Key to tables

Name

It cannot be stressed too strongly that the name of a solvent should be easily used and recognized by all, from the graduate in the research laboratory to the plant operator who may have difficulty in reading a language which is not his or her own. Once a name, or worse still a set of initials, has become standard usage on a site it is very difficult to make a change.

The use, for instance, of IPA for isopropanol or isopropyl acetate of tri or TC for trichloroethylene or 1,1,1-trichloroethane can lead to errors that are very serious. Highly toxic benzene can all too easily be confused, in dealings with Europe, for benzin, a comparatively low toxicity material.

Hazchem code

This is a code informing U.K. emergency services of the action to be taken when dealing with transport emergencies and can be a useful method of labelling storage tanks on a site where many different solvents are handled. It consists of a number and one or two letters (see Table 1).

Explanation:

- It can be seen that breathing apparatus (BA) should be available in all cases.
- E after the code indicates that evacuation of people should be considered.
- 'Contain' means that any spillage should not enter water courses or drains.
- 'Dilute' means that a spillage should be washed away to drain with plenty of water.

Table 1 Hazchem codes

Number	*Firefighting medium*
1	Water jets
2	Water fog
3	Foam
4	Dry agent

Letter	*Explosion risk*	*Personal protection*	*Action*
P	Yes	BA + Full	Dilute
R	No	BA + Full	Dilute
S	Yes	BA + Gloves	Dilute
(S)	Yes	BA (fire only) + Gloves	Dilute
T	No	BA + Gloves	Dilute
(T)	No	BA (fire only) + Gloves	Dilute
W	Yes	BA + Full	Contain
X	No	BA + Full	Contain
Y	Yes	BA + Gloves	Contain
(Y)	Yes	BA (fire only) + Gloves	Contain
Z	No	BA + Gloves	Contain
(Z)	No	BA (fire only) + Gloves	Contain

Molecular weight

On many occasions the effectiveness of a solvent will be compared on a molar rather than on a weight or volume basis.

Purchases are, however, always by weight or by volume so that a low molecular weight solvent may have a significant cost advantage in use. On the other hand the low molecular weight of water, present in all solvents at parts per million level at least, may be surprisingly damaging when processing, for instance, high molecular weight Grignard reagents or urethanes. When a solvent is used at a high mole fraction, as for instance in extractive distillation where solvent mole fractions of 0.9 are common, the cost-effectiveness of a low molecular weight solvent such as monoethylene glycol can be remarkable in comparison with some other entrainers.

Boiling point

Many operations with solvents involve boiling the liquid solvent and this requires a heating medium (hot oil or steam) at a temperature 15 or 20°C above the solvent's boiling point. It should be borne in mind that some solvents (e.g. DMF and DMSO) are not stable at their atmospheric boiling points and if necessary must be boiled at reduced pressure.

The normal factory steam pressure is about 10 bar and this should yield a temperature of 160°C at the point of use and boil a solvent at 140–145°C. If a higher temperature than this is necessary hot oil, stable to 300/320°C, will provide heat usable at 270/280°C. A solvent in which an involatile solute is dissolved will boil at a higher temperature than the pure material. Typically, the boiling point will be raised from 140 to 150°C if the mole fraction of the solvent in the mixture is reduced by 20%.

If solvents need to be separated by distillation it is not a reliable guide to assume that because their boiling points are widely different the split will be easy, particularly when water may be present.

Freezing point

Several solvents (e.g. dimethyl sulphoxide and cyclohexanol) are solid at ambient temperature and therefore need to be stored and handled in heated storage and pipelines and particularly with heated tank vents.

For certain materials, such as benzene, that combine a high freezing point with high toxicity, the thawing of blocked pipelines can be a difficult and potentially dangerous task. It should be noted that some solvents even when solid give off an explosive vapour. Thus, the vapour pressure of solid benzene is given by

$$\log_{10} p\ (\text{mmHg}) = 9.85 - 2309/T$$

and the concentration of benzene at 0°C is 7600 ppm, which is well above its lower explosive limit.

Air-cooled condensers can be severely damaged if some of their tubes become blocked while others are still handling hot vapour causing high stresses in the tube bundle. Drums of solid flammable solvents pose handling and emptying problems.

Specific gravity

Storage tanks and their surrounding bunds are normally tested using water and are designed for a liquid of density 1.0. While most solvents have specific gravities below this, the chlorinated solvents are much denser (e.g. perchloroethylene, specific gravity 1.62) and tanks may need to be derated if switched to storing such materials.

For the same reason 200-litre drums of chlorinated solvents may be too heavy to handle, either manually or palletized on a fork-lift truck and existing pumps may be overloaded.

