HSP PowerPoint presentation

Comments to accompany the HSP PowerPoint presentation:

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.

2. The wisdom of why one who could be retired chooses not to do so. The HSPiP eBook/software has been used very frequently to produce the figures and data used in this presentation.

3. Summary of the Hansen solubility parameters (HSP) concept emphasizing that the energy of evaporation must be accounted for, no more or no less, and is indeed accounted for quantitatively by the three HSP parameters. There is also an inherent emphasis on the importance of the cohesion energy density rather than the strength of a given type of bond. δ is the Hildebrand or total solubility parameter.

4. The methods used to calculate the D-parameter. The corresponding state reference is the reduced temperature ($298.15/T_c$) for hydrocarbon solvents (aliphatic, cycloaliphatic or aromatic).

5. The plot used for the dispersive (London, Van der Waals, hydrocarbon) energy. One needs the critical temperature, T_c, and the molar volume of the solvent in question to use this kind of figure.

6. The equations used for the P-parameter, depending on available data.

7. The methods used to estimate the H-parameter. The Panayiotou method is available in the HSPiP software. More recently the Y-MB method (Yamamoto – Molecular Breaking) has become available in the HSPiP software. This is based on correlations with the HSP solvent data file. Both of these methods predict all three HSP parameters. The Hoy and Van Krevelen approaches are also included in the HSPiP software for completeness, even though they are not the preferred methods.

8. Summary of important equations leading to the present state. The importance of the Patterson/Delmas contribution is to show that negative heats of mixing are, in fact, predicted by the solubility parameter theory, thus refuting the commonly held belief that negative heats of mixing are not possible with this theory. Patterson/Delmas differentiated the free energy equation, which includes both the combinatorial factors (entropy effects) and the noncombinatorial factor to show this.

9. Important relations summarizing the further development of the solubility parameter concept. The "4" in the key equation for Ra is justified/supported by many (thousands of) successful correlations, also for surfaces, as well as appearing in the Prigogine theory of polymer solutions, and earlier in the Lorenz-Berthelot theory of mixtures. The geometric mean assumption is necessary to arrive at these results. The use of the geometric mean is thus experimentally

confirmed for hydrogen bonding effects. In the past only dispersive energies were accepted as following this average. Later it was accepted that the dipolar energy contributions to the cohesive energy also followed this average. All three of the energy types leading to the HSP are now shown to follow this geometric mean average. But then why should the directional molecular polar forces and the directional molecular hydrogen bonding forces differ in this respect?

10. Please refer to Chapter 3 in the handbook or to original articles having Prof. Panayiotou as author.

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12. Agreement between the Panayiotou approach and that of Hansen. See Chapter 3 in the handbook.

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14. A reminder that it is the condition where the free energy change is zero that determines the boundary of the HSP (solubility) spheres as they are usually determined. The HSP calculation for the chi parameter is also given. Some authors "intuitively" omit the 0.25 factors. This could lead to problems when considering or comparing with systems where others have used the 0.25 factors. The validity of the "4" discussed above and in Chapters 2 and 3 of the handbook would appear to be decisive for its use.

15. An overview showing the relative positions of common solvents in a two dimensional P-parameter versus H-parameter plot.

16. The sketch shows how to use the HSP data to predict solubility, chemical attack, barrier properties, etc.

17. Summary of key equations.

18. A plot showing what happens if the "4" is not considered. The result is a spheroid.

19. A sketch showing the effect of increased temperature.

20. Data from Chapter 10 of the handbook illustrating calculation of HSP at higher temperatures. Dr. Laurie Williams calculates HSP for supercritical carbon dioxide.

21. A list of some of the types of materials that have been assigned HSP.

22. A list of uses for HSP.

23. HSP sphere for cholesterol showing that synergism can occur, and does occur, when the given non-solvents are mixed. The beneficial effects from (small) amounts of ethanol for

potentially reducing a (human) cholesterol problem can be predicted if one considers n-hexane as a model for the lipid layers in the human body. Very small additions of ethanol to n-hexane result in complete cholesterol solubility. This plot also confirms experimentally that the HSP split into three parameters is required to explain the synergism found in mixtures of the three solvent pairs. The single Hildebrand parameter could not do this, since the values for ethanol and 2-nitropropane are so close.

