Case II absorption in polymers.
35. Calculations using the data of Thomas and Windle for the absorption of methanol into PMMA at 30°C that reproduce the uptake curve and show concentration gradients for methanol that are not step-like – quite to the contrary. Iodine is not suitable for this purpose and has led to erroneous conclusions.
36. The widely cited Super Case II example of Hopfenberg and coworkers is given. See the download Reexamination of Super Case II for further details and additional examples.
37. The result of modeling the data in the previous slide. All the verifiable parameters including the uptake curve, D_0, and h (from the initial uptake rate) are very close to what can be found or derived from the literature. See the download Reexamination of Super Case II for further details and additional examples.
38. The conclusion to be drawn is given in the slide. This author has yet to see a report that would not be explainable by solutions to the diffusion equation, perhaps with the simultaneous inclusion of concentration dependent diffusion coefficients and/or a significant "external" surface condition or a significant "entry" surface condition. Both of these fortunately or unfortunately are described by the same equation, and this equation has also been invoked by Petropoulos and coworkers but with a completely different interpretation. Quoting the slide:

    Stress relaxation phenomena need not be invoked to explain the cases examined including Thomas and Windle Case II, Super Case II, and Sigmoidal examples or the studies of Petropoulos and coworkers.
39. The presentation is summarized.
40. Contact is always possible. I am willing to analyze a report where sufficient data are presented to do so in agreement with the above. Unfortunately many older reports do not do this, as I confirmed in 1980.

Appendix: A rejected manuscript:

There are numerous key points in the manuscript rejected by the European Polymer Journal that I feel should be in the literature. The following are the comments by the two reviewers:

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Reviewer #1: This is a paper in a series between two groups. I believe that the
issues dealt with and the discussions between the groups is more appropriate to
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deal with outside a journal. Whether it is the stress relaxation or the mass transfer resistance that are the rate determining steps during sorption is in my opinion, with this paper, still not determined.

Now who would come up with such a comment? This is a stopper. The discussion is being continued here, but the audience is very much more limited than in an international journal. I am sorry for this!

This manuscript aims to reply to some of the conclusions stated in a recent work by Petropoulos and co-workers [Physically insightful modeling of non-Fickian kinetic energy regimes encountered in fundamental studies of isothermal sorption of swelling agents in polymeric media, Petropoulos et al. (2011), Eur Polym J, vol 47, pag 2053] and, in that attempt, it addresses a comparison between "stress relaxation" and "significant surface condition" models. The latter are two different approaches to the interpretation of so called anomalous absorption/desorption kinetics in polymers, and this paper gives a rather specific discussion which refers to their prediction ability and the feasibility of physical picture they offer for the interpretation of overall transport phenomena.
The manuscript also presents few correlation results, by the "significant surface condition" model, of sorption kinetics for the case of dichloromethane in stretched cellulose acetate (reference experimental data from the work by Petropoulos) and for one pure hypothetical sorption case in which a Super Case II kinetics (mass sorption rate increasing with time) is obtained by the model.
Just as in previous papers in which the "significant surface condition" model was introduced, it is here stated that equation used to describe the evolution of the penetrant flux at the surface (equation 3 in ref.[1]) may apply both to the case of non-negligible resistance to mass transfer in fluid phase out of the polymer sample and to the case of entry resistance for penetrant into the polymer sample surface. THIS IS HOW THE MATHEMATICS SPECIFIES THE SITUATIONS, ONE HAS ONLY TO ASSIGN THE PARAMETERS FOR THE GIVEN SET OF EXPERIMENTAL CONDITIONS.
Conclusions of the manuscript state that several specific correlation results for vapour sorption processes in polymer samples obtained through "stress relaxation" model can be obtained as well from the application of "significant surface condition" model. Comments are also offered in the submitted paper to underline the existence of experimental data for vapour sorption/permeation in polymers for which "stress relaxation" model would result unsuitable.
Content of the paper which refers to description of characteristics and ability of the "significant surface condition" model does not add much to what already reported in paper [1], published two years ago in the same journal and, on the other hand, replying to comments stated in a recent paper results here a rather weak motivation for the publication of a research full article, as proposed in this case. Indeed, this kind of dispute between authors for the best approach to the representation of anomalous sorption in polymers cannot be really conclusive, as the set of so called non-Fickian features for sorption in polymers include several rather different phenomena, which may indeed have different origin. In this view, judging proposals of mathematical descriptions of elementary processes for their ability to account for the whole set of phenomena is not a fruitful approach. I DISAGREE.
That reported above is the major motivation for this reviewer to suggest the proposal of publication of the manuscript as full article is rejected. A SHORTENED PAPER WOULD ALSO BE OK WITH ME, BUT APPARENTLY NOT WITH THE EDITOR.