On the other hand, a change to a less dense solvent may mean that a full tanker load of solvent cannot be accommodated in an existing tank built with a denser solvent in mind.

When compositions are quoted as percentages it is important to know whether these are by mole, weight-by-weight (w/w), volume-by-volume (v/v) or weight-by-volume (w/v) and, in the last case to appreciate that the sum of the components will not add up to 100.

Liquid expansion coefficient

Organic solvents have an expansion coefficient five to seven times greater than water. The increase in volume when a high boiling solvent is heated from cold to its boiling point is significant and has been known to cause damage in batch-still operations when sufficient ullage has not been allowed.

When purchasing solvents by volume rather than weight it may be necessary to use temperature correction.

Flash point and explosive limits

The lower explosive limit (LEL) of a solvent corresponds to the vapour concentration above the liquid at its flash point at which a source of ignition will set off an explosion. The upper explosive limit (UEL) is the vapour concentration that is just too rich to explode and an 'upper flash point' of a pure solvent can be calculated if the UEL and the Antoine constants are known.

If the atmosphere should be enriched with oxygen it will form an explosive mixture over a wider range than that between LEL and UEL and if the 'air' is less than 8–10% oxygen, depending on the solvent, no explosion can take place at any solvent content. It is common when the likely ambient temperature lies in the range between the two explosive limits to blanket the vapour space in a storage tank with inert gas. For safety a gas with about 3% oxygen is used, but it should be remembered that this 'nitrogen' is not free of oxygen so that solvents that form peroxides very readily (e.g. ethers) can be damaged if pure nitrogen is not used as the blanket over them.

Testing for flash point is carried out using laboratory equipment of a range of designs. Those that are easier to use do not necessarily correspond to the standard test methods laid down by regulatory authorities, but are adequate for internal purposes on site. The standard methods are difficult to use for an inexperienced operator, but all common mistakes tend to give a test result lower than it should be and therefore err on the side of safety. The figures quoted here are ones using the tag closed cup method which tend to give rather lower results than the tag open cup and the Cleveland open cup methods. There is no reliable conversion factor between the various methods.

Mixtures of two or more solvents may, because of the presence of azeotropes, have a lower flash point than their components have separately.

When handling solvent-laden air, as is common in activated charcoal recovery plants, it is normal to operate with a flammable solvent content in the range of 25–40% of LEL. If information on the flash point of a mixture is not available the great majority of solvents have an LEL of 10,000 ppm (1%) with a few in the range of 7000–10,000 ppm. The flash point of straight run hydrocarbon solvents (e.g. white spirit) can be estimated from their initial boiling point (IBP)

$$\text{flash point} = 0.73 \times \text{IBP} - 72.6$$

where both temperatures are in °C. Common practice in United States is to quote petroleum temperatures in °F.

Autoignition temperature

While generally a spark or flame is needed to set a flammable liquid on fire, almost all solvents can be ignited by a very hot surface and some by heat sources that are commonly met on industrial sites such as steam mains, hot oil pipelines and items heated by electricity, including laboratory heating mantles.

Steam pipes routinely have temperatures between 160 and 200°C and may be considerably hotter where high pressure steam is used. Hot oil reaches 300°C or a little higher. Solvents such as ether with an autoignition temperature of 160°C and dioxane (180°C) are therefore liable to catch fire if dripped on to a heating medium line. Their use on a site may require major changes to plant layout. Carbon disulphide has an autoignition temperature of 100°C and cannot safely be used except in a purpose-built plant. The glycol ethers also present a hazard when hot oil heating is used.

Electrical apparatus that is correctly described as flameproof can reach the autoignition points of some solvents and a change of solvent in a manufacturing facility should not take place without this being considered.

Electrical conductivity

When solvents are moved in contact with another phase static electricity is generated. This can occur in a number of circumstances in industrial operations such as

1. A hydrocarbon/water mixture is pumped in a pipe.
2. A solvent is stirred or pumped in contact with a powder.
3. A solvent is sprayed into air.
4. A solvent is contacted with an immiscible liquid (e.g. water) in an agitator.

If the static produces a spark which contains enough energy and if the vapour phase in contact with the liquid is between its LEL and UEL an explosion may occur. It is also possible that a fine mist of flammable liquid below its LEL can be ignited by a static spark.