24. Boundary solvents with a maximum of cheaper hydrocarbon solvents have traditionally been mixed with a minimum of oxygenated solvent to just achieve the required solubility. This is also an advantage in terms of improved pigment dispersions and improved pigment dispersion stability as shown in Figure 27.

25. An older figure shows that xylene (x) plus n-butanol (b) mixed in about equal amounts can be used, perhaps with a small amount of a third solvent with a higher P-parameter, to dissolve almost any commonly used binder in the coatings industry. Parenthetically it should be noted that there are also HSP applications in water-reducible coatings including compatibility of components, the function and distribution of coalescing solvents, and surface effects related to adhesion and dispersion.

26. It has been possible to dissolve two incompatible polymers in a mixture of two non-solvents. Attempts to form a film on solvent evaporation are doomed to failure, but the solution is clear.

27. Pigment dispersion and pigment dispersion stability are affected by choice of solvent. The goal is to have a larger molecular weight species (the binder) adsorbed onto the pigment surface to help keep the particles apart.

28. Those solvents called designer solvents are not sufficiently good, having very low D-parameters, to dissolve many soils in cleaning operations. Dr. John Durkee in Chapter 11 of the handbook describes ways to use them in effective azeotropes. The figure shows that Ra less than about 8 is required to provide a suitably clean surface in most cases. This supports other experience that this is a useful rule of thumb for solubility or not. One can also compare with the HSP data for Ro in Table A.2 in the handbook.

29. The bitumen/asphalt used in road surfacing must have good properties at both high and low temperatures. This is accomplished by adding an SBS polymer such that it is only marginally compatible. Per Redelius in Chapter 9 of the handbook describes how the HSP of bitumen/asphalt can be adjusted appropriately by blending bitumen/asphalt from different sources to accomplish this. It is also confirmed that crude oil and related products are not colloidal mixtures, but are true solutions with components having widely different HSP.

30. Jean Teas very rapidly recognized the value of the division of the Hildebrand parameter into the D-, P-, and H-parameters, and his triangular plots gained wide usage already in the late 1960's. The methodology for doing this is given in the figure.

31. Teas plots are frequently used by those who conserve (older) paintings since this methodology appeared in a book by Torraca that has traditionally been used during their

schooling. This Teas plot shows how a mixture less harmful than toluene, for example ethanol plus cyclohexane, can be used to remove the Paraloid B-72 (Rohm and Haas) varnish from a painting without attacking the painting itself. Teas plots are available in the HSPiP software.

32. The solubility of Carbon-60 can be correlated using HSP. The HSPiP eBook/software has a version of this plot that includes still more data.

33. The solubility and stress cracking of the COC (cylic olefinic copolymer) Topas 6013 (Ticona) can be portrayed in a three dimensional plot to show that the stress cracking agents are those that swell the polymer, having RED numbers slightly greater than 1.0 for the HSP correlation based on solubility. An alternative plot of this same data is given in the next figure.

34. There are three regions in this plot of RED number for a solubility correlation versus molar volume of the solvent. The COC polymer is dissolved in the lower region. Solvents in the upper region have RED numbers that are so large that there is no significant effect. Solvents in the intermediate region can give environmental stress cracking (ESC). Those solvents that do not give ESC, that might be expect to do so, have cyclic (aromatic) or branched chain structures. Some of these in fact do not even enter the polymer on extended exposure or only slowly with a sigmoidal-shaped absorption curve (absorbed amount versus square root of exposure time). See Chapter 16 of the handbook. This is proof positive that a surface entry effect can be dominant in solvent absorption into polymers. Later in the presentation it will be shown (again) that a significant surface condition can lead to sigmoidal absorption curves, as well as to what have been called Case II and Super Case II absorption behavior. These are found when the surface condition becomes still more significant than in the sigmoidal case.

35. Polycarbonate is especially prone to ESC. There are no dissolving solvents for this polymer. A correlation was made based on the critical strain leading to ESC, using solvents with critical strains less than 0.6% as "good". This plot shows that higher strain (key under the figure) allows still more solvents to give ESC. The ESC phenomena occur for tensile stress only, and factors such as eliminating stress concentrating sites and appropriate design, as well as lower inherent stress from fabrication, are all important to reduce this kind of problem. The recommendation is to try to avoid contact with solvents where the HSP match is too good.