Further relevant question which, in case, should be specifically considered before the manuscript is published are listed below:

- in Eq.(2) in the manuscript, which should emphasize the numerical equivalence, in some respect, of "stress relaxation" and "significant surface condition" models, is stated mistaking the time derivative of the penetrant concentration at the surface with the corresponding spatial gradient; I DO NOT BELIEVE SO
- in "significant surface condition" model, results for Case II and Super Case II kinetics, which refer to the case of penetrant flux at the surface Fs which is constant (Case II) or increasing with time (Super Case II) in a rather large time interval, are only consistent with time-increasing value of mass transfer coefficient h. THIS IS NOT CORRECT. A SLOWLY RISING SURFACE CONCENTRATION WITH THE SAME MASS TRANSFER COEFFICIENT WOULD DO IT, AND APPARENTLY DOES DO IT. Indeed, if h would be constant in time, according to Eq.(2) Fs should decrease as surface concentration Cs approaches equilibrium concentration Ceq. On the other hand, no information is given about assumed time dependency of h in the discussion of the example in which Super Case II kinetics is represented (see Fig.1 in the manuscript); h COULD BE TIME DEPENDENT, BUT MORE DETAILED STUDIES WOULD BE REQUIRED TO ELUCIDATE THIS. THE SOLUTIONS PRESENTED IN THE PAPER ARE THOSE GENERATED BY THE SURFACE CONDITION MODEL. I ONLY REPORT THE SOLUTIONS THE SOFTWARE PROVIDE WITHOUT ANY FURTHER CONSIDERATION, NOT TRYING TO ARGUE THEIR INCORRECTNESS IN THIS WAY. I ACCEPT THE SOLUTIONS TO THE DIFFUSION EQUATION AS GIVEN. NOTE THE COMMENT ON SLOWLY INCREASING SURFACE CONCENTRATION ABOVE.
- use of the same mathematical expression (Eq.(2)) to deal either with a significant mass transfer resistance in the external fluid phase or with relevant penetrant entry resistance at the sample surface, as proposed in the model, puzzles the possibility to compare values of model parameter h in different conditions (see parameters used for calculation represented in Fig 2 and 3); I HAVE NO PROBLEMS KEEPING THEM STRAIGHT. THE BETA PARAMETER IS IMPORTANT IN SOME CASES WHERE SEMI-INFINITE SOLUTIONS ARE NOT THE ONLY THING OF INTEREST.
- the author claims that representation of entry resistance, through model parameter h, can describe Case II kinetics for the case of penetrant sorption from pure liquid source. On the other hand, best known evidences of similar phenomena refer to Case II kinetics in which no appreciable change of the surface concentration is observed (see for example works by Thomas and Windle for sorption of liquid alcohols in PMMA published in Polymer in years 1978-82). IF SUFFICIENT DATA ARE AVAILABLE IN THESE WORKS, I AM SURE THE SURFACE CONDITION MODEL WILL RESPOND CORRECTLY, BUT I FEAR THE DATA ARE NOT THERE, BASED ON A VERY OLD SEARCH AND MY MEMORY. I AM NOT IMMEDIATELY FRIGHTENED WHEN SEEING THE CURVES IN (Windle, A.H. Case II Sorption, in Polymer Permeability, J. Comyn, Ed., Elsevier Applied Science, London, 1985). I MAY GET AROUND TO LOOKING INTO IT, BUT SEE NO IMMEDIATE NEED. It should be underlined in the paper that this is different from what embedded in the "significant surface condition" model, for which sorption order kinetics larger than 0.5 (anomalous, Case II or Super Case II) is invariably associated to convenient variation in time of surface concentration; I DO NOT SEE THAT THIS IS CORRECT. I ONLY REPORT WHAT THE COMPUTER GIVES BACK IN TERMS OF THE SPECIFIED MODEL. THIS MODEL TAKES ALL OF THE CHOSEN PARAMETERS AND EQUATIONS INTO ACCOUNT TO GIVE THE OUTPUT REPORTED. I HAVE NOT ATTEMPTED TO ADJUST CHANGES IN MASS TRANSFER COEFFICIENT OR CHANGES IN SURFACE CONCENTRATION, I ONLY ACCEPT WHAT THE DIFFUSION EQUATIONS SAYS.
- It should be then accounted for the fact that variation in surface concentration (similar to those produced by "significant surface condition" model) can be also obtained through approaches which focus on bulk properties of