The chance of such an explosion depends largely on the electrical conductivity of the solvent (see also the section on *Dipole moment*) since a high conductivity allows the charge to leak away. Some solvents have naturally high conductivities and a few develop high conductivity over time in storage, although the latter cannot be relied on as a safety measure. It is also possible to add a proprietary anti-static additive at a level of about 0.15%. Small impurities of alcohols in esters or of inorganic salts can also increase conductivity by orders of magnitude. Freshly distilled water has a conductance of 5.0×10^{-8} siemen, but this rapidly increases as it picks up CO_2 from the air.

The conductivity limit that is usually regarded as safe is 1.0×10^{-10} siemen/cm (100 picosiemen/cm) and above this level it is not necessary to earth the equipment handling the solvent.

Resistivity, the reciprocal of conductivity, is also often quoted and the danger limit in various resistivity units is

100 megohm metre	(MΩ m)
$1.0 \times 10^{+4}$ megohm cm	(MΩ cm)
$1.0 \times 10^{+10}$ ohm cm	(Ω cm).

In general, all hydrocarbons and ethers (but not glycol ethers) have conductivities of 1 picosiemen/cm or less and are liable to generate static electricity. The higher molecular weight esters are at or near the limit. The unit used in the tables is siemen/cm.

The minimum ignition energy of the spark required to cause an ignition for most solvents lies in the range of 0.2–1.5 mJ, but carbon disulphide which has a very low conductivity (1.0×10^{-16} siemen/cm) also has a very low minimum ignition energy (about 0.015 mJ) and a very wide range between LEL and UEL. It thus represents an exceptionally high electrostatic hazard.

Immediate danger to life and health (IDLH)

The IDLH value represents a maximum vapour concentration from which a person can escape within 30 min without irreversible health damage or effects that would impair the ability to escape. Such information is clearly important in rescues and emergencies. It should be compared with the LEL and the saturated vapour concentration at the ambient temperature. Since a spark might cause an explosion in an atmosphere within the flammable range even if the IDLH is greater than the LEL other considerations than the IDLH may prohibit entering a solvent-laden atmosphere.

Occupational exposure standard (OES)

An OES is the exposure to a solvent in air at which there is no indication that injury is caused to people, even if it takes place on a day-after-day basis.

The long-term exposure limit to solvent vapours sets a limit for the average exposure over an 8-h working day. It applies to workers in a plant and not to people living in the neighbourhood.

The short-term exposure limit (STEL) also applies to some solvents and refers to an average over a peak period of 15 min. This is meant for the type of exposure that occurs when cleaning a filter press or doing other regular, but short-term tasks. The average over the peak would be counted as part of the 8-h exposure.

The limits vary from country to country and are constantly being reviewed in the light of experience. The figures quoted in this book are those applicable in the U.K. in 1996 and are expressed in ppm. Where a British figure is not available U.S. TLV-TWA figures are used.

Odour threshold

This is extremely subjective and hard to define accurately. In one reported test 10% of those taking part could detect an odour at 1 ppm while 50% could do so at 25 ppm. At 500 ppm there was still 10% of those exposed who could not detect it.

There is further a difference between identifying a smell and just detecting it so that complaints of an odour are hard to refute reliably and smell cannot be relied upon as a warning of potentially dangerous exposure. This is particularly true in the case of long periods of exposure since the nose becomes desensitized.

The figures quoted here are for concentrations where all the people exposed could detect, although not identify, an odour.

Solvents are not, as a class, very odiferous materials and few can be detected at much below a 1 ppm level unlike mercaptans (which can be smelt at the low ppb level), sulphides and aldehydes. The latter are often detectable in solvents that have been recovered and recycled and make such recovered solvents unacceptable for use in household formulations.

Some solvents, such as dimethylformamide (DMF), have very low odours themselves but contain trace quantities of impurity (dimethylamine in the case of DMF) which are much easier to detect. Others, e.g. dimethylsulfoxide, produce very unpleasant smells when they are degraded biologically so that even small quantities getting into an aqueous effluent are unacceptable.

Saturated vapour concentration (SVC)

The concentration of vapour in equilibrium with liquid (or solid) solvent is important for a number of reasons:

1. Fire and explosion.
2. Toxicity.
3. Smell.
4. Loss in handling.

Vapour concentration can be expressed in mgm/m^3, ppm or %. The former lends itself to ventilation calculations where the quantity of solvent being evaporated into a body of air is known.

Both ppm and percentage figures are based on volumes of solvent vapour in air and the conversion is given by

$$\text{ppm} = \text{mgm/m}^3 \times 24.04/\text{solvent molecular weight}.$$

All the SVC quoted here are at 21°C (equivalent to 70°F).

1. *Fire and explosion*. The concentration leading to a fire hazard is very much greater than that leading to a health hazard. It is unusual for someone exposed to a fire hazard not to be able to detect solvent odour by nose although, since all solvents are denser than air, the concentration at floor level may be very much greater than that at head height.