36. Materials nominally called "carbon" can have a wide variety of surface and solubility properties depending on raw material source and degree and kind of oxidation of the surface, as well as the degree of surface coverage if there is a special treatment.

37. The one end of a surfactant can have very low HSP (hydrocarbon chains) while the other end can have very high HSP (in this case lithium). When the surfactant is also considered to be a solvent, it is the total HSP that is important.

38. Spontaneous spreading and film retention on surfaces can also be correlated with HSP. The ASTM wetting tension test corresponds to the boundary between regions B and C on this plot. The boundary between regions A and B is presumed to be more important for adhesion phenomena.

39. Fibers can be readily characterized by HSP either by long-time suspension or by normalized sedimentation rate measurements in a well-chosen set of solvents. The same is true of pigments. Nano-sized materials are imminently suitable for HSP characterization since they sediment so slowly compared with untreated glass fiber, for example, where sedimentation is so rapid that characterization is difficult, if not impossible, by this method. See Chapter 7 in the handbook for more details. It is fortunate that carbon fibers and glassy carbon can have essentially the same HSP, although this may differ from case to case depending on number/density and kind of oxygen groups in the fiber surface. Glassy carbon is often used as a model material to study the behavior of carbon fibers. It might also be added that the HSP of a typical epoxy material is also (fortunately for good adhesion) similar to the HSP of these carbon materials.

40. Self-assembly can be controlled by suitable choice of materials. In this case use of a single solvent can result in a homogeneous solution that will spontaneously separate into a primer layer and a topcoat layer shortly after evaporation starts. The polymer with the lower surface energy will be the topcoat.

41. Thixotropic paints make use of partial solubility of polyamide block segments attached to polyesters (alkyds). When the solvent is mineral spirits, the polyamide blocks are not soluble and associate, but this association is easily broken by modest shear forces during brushing or by spraying. The broken polyamide to polyamide associations are readily reestablished when the shear forces are reduced. Additions of alcohols can destroy the effect since the solvent can then truly dissolve the segments that are to associate because of insolubility. Such effects are also found in proteins with so-called "hydrophobic bonding". This type of "bonding" can also be used to regulate rheology in water-reducible paints although any solvent content can disturb the effect if it tends to locate/associate at the water-insoluble blocks. As discussed in detail later, DNA is "bonded" at the base sites, not by hydrogen bonds, but because these segments are simply not soluble in water. The base segments seek regions with similar HSP when they cannot reside in the aqueous phase.

42. PTFE is not a particularly good barrier for solvents and gases with low molecular volume. The figure shows a HSP correlation of breakthrough times of less than three hours for a body suit (previously) used by the United States Coast Guard. There is a region at low molecular volume, V, where breakthrough is almost independent of the RED number. At higher V breakthrough is not found regardless of the RED number. There is an intermediate region where monomers having terminal double bonds have breakthrough times of less than three hours whereas solvents that do not have this characteristic, but do have similar HSP and size, are stopped. This clearly points to a unidirectional preferred diffusion process in the direction of least resistance (needlepoint).

43. HSP for drugs used in chemotherapy were calculated to help confirm suitable glove selection for handling them. It was striking that most of these drugs have very similar HSP, or had segments or organic parts with these same approximate HSP. This led to the studies and analyses in the following figures.

44. Breakthrough correlations of the common glove types with HSP are given in the handbook and in the software for the HSPiP. It can be seen that butyl gloves would be very good for

handling cyclophosphamide since the RED numbers are much greater than 1.0 for each of the correlation types. Butyl rubber does not allow the required dexterity however. These HSP correlations consider breakthrough at less than 20 minutes as "good" (meaning inside the HSP sphere with Ra less than Ro), less than 60 minutes as "good", or less than 240 minutes as "good", respectively. A plot of respective RED numbers versus these times for the Nitrile glove type was interpolated to 45 minutes for the breakthrough time. This can then be adjusted upward for larger V, but represents a minimum to help in decision making. The diffusion/permeation software in HSPiP have recently been used to find the concentration dependent diffusion coefficients required to simultaneously yield reported breakthrough times and steady state permeation rates using film thickness and equilibrium swelling as inputs. A chapter on this is planned for the next edition of the HSPiP.