penetrant-polymer mixture (similar to what it is done in "stress relaxation" model). I DO NOT INTUITIVELY SEE WHY, BUT YES, WHAT GOES ON WITHIN THE FILM WOULD AFFECT THE RATE OF REMOVAL FROM THE SURFACE TO THE BULK. For a similar approach see, for example, "Modeling Sorption Kinetics of Carbon Dioxide in Glassy Polymeric Films using the Nonequilibrium Thermodynamic Approach" Carlà et al., Industrial and Engineering Chemistry Research (2009), vol.48, pag. 3844, which deals with the description of a two stage sorption process, and see specifically the last figure in the paper for the representation of change in penetrant surface concentration. I DO NOT CONSIDER THE EXPERIMENT IN THIS REPORT A DIFFUSION EXPERIMENT. THE FILM THICKNESS IS 1 MICRON (ok, BUT) AND THE TEMPERATURE VARIES TOO MUCH DURING THE EXPERIMENT. IF ONE HAS TO CONTINUALLY SUPPLY CARBON DIOXIDE FROM SOME EXTERNAL SOURCE, THIS IN ITSELF IS AN INDICATION THAT TRANSFER TO THE FILM SURFACE IS IMPORTANT. IT MAY BE POSSIBLE TO ANALYZE THIS IN TERMS OF THE PRESENT PROCEDURE, BUT IT WOULD INVOLVE A GREAT DEAL OF GUESSING, WHICH WILL THEN THE CRITICIZED BY ANYONE WHO SO DESIRES TO DO SO. I SENSE THAT THIS REVIEWER IS ONE OF THE (VERY) MANY WHO HAVE THEIR OWN APPROACH.

I AGREE THAT FURTHER DISCUSSION WITH EITHER OF THE TWO REVIEWERS WOULD NOT BE PRODUCTIVE.

I suggest that those very much interested in this discussion review the contents of the Tamura et.al. article found so important by Petropoulos et.al, (Tamura M Yamada K Odani J. Tensile creep measurement on the system polystyrene and benzene. Rep Prog Polym Phys Japan 1963;6:163–6.). My comments on this in the rejected manuscript are as follows, with apologies for the references that those well into the situation will recognize:

The following is a quote from [Petropoulos et.al, 3] regarding the work presented in Tamura et al [15].

Quote:

“ Accordingly a study of Stage II absorption enabled Tamura et al [Ref. 28 in 3] to report viscous swelling kinetics practically *coincident* with those exhibited by parallel mechanical tensile creep experiments; thus unmistakably pointing to a swelling relaxation process having a *common* physical origin with that governing mechanical creep (and excluding potential alternative interpretations e.g. in terms proposed in [10,11].”

End of quote.

The references [10,11] in the quote are references [16,1, respectively] in this document (both to Hansen).

One is led by the above quote to believe that Tamura et al [15] actually performed Stage II absorption experiments that paralleled a mechanical study. In fact this was not done.