2. *Toxicity*. This is discussed elsewhere. Above the normally quoted health levels asphyxiation can take place at an SVC of about 150,000 ppm. A high concentration of inert gas (or CO_2) used for blanketing the vapour space in a tank can also be dangerous in this way.

3. *Smell*. This is discussed in the section on *Odour threshold*.

4. *Loss in handling*. Every time a bulk liquid is transferred between road tanker and storage tank or between storage and process there is a potential discharge of vapour. In addition, solvent vapours are discharged when the storage tank 'breathes' with the daily change of temperature.

Increasingly it is becoming unacceptable that this discharge goes directly into the atmosphere and the alternatives are to return the vapour to the vapour space of the vessel from which the liquid comes or to pass the solvent-rich ventings to recovery or destruction. The linking of vents and recovery can become very complicated if more than one solvent is involved in the system and destruction of the solvent in the ventings before their discharge to atmosphere is the most common solution. The loss of solvent is no greater than it would be if the ventings were discharged directly but, to design a destruction plant, the amount of discharge must be known. The most volatile solvents (pentane, ether, dichloromethane) can lose 0.3% of the liquid transferred on each occasion and in a good recovery system the handling loss can be the largest contribution to the total losses of solvent.

Vapour density relative to air

This is the ratio between the molecular weight of the solvent and the molecular weight of air. Apart from methanol which has the lowest vapour density, all organic solvents are much heavier than air.

This means that spillages, whether on a small scale in the laboratory or on a large scale in an industrial plant, will give rise to vapour at a low level. Ventilation should therefore be designed to draw from this level and tests for flammable or toxic concentrations should be made at a low point.

Heavy vapours can spread for long distances in ditches, pipe tracks and drainage pipes and can accumulate in bunded areas, particularly if the bund walls are high. The manual clearing of sludges and deposits in the bottoms of storage tanks which have contained low-flash point solvents is particularly hazardous if low-level ventilation is not provided.

Photochemical ozone creation potential (POCP)

POCP is an arbitrary scale of atmospheric chemical activity based on ethylene at 100 and the very stable organics at 0. The 'natural' products such as alpha-pinene and dipentene have a POCP of about 50.

A significantly large contribution to the total of volatile organic compounds (VOCs) in industrial countries is derived from the use of solvents. Since VOCs are an essential ingredient of smog both legislation and public opinion will lead to the choice of solvents which have a low POCP.

This is particularly true for paints and for domestic uses where recapture and recovery of the used solvent or its destruction before discharge are impractical. Since there is little correlation between the toxicity, evaporation rate, solvent power and POCP of solvents this entails a further independent restriction to the choice of solvent for domestic purposes.

The POCP should not be confused with the ozone depletion potential (ODP) which depends on the extreme stability of various halogenated solvents in the atmosphere, but, because POCP is a measure of reactivity in the complex chemistry of the lowest level of the atmosphere, solvents with a high ODP (see Table 2) do have a very low POCP.

Table 2

	POCP	*ODP*
CFC113		0.80
Methylene chloride	0.9	<0.05
1,1,1-Trichloroethane	0.1	0.15
Chloroform	1.0	
Perchloroethylene	0.5	0
Carbon tetrachloride		1.04
Trichloroethylene	6.6	0

The class of solvents with particularly high POCP is made up off aromatic hydrocarbons with methyl sidechains such as trimethyl benzenes and the xylenes. Legislation has restricted their use in Los Angeles for many years and their widespread use in paint formulations is steadily being reduced. Developments in the resins used in paints will reduce the proportion of solvents and demand increased use of more sophisticated solvents and of water in their place. If such improvements cannot replace, say, xylenes, careful fractionation can, at a price, reduce the POCP as Table 3 shows. Since *m*-xylene is usually the most common isomer in solvent C_8 aromatics, the improvement may be considerable.

Table 3

	POCP
Ethylbenzene	59.3
o-xylene	66.6
p-xylene	88.8
m-xylene	99.3

Methyl sidechains on paraffins or naphthenes do not have the same harmful effect. The replacement of acetone (POCP 17.8) by methyl acetate (POCP 2.5) or the use of isobutyl acetate (POCP 33.2) for MIBK (POCP 63.3) is typical of what may be achieved in reducing the adverse impact of solvents on the environment.

Miscibility with water

All solvents are at least partially miscible with water and most of those with a polarity of more than 36 (on a scale of water = 100) are wholly so. Moisture levels as low as 200 ppm can easily be measured by the Karl Fischer method. Only solvents with a very low solubility in water and densities of less than 1.00 should be tested by the Dean and Stark method.