45. This correlation for permeation through the biological membrane called viable human skin is given in anticipation of what follows. The HSP found here are very close to the average HSP found for the cytotoxic drugs used in chemotherapy. This makes good sense since the cytotoxic drugs must pass through biological membranes, in this case cell walls, in order to be effective. Unfortunately most studies of skin permeation do not include a sufficiently broad selection of HSP in the test solvents used, particularly neglecting the high P-parameter region. If such studies were implemented they would be expected to confirm this correlation.

46. At this point there is a short excursion in the presentation into diffusion phenomena where the software provided with the HSPiP has confirmed the need for the including a surface condition for appropriate solutions to the diffusion equation (Fick's Second Law). This figure matches data reported in the literature (Hasimi A, Stavropoulou KG, Papadokostaki M, Sanopoulou M. Transport of water in polyvinyl alcohol films: Effect of thermal treatment and chemical crosslinking. Eur Polym J 2008;44:4098-4107) to show that for absorption to concentrations significantly over 10% water in polyvinylalcohol, in this case to 0.748 volume fraction water at equilibrium uptake, the surface condition completely dominates the process. The S-shaped curve, sometimes called sigmoidal absorption, is not an artifact or an anomaly. Such S-shaped absorption curves are predictable using reasonable values for the surface mass transfer coefficient, h, and concentration dependent diffusion coefficients as shown in the figure. See also Chapter 16 in the handbook.

47. The diffusion coefficients measured over the entire concentration range for chlorobenzene in polyvinylacetate that can be considered typical for solvent diffusion in many rigid polymers (See Chapter 16 in the handbook). These are used in this figure, and the one that follows, to show that the phenomena called Case II and Super Case II absorption are not anomalies. These are fully predicted using these reasonable, experimentally determined diffusion coefficients and reasonable values for the surface mass transfer coefficient. In Case II type diffusion the uptake to an equilibrium concentration (here 0.6 volume fraction) is linear with linear time rather than with the square root of time (so-called Fickian diffusion). Slight bending of the uptake curve either upward or downward at the start is found for different values of h. It is concluded that Case II should be called Fickian diffusion since it follows a simple solution to Fick's second law (the diffusion equation).

48. Super Case II, where the absorption takes place at rates faster than with linear time, is demonstrated in this figure as being caused by a still more significant surface condition than that typical of Case II type diffusion. At some condition in some polymers there is no solvent absorption, even though this is predicted by HSP. This effect was seen for the COC polymer discussed earlier where solvents with aromatic rings are simply not absorbed. Other solvents are absorbed by this polymer with the characteristic S-shaped curve indicating some degree of control by the surface condition. Likewise as molecular size goes up, it becomes more and more difficult to absorb into any polymer surface, and at some point increasing V will dictate a significant surface condition. It appears proven beyond doubt that Case II and Super Case II are not anomalous. It is concluded that both Case II and Super Case II should be called Fickian diffusion since this behavior follows a simple solution to Fick's second law (the diffusion equation). It should be recognized that the surface condition can be important when solving the usual diffusion equation (without any added terms to account for "time-dependent" diffusion, for example). The software provided in the HSPiP can handle these situations as demonstrated in this and previous figures.

49. Coming back to the HSP topic, this figure shows that organic salts have experimentally determined HSP that are higher than the HSP of either the acid or base that make them up.

50. So-called ionic liquids have been assigned HSP in a chapter planned for the next edition of the HSPiP eBook and software package. Some results are given here based on a collection of literature data. These HSP are slightly higher than what is typical of what might be called reaction solvents (DMSO, DMF, DMAc, NMP, gamma butyrolactone, etc.). The methods useful for assigning these include solubility in organic solvents, measuring intrinsic viscosity in organic solvents, and measuring reaction rates. The important thing in each of these methods is to include a sufficient number of test solvents and most certainly a sufficient number with relatively high P-parameter. This is almost never done, and most of the literature studies are close to being worthless for the purpose of assigning reliable HSP for this reason. When simply averaging HSP for test solvents, perhaps weighted by their response, one must be aware that values outside the HSP range of the test solvents cannot be found. This is particularly problematic when the sample has a high P-parameter and no solvents with high P-parameters are included in the study. This problem also occurs for most skin permeation studies. Please be very careful to include sufficient and suitable test solvents in your studies! The HSPiP software can also be used to analyze data obtained by any of the methods discussed here.