Tamura et al [15] studied tensile creep in atactic polystyrene that had been saturated in advance to given equilibrium amounts with benzene at two temperatures (25°C and 35°C). Retardation (relaxation) times for use in a mechanical (Voight) model for stress relaxation are reported. There are no absorption experiments. There is no report of viscous swelling kinetics.

The experiments reported by Tamura et al [15] were all done at concentrations low enough so the system was below the glass transition temperature, but the results have been applied to the second stage of absorption where the concentrations would be somewhat higher, and presumably above the concentration giving a glass transition temperature. This is true for the data presented in [2 Hasimi A Stavropoulou A Papadokostaki KG Sanopoulou M. Transport of water in polyvinyl alcohol films: effect of thermal treatment and chemical crosslinking. Eur Polym J 2008;44:4098-4107] as an example. The consensus of researchers at that time was that stress relaxation was a viable explanation for the second stage of the absorption curves, that is, where the concentrations are highest.

Quoting from Tamura et al [15]:

“Recently, Long and Richman5) have shown that the two-stage absorption curves can be derived from Fick diffusion equation with the concept of variable surface concentration. They expressed the dependence of surface concentration, c_1^s, on time by the following equation: $c_1^s = c_1^i + (c_1^\infty - c_1^i)[1 - \exp(-\beta t)]$. Here, c_1^i is the concentration at the quasi-equilibrium and is only a small fraction of the final equilibrium value c_1^∞, and β is a rate parameter.”

The authors find that:

“These results, though yet of a preliminary nature, may give clear evidence that the second portion of the two-stage absorption is primarily caused by slow rearrangements of polymer network chains.”

Tamura et al [15] find a correlation between the measured mean retardation times and the concentrations at which they were measured and there also is a correlation with $1/\beta$. This is interpreted by Petropoulos and coworkers as proof positive of the stress relaxation mechanism at much higher concentrations in the second stage. The Long and Richman article above is cited in [1] as reference [15], and here as [17], because it presented the possibility that both the prevailing stress relaxation mechanism and an exponential increase in the surface concentration could correlate the two-stage absorption behavior. That this latter proposal could be the case can also be seen in Crank [18] where several two stage curves are calculated for different rates of exponential increase of the surface concentration. A significant mass transfer coefficient leads to an exponential increase in the surface concentration, in agreement with the possibility expressed by Long and Richman. This was not recognized at the time, however. The β (retardation times) could in principle equally well have been used to estimate the exponentially rising surface concentration and resulting absorption.

CONCLUSION:

The first section is not changed from that posted on May 20, 2012. The second section was added on July 4, 2012.

Section 1:

The diffusion community has been too diverse for so many years that there are many, including myself, who think they have the answer. This means one will continue to discuss with reviewers in an atmosphere more akin to religion than to science. I am sorry my presumably last attempt to publish in the scientific literature in the area was rejected. I think the diffusion community is the loser in the long run. I naturally accept this, and recognizing the difficulties of publishing, have decided to refrain from so doing in the future. This powerpoint presentation with comments is my last effort in the area. The last remnant of regret is not having conclusively treated the older Thomas and Windle data. I do not have copies of these but I do have suspicions of lack of relevant data. This would mean guessing at some parameters, and these guesses would always be open to criticism, witness the two reviewers above.

Section 2:

I had some exchanges of emails with Prof. Vesely, Oxford University, who previously had questioned my thoughts on the Thomas and Windle results. I decided to look at what Windle had included in a chapter in Comyn's book *Polymer Permeability*. It turned out there were enough data to do the calculations for the Case II example in this chapter. I sent a temporary sketch of this to both Prof. Vesely and to Prof. Abbott. Prof. Abbott then supplied me with the Thomas and Windle articles that were relevant. I could then correlate data for several of the experiments and interpret them in the usual way. The report that can be downloading elsewhere from www.hansen-solubility.com is much more complete in analyzing the Thomas and Windle data than what is given in this presentation. It has the title "Reinterpreting Case II Absorption in Polymers – An Examination of the Thomas and Windle Data."

I do not know what to do with all of this at this point.

Charles M. Hansen