The requirements for dryness in a solvent range from the low ppm for a Grignard reagent solvent to 2 or 3% for cellulose paint thinners or gun washes. While most can be dried by various forms of distillation, there are also many solid dessicants using chemisorption or hydration effects, although none of these dessicants are general purpose. Molecular sieves are very effective and are suitable to dry the great majority of solvents. However, unless regeneration plant is used to recover the molecular sieve, their cost is about £10,000/tonne of water removed.

Many solvents are hygroscopic and if moisture is to be kept at a very low level, the vents of storage tanks should be fitted with silica gel or molecular sieve-filled canisters. For the removal of small amounts of solvents from water see the section on log activated carbon partition.

Knowledge of the solubility of solvents in water is useful in predicting their behaviour in several fields. Highly water-soluble solvents carry materials and migrate themselves into the biosphere. They are both more easily leached from soil and less easily volatilized into air. The large number of solvents that are not fully miscible with water at 25°C is a measure of the high difference between the polarity of water and that of many organic solvents. Table 4 lists a number of other solvent pairs that have an upper critical solution temperature at a temperature within normal industrial operating range.

The polarity of the non-polar solvents are all less than 6.5 (on the scale of water = 100), while the polar solvents have a polarity of 30 or more.

Log$_{10}$ activated carbon partition

While aqueous effluents containing highly volatile solvents can be stripped using air or steam preparatory to being discharged, the less volatile and particularly those that are polar, are difficult to strip and are more economically removed from dilute solution using activated carbon- or ion-exchange resins.

To get an idea of the effectiveness of activated carbon adsorption, one can use the following equation as a preliminary guide, although an experiment using the grade of carbon to be used is vital to get a sound design

Table 4 Upper critical solution temperature (°C)

	nC_5	nC_6	nC_7	nC_8	nC_9	nC_{10}	C_6	CS_2	2,2,4-TMP
Methanol	14.8	35	51	67		76	45	36	42.5
Ethanol	<–78	–65	–60			–15	–16	–24	–70
EGME		28	49					25	40
EEE		–32	–12				–60		–15
Carbitol		12	25					<–1	28
Acetone		–39	–28	–6		–6	–40	–29	–34
Acetophenone		3	4			10		–16	14
DMF	63	68	73					50	
Acetic acid		–4	–8	19	29	41	3.9	7	7
Aniline	72	69	70	72	75	78		30	80
Nitrobenzene	25	20	18	20	22	24		–4	29
Pyridine		–25	–22					–36	–15
Acetonitrile	60	77	85	92	100	108		77	81
Furfural		92	94					66	101
Phenol	57	51	60						

$$P_{AC} = \frac{x}{m} \cdot \frac{1}{c}$$

x/m is the weight of adsorbate in mg per kg of charcoal, c is the concentration in ppb of the solute remaining in the effluent, and P_{AC} is the activated charcoal partition coefficient.

The values of P_{AC} are usually quoted in logarithms to the base 10. For a rough preliminary estimate

$$\log P_{AC} = 6 - \log S$$

where S is the solubility of the solvent in water in ppb. This relationship is not valid if the solute is wholly water miscible, and clearly shows that the more water-soluble a solvent is the less easy it is to remove it from water by adsorption.

The partition coefficient is affected by temperature, pH and the type of activated charcoal used.

Log$_{10}$ partition between octanol and water

A great deal of work on the partition of solutes between water and other solvents has been done by Pomona College. The main solvent used is *n*-octanol giving the relationship

$$P_{ow} = \frac{\text{concentration of solute in } n\text{-octanol}}{\text{concentration of solute in water}}$$

Originally the work was done as a guide to the biological effect of the solute. A high value of P (i.e. $\log P > 1.5$), corresponding to a low concentration in water, means that the material in solution cannot easily invade living organisms and therefore has a low biological effect. On the other hand, a negative value of $\log P$ indicates a very hydrophilic compound, difficult to extract from water using any third solvent, not just *n*-octanol.

The values of P_{ow} are expressed as logarithms to base 10 and the logarithms have a range of −1.93 to +4.15, a range of a million.

A reasonable estimate for P, if experimental results are not available, is

$$\log P_{ow} = 6.75 - 0.75 \log S$$

where S is the solubility of the solute in water in ppb.

Oxygen demand

The biodegradability of solvents to the simplest molecules, primarily CO_2 and water in a given time (here the quoted biological oxygen demand figure is for five days except for a few instances where 10 days are quoted) vary widely and the correlation between laboratory and plant-scale results for the amount of oxygen removed from the aqueous phase is not very reliable.