51. Coming back to carbon dioxide (or other gases), one can determine their HSP based on solubility in test solvents, or from a collection of data from the literature as is done here by Dr. Laurie Williams (See Chapter 10 in the handbook). The good solvents are those with solubility greater than the so-called theoretical value. These are shown in the figure. Who would have expected that this grouping should ever have been found and exhibit HSP similarity to carbon dioxide?

52. Once the HSP for carbon dioxide (or other material) have been found one can arrange the test solvents or the entire solvent file (more than 1200 solvents) in order of best to worst (or vice versa). In this case the correlation is perfect with all "good" solvents having Ra less than Ro.

53. The HSP at room temperature for carbon dioxide leave some important questions unanswered. The fact of no dipole moment and a significant P-parameter is one. Experience has also shown that other solvents with zero dipole moment behave as expected with a P-parameter found with the Beerbower group contribution method (or perhaps other method). So it appears not to be such a difficult problem to explain the significant P-parameter, especially if induced dipoles are considered. The significant H-parameter in the absence of any hydrogen atoms requires terminology recognizing the electron exchange that occurs rather than calling whatever is not D-parameter or P-parameter as H-parameter. Some would prefer to divide the H-parameter into parts (acid and base), but a completely satisfactory procedure to do this does not seem to be currently available. The radius for this carbon dioxide correlation is very small, meaning very good matches in HSP are required for the good solvents.

54. The HSP data reported in the previous figures for carbon dioxide are summed up here with a three-dimensional figure that clearly shows sharp boundaries.

55. This figure lists examples of materials that have been assigned HSP. It may be that some revision in some of these values will take place, but they are not thought to be very much in error.

56. Chemicals for which HSP are available. These HSP allow prediction of how these will interact with any other material with known or estimated HSP.

57. It was stated many years ago that brominated fire retardant additives (or unreacted monomers) would follow the environmental path of pentachlorophenol since they have similar HSP. Other predictions of the behavior of TBBPA, in this case, are ready absorption into both plant material and human skin.

58. The HSP for dioxin clearly suggest ready absorption into human skin (slowed somewhat by the large size) and plant matter. These are in agreement with the human blistering and plant damage/death found in the Sevesso incident.

59. Nature has arranged the ultrastructure of wood in a manner consistent with the HSP of the components. Hemicelluloses function in a manner comparable to surfactants or coupling agents with HSP intermediate between the HSP of lignin and the HSP of cellulose. There are short side groups on the hemicelluloses. Some of these have HSP approaching the HSP of lignin, but there is poor compatibility. This allows for motion without tearing structure apart on a permanent basis when movement is required (wind). There are also short side chains with alcohol groups that orient toward the cellulose fibers where there also are alcohol groups, and the binding is stronger. These physical bonds are weakened with water exposure, since water will tend to locate in these higher HSP regions, and not in the lignin.

60. Water appears to have a chameleonic behavior adjusting to the given environment with structures or perhaps lack of same at higher temperatures. At the normal boiling point the H-parameter for molecular water is high (42.3 MPa$^{1/2}$). The HSP for molecular water also appear useful for subcritical water and perhaps in other situations. At room temperature the HSP correlations considering total miscibility as indicative of a "good" solvent or even 1% miscibility

as being indicative of a "good" solvent, are consistent with 6 molecules of water being associated by hydrogen bonding into a rather unique entity. The HSP for these correlations are consistent with this model since larger entities have larger D-parameters, and the P-parameter is essentially unchanged. The H-parameters suggest 6 molecules are associated in some way since this is approximately given by $(42.3/16.5)^2 = 6.3$ as a ratio of molar volumes for the associated species versus molecular water.