The theoretical oxygen demand (ThOD), is solely the oxygen needed on a stochiometric basis to oxidize the solvent completely, and is thus the worst possible effect, but may be useful if no laboratory results are available. In this book the values of ThOD do not include for the oxidation of the nitrogen where it exists in the solvent's molecule. This tends to be a slow reaction and seldom is represented in the five-day BOD test.

BOD depends on the effectiveness of the organisms that may be present and which may be killed by a change of the solvent in the effluent and starved to death by a lack of the solvent to which it is accustomed. Results for BOD can be measured over a time period measured in days, usually five or 10, and is clearly a time-consuming test.

A high BOD solvent sparingly miscible in water and with no solvent-rich phase present to replenish the aqueous phase may be less harmful than a low BOD solvent that is readily soluble in water.

Antoine vapour pressure equation

There is one very widely used equation for estimating the vapour pressure of organic liquids, the Antoine equation

$$\log P = A - \frac{B}{C + T}$$

where A, B and C are constants.

P is the vapour pressure of the solvent at temperature T which can be expressed in a number of pressure units which, of course, refer to different values of A. It is therefore most important to know what pressure units are in use when getting values of the constants from the literature.

In this book logarithms to base 10, mmHg and °C are used.

Cox chart equation

As an alternative to using the Antoine equation it is possible to employ an equation based on the Cox chart

$$\log P = A - \frac{B}{T + 230}$$

These constants are not the same as the Antoine ones although they tend to coincide when $C = 230$. In this book the same units for P and T are used and the logarithms are also to base 10. Since another correlation gives a value for C of

$$C = 239 - 0.19T_b$$

A and B from the two systems will be close together for solvents boiling near 50°C.

Since both Cox and Antoine equations are based on the Clausius–Claypeyron equation the values for B are related to the latent heat of the solvent.

The Cox equation lends itself to calculating relative volatilities

$$\log \alpha^* = \log \frac{P_1}{P_2} = A_1 - A_2 - \frac{B_1 - B_2}{230 + T}$$

and the sensitivity of the value of the relative volatility to temperature tends to be high when the difference in latent heats is high. Alcohols tend to have higher molal latent heats than other groups of solvents and therefore to have large changes in α^* with changes of temperature and pressure.

Solubility parameter (δ)

In choosing a solvent for a particular duty, knowledge of its solubility parameter can be of considerable assistance. A resin, a polymer or any other non-electrolyte is likely to be most easily soluble in a solvent if the solubility parameters of the solvent and the solute are similar. It follows that two solvents with similar parameters will have similar dissolving powers for a given resin

$$\delta = \left(\frac{L - RT}{V}\right)^{1/2}$$

where L is the molal latent heat of the solvent, T the absolute temperature and V its molar volume. The value of is normally expressed in units of cal$^{1/2}$ cm$^{-3/2}$.

The solubility parameter is a blendable property so its value for a blend can be calculated and a blend of solvents can be made to suit the solute more closely if necessary. While the value of δ can be calculated knowing only readily available information, it can also be found experimentally for hydrocarbons and chlorinated hydrocarbons by measuring the Kauri Butanol number (KB) since

$$KB = 50\delta - 345 \text{ (for } KB > 35\text{).}$$

Just as a solute with a similar value of δ to the solvent will dissolve so two solvents of similar δ will be miscible. The limit of difference beyond which total miscibility will not be achieved at 298 K is about 2.5, but as the values of UCST show (*Miscibility with water* section), at higher temperature miscibility becomes easier.

Dipole moment

The figures quoted here are for liquids at 298 K. The dipole moment is proportional to $1/T$ where T is the absolute temperature.

Along with a number of other properties, dipole moment contributes to the ‘polarity’ of a solvent.

Dielectric constant

The dielectric constant of a solvent reflects its molecular symmetry and is comparatively easy to measure. It can thus be used to calculate molar polarization and, from it, dipole moment (*P*).

$$P = \frac{\varepsilon - 1}{\varepsilon + 2} V$$

where ε is the dielectric constant and *V* the molecular volume.

Dielectric constant is also a factor in considering a solvent's electrostatic hazard. A solvent's relaxation time, which is a measure of the rate at which an electrostatic charge will decay, is a product of dielectric constant and resistivity. The higher this product the higher the relaxation time.

However, the range of values of the dielectric constant is about 2–180, which is a small range compared to the range of resistivity (see *Electrical conductivity* section). Nonetheless if a solvent is being changed in an existing process the possible increased risk of electrostatic problems should not be ignored.