61. The reference cited lists the activity of the given compounds with respect to DNA in the order given. A correlation with HSP was made considering the green chemicals as "bad", the yellow chemicals as being too difficult to work with reliably for present purposes, and the red chemicals as being "good". The result of this correlation is seen in the next figure.

62. The chemicals are ranked in exactly the same order as in the previous figure, giving considerable evidence that the HSP for DNA found in this way are not too far different from what might be found with a significantly larger data set. The results are reported and discussed in the next figure.

63. The (perhaps) surprising result of this correlation is that the D-parameter and the P-parameter are about equal and both much larger than the H-parameter. Converting these solubility parameters to cohesive energies, shows that only about 14% of the cohesive energy of DNA is attributable to hydrogen bonding. The frequently used figures showing hydrogen bonding as the primary source of the "bonding" in DNA are completely misleading! Well, what then is the reason for the "bonding"? The next figure answers this question.

64. Not even one of the 4 traditional model compounds for the 4 base segments of DNA is soluble in water. Therefore the base segments of DNA are simply not soluble in the continuous media (water) and precipitate/associate to regions of similar HSP. Nature has arranged this precipitation/association such that there are matching pairs with the double helix structure. There is no reason to invoke hydrogen bonding as the dominant factor for this "bonding". The average of the HSP of these four bases is used in the following figures as being characteristic for the adsorption/association characteristics of the DNA segments, recognizing that the variation in the estimated HSP among them could also be important in given cases.

65. This figure shows that the HSP average of the DNA base segments is very similar to the average of the chemotherapy (cytotoxic, cell membrane penetrating) drugs, and that these HSP are very similar to the HSP found for rapid permeation of viable skin. This similarity strongly suggests the mechanism of the function of the drugs is rapid cell wall permeation with preferential adsorption at the DNA base sites. Synergism is mentioned. Mixtures of given chemicals with alcohols have average HSP close(r) to the HSP of the DNA bases (and cell wall permeation potential) than do either component. An example is given in the following.

66. This figure shows that the HSP for DNA, proteins, and fatty material are significantly different, such that given chemicals will have different affinities for these common biological materials.

67. The HSPiP software was used to provide the green sphere correlation for the chemotherapy drugs. This is a small sphere with an excellent data fit. In agreement with previous figures this correlation will also resemble those that would be found or have been found for skin permeation and the DNA bases. There is similarity among all of these. The red points in the plots are for dioctyl phthalate and ethanol, with the red point in the middle being a mixture of the two that has obvious synergism compared with the HSP of the drugs. This strongly suggests that such mixtures can be potentially more harmful than either of the components alone. The warning for pregnant women to avoid use of alcohol may be partly justified by the condition shown in this figure.

68. The solvent optimizer in the HSPiP software was used to produce this figure. It can be seen that a mixture of methyl paraben (66%), dioctyl phthalate (20%) and ethanol (14%) has HSP that are effectively identical to the target value – the HSP average of the chemotherapy drugs. The methyl paraben is already within the green sphere of the previous figure.

69. The solvent optimizer in the HSPiP software can be used to optimize solvent mixtures for many purposes (REACH, VOC, cost savings). A special case where it may be found helpful is to locate mixtures of solvents suitable for NMR analyses, such that a sample can be dissolved suitably, where it could not be in any of the useful pure NMR solvents alone.

70. The HSPiP software includes a calculation of retention times for HPLC analyses as well as an analysis of IGC data to find the HSP rather than just the Hildebrand parameter (which is not useful for mixtures or in reality anything but hydrocarbon solvents).

71. This figure is a repeat from the start of the presentation to emphasize what has been done with theory based on the interaction of the molecules of a pure liquid with each other. It also emphasizes again the requirement that the total cohesive energy measured by evaporation of the liquid in question is what is divided into three separate, independent parts. Evaporation breaks all of the bonds holding the liquid together, including hydrogen bonds. It is also emphasized that the dispersion forces are not oriented in any particular direction, while the polar and hydrogen bonding interactions are inherently molecular and oriented with (directional) association among the molecules. Just look at what has been done with this simple approach!

72. This summary figure could be expanded with still more examples, but then the readability would suffer. Again, just look at what has been done!

73. The HSPiP software can do many more things than are included in the presentation.

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