Polarity

Polarity is a widely discussed and quoted property of a solvent but it is used loosely to cover a number of different effects, including those covered by dielectric constant and dipole.

The figures quoted here are comprehensively discussed in reference 14 of the bibliography.

Evaporation time

There is no satisfactory method of calculating the rate of evaporation of a solvent, since it depends on the equipment in which evaporation takes place as well as a number of properties of the solvent.

There are two widely used standard solvents – diethyl ether and butyl acetate – against which other solvents' evaporation times can be compared. Somewhat confusingly, a low rate of evaporation on the ether scale corresponds to a high number (i.e. the time it takes to evaporate is many times the time ether takes), while on the butyl acetate scale a low rate of evaporation corresponds to a low number (i.e. the rate of evaporation is lower than that of butyl acetate).

An approximate relationship between the two scales is

$$B = 15/E$$

where *B* and *E* are the butyl acetate and ether numbers.

Nett heat of combustion

For the eventual disposal of used solvent, whether in liquid or vapour form, the preferred method is usually burning. This may involve using the solvent as a fuel, possibly in a cement or lime kiln in which it may be used as a replacement for a more conventional, and more costly fuel. Alternatively, to reduce VOCs to a very low level in solvent-laden air, combustion in an incinerator, with or without added fuel, may be used.

A less common alternative is oxidation in the liquid phase which also gives rise to heat.

In all cases the heat of combustion of the solvent to be destroyed needs to be known. Since in almost every case the water generated in the destruction will be discharged as vapour, the lower or nett calorific value is the appropriate one to use and it is the one quoted here.

Heat of fusion

It may be theoretically important to know how much heat will be required to thaw out the solvent should it freeze, but the most frequent use of the heat of fusion is to estimate the freezing point depression when the solvent dissolves a solute.

The freezing point depression per gram-mole in 100 grams of solvent can be adequately calculated up to a mole fraction of solute of 0.10 by the expression

$$\frac{RT^2}{100H}$$

where *R* is the gas constant (1.987 cal/g units), *H* is the latent heat of fusion in cal/g and *T* is the freezing point of the pure solvent in K.

For some commonly used solvents with high melting points the freezing point depression coefficients are listed below.

Acetic acid	39.0
Benzene	49.0
t-Butanol	80.6
Cyclohexane	208
Cyclohexanol	420
Dimethylsulphoxide	40.9
1,4-Dioxane	46
Nitrobenzene	70
Phenol	74
Sulfolane	641
Water	18.6

Azeotropes

The presence of an azeotrope between solvent components can have three important effects:

1. It makes the recovery by distillation of one of the solvents to a high degree of purity and a high yield difficult. Azeotropic mixtures should therefore be avoided if possible in pharmaceutical production where recovery is important.
2. It increases the rate of evaporation in the great majority of cases since the azeotrope is usually a low boiling one in which the boiling point of the azeotrope is below that of both pure components.
3. It decreases the flash point of the mixture and can therefore have an important influence on safety when the solvent mixture may be used at a temperature about ambient. It is important, therefore, to know when an azeotrope exists and also when its absence is confirmed.

In this book binary azeotropes mostly drawn from *Horsley's Azeotropic Data* are listed. There are a great number of possible ternary or more complex mixtures of solvents that are used, and some ternary azeotropes have been recorded. It is extremely rare for a ternary azeotrope to occur if all three binary mixtures which its components can form are not also azeotropic.

In the absence of information on the existence of an azeotrope in a binary mixture of solvents it is possible to estimate whether an azeotrope will exist if activity coefficients at infinite dilution (γ^∞) and pure vapour pressures of the solvents (P) are available.

In an ideal vapour–liquid system of two solvents the relative volatility (α^*) is equal to the ratio of the vapour pressure of the components and is not affected by composition

$$P_1/P_2 = \alpha^*$$

An azeotrope occurs in a non-ideal system when the vapour phase and the liquid phase in equilibrium with it have the same composition

$$\alpha = \frac{\gamma_1 P_1}{\gamma_2 P_2} = \frac{\gamma_1}{\gamma_2}\alpha^* = 1.0$$

The values of γ vary throughout the concentration range. By definition $\gamma_1 = 1.0$ for pure component 1 at the composition at which component 2 is infinitely dilute and has an activity coefficient γ_2^∞ and vice versa.

A low-boiling azeotrope (much the more common) will occur if $\gamma_2^\infty > \alpha^*$, while a high-boiling azeotrope will occur if $1/\alpha^* > \gamma_1^\infty$.

Activity coefficients (γ)

Activity coefficients are described as a measure of the relative escaping tendency of a compound. This may be escape from a liquid phase to a vapour phase (which can also be quantified by Henry's law coefficient) or from one liquid phase to another, which is the basis of liquid–liquid extraction.

The data sheets list the experimental values of γ^∞ which are obtained by a variety of methods. These can show an appreciable difference one from another, particularly when the mixtures they refer to are very non-ideal with values of γ^∞ of 10^3 or more. There is also a considerable temperature effect on values of γ.

The two major sources of the values listed here are references 2a and 2c. Those from 2a, which have reference numbers 1/1 to 8/381 are derived from distillation data and are at temperatures near boiling point, although these may be at pressures lower than atmospheric for high boiling or unstable solvents. Those from 2c are measured at 25°C and have reference numbers commencing 1X. The latter are more useful for liquid–liquid extraction calculations.

If no experimental results are available for particular solute/solvent mixtures UNIFAC provides a method of calculating γ^{∞} values.

Partition coefficient (K)

There are an almost unlimited number of systems which can involve solvent extraction, but those listed here are restricted to the ones which have water as phase 1, an extraction solvent, sparingly soluble with water, as phase 2 and a solute partitioned between the two phases.

$$K = \frac{\text{molar concentration of solute in water}}{\text{molar concentration of solute in X}}$$

If the objective is to remove the solute from phase 2 and concentrate it in phase 1, K needs to be as high as possible and a target minimum of 5.0 is appropriate. On the other hand, if the solute needs to be removed from the water phase, K should be 0.2 or less.

The values of partition coefficient listed are for 25°C and the most dilute solutions for which information was available. K is temperature dependent and tends to 1.0 as the concentrations of solute in the two phases increase. Since the two phases each containing solute are in equilibrium, the product of the mole fraction of solute and its activity coefficient in each phase is the same. Hence

$$K = \gamma_2/\gamma_1$$

For dilute solutions the activity coefficients can be used to assess the likely performance of the system. Thus for the system water (1)–heptane (2)–MEK (solute)

$$K = \frac{\gamma_2^{\infty}}{\gamma_1^{\infty}} = \frac{3.91}{27.2} = 0.14$$

This would indicate that it was possible to remove MEK from water using heptane as an extraction solvent.

The references which give the source of the information are from three sources in the bibliography. These are:

1. CEH: *Perry's Chemical Engineering Handbook*
2b. V2, 3 and 4: *Dechema Liquid/liquid Data Collection*
17 P: *Pomona College Collection.*

Henry's law constant (H)

Particularly in dilute solutions in water, solvents tend to behave in a very non-ideal way and their equilibrium vapour pressure has to be calculated either using an activity coefficient or Henry's law constant (H). The literature contains compilations of the latter for aqueous solutions but they are reported in several different units, all of which are a pressure divided by a concentration, i.e. $H = P/x$, where P is the vapour pressure of the pure solvent at the solution temperature and x its concentration in the liquid phase.

In this book H is expressed in atmospheres divided by mole fractions. Alternative units are

1. Atmospheres per g-mole of solvent per 100 m^3 of water. Convert by multiplying by $10^6/18$.
2. Kilopascals per g-mole of solvent per 100 m^3 of water. Convert by multiplying by 548.
3. Atmospheres per lb-mole per ft^3. Convert by multiplying by 6.25×10^{-5}.

The value of H increases with temperature and the figures here are for the system temperature of 25°C.

Figures for H quoted in the literature for apparently identical systems vary widely, sometimes by an order of magnitude or more, but, if the information is available there are two ways of checking it.

1. Since H is only suitable for use in dilute solutions

$$H = P\gamma^{\infty}$$

If therefore figures for the activity coefficient at infinite dilution and 25°C and the Antoine coefficients are available, the value of *H* can be compared.

2. Many solvents, particularly hydrocarbons, chlorinated, and the higher molecular weight oxygenated ones, are so insoluble in water that their aqueous solutions are always dilute. At saturation, therefore

$$H = P/S$$

where *S* is the solubility of the solvent in water expressed as a mole fraction.

High values of *H* (e.g. > 50) indicate a dis solved solvent that can be stripped easily either by air or steam. Such a solvent will also evaporate quickly from water.

H can also be used to calculate the composition of solvent-laden air in contact with water at levels appropriate to TLV calculations thus

$$C = \frac{(\text{TLV in ppm}) \cdot (\text{mol. wt of solvent})}{H \cdot 18}$$

where *C* is the concentration of solvent in water which corresponds to the TLV.

Similarly the flash point of a dilute aqueous solution can be seen to be above or below 25°C given a value for the LEL of the pure solvent.