F2 Chemicals Ltd - Technical Article

Dissolving gases in FLUTEC™ liquids

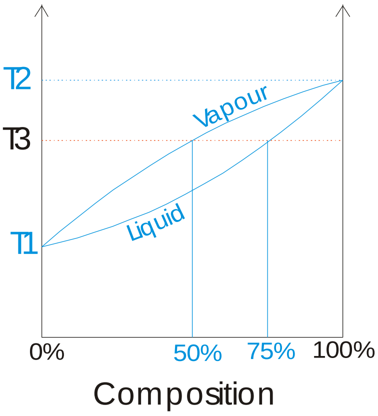
Perfluorocarbons have a remarkable ability to dissolve gases, and, coupled to their very low toxicity, this has generated a lot of interest in medical applications including blood substitutes and liquid ventilation. This paper discusses the factors that determine solubility.

This is a lengthy document, as it collects together a lot of different concepts.

Liquid-vapour diagrams

The way two fluids behave is best explained by referring to a liquid-vapour diagram, such as the one below. This shows the composition against temperature when boiling two liquids, A and B, where A is lower boiling, and the composition is the percentage of B in the mixture.[1] The upper curve is the composition in the vapour, the lower curve for the liquid composition. If you know the composition of the liquid, then you can use the diagram to determine the boiling point for the mixture and the composition of the vapour.

At the far left the composition in the liquid is 0% B, 100% A. In this situation, the boiling point is T1, the boiling point of A, and the vapour is 100% A. At the far right the composition is 100% B in both the liquid and gas phase. Suppose the liquid is 75% B, 25%A: You can read up the 75% line to the curve, then read across to find the temperature, T3, the boiling point for this composition. If you follow the horizontal lines across to the vapour curve, you can also get the vapour composition, in this case 50%. If the system is at a pressure of 1.0 bar, then the partial pressure of A is 50% of that, 0.5 bar.



---

[1] Note that there are several ways to quantify the solubility of a gas, such as ml of gas per 100 g of liquid, or ml of gas per ml of liquid. In this discussion, the composition indicates the number of moles of a component divided by the total number of moles.

How Solubility Changes With Temperature

Gas solubility decreases with increasing temperature, falling to zero at the boiling point of the perfluorocarbon.

Suppose now that A is nitrogen (boiling point –196°C; T1) and B is perfluorohexane (boiling point 56°C; T2).[2] At the far left, we have pure nitrogen at –196°C, at the far right pure perfluorohexane at 56°C, and the dotted line is some temperature of interest, T3 (a pretty low temperature, for clarity in the diagram). In the liquid we have predominantly perfluorohexane with some nitrogen. Before we worked out the temperature based on the composition, but this time we know the temperature, T3, and want to know the composition. Notice how, as the temperature rises, the composition becomes more and more perfluorohexane, until, at the boiling point, there is no nitrogen present. **As temperature rises, gas solubility decreases, falling to zero at the boiling point**. This means that if you want to ensure there is no gas present in your liquid, you can boil it up for a few minutes, then seal the container as it cools (do not seal the container while it is still being heated) to prevent gas getting back in.

In the vapour phase, it is mostly nitrogen with some perfluorohexane. Incidentally, as before the amount of perfluorohexane in the vapour phase can be expressed as the partial pressure. But in this case, the partial pressure is the same as the vapour pressure. At the boiling point, the vapour pressure is equal to the total pressure, so the composition of the vapour is 100% perfluorohexane.

In fact, the difference between the liquid and vapour curves is very big for a perfluorcarbon and a low boiling gas like nitrogen; at 25°C the liquid composition is 99.886% perfluorohexane (corresponding to a solubility of 26.3 ml in 100 g) while the vapour is 23.5% perfluorohexane (corresponding to a vapour pressure of 0.294 bar).

You might wonder what happens below the boiling point of the gas. Carbon dioxide boils at -78°C (actually it sublimes); does this mean that the solubility is 100% carbon dioxide at -78°C? What happens below –78°C? The answer is that of the liquid-vapour diagram is for a boiling mixture. If the temperature is –78°C and the pressure is atmospheric, if it is boiling then you must necessarily have only carbon dioxide present. If you have perfluorohexane as well as carbon dioxide at –78°, then they will not be boiling.

There is a further complication if the condensed gas is not miscible with the liquid. This will change the liquid-vapour diagram dramatically, the curves will dip in the middle, with the liquid composition being flat across the composition range for which there are two phases. However, as the important part of the diagram is the far right, in practical terms it makes little difference.

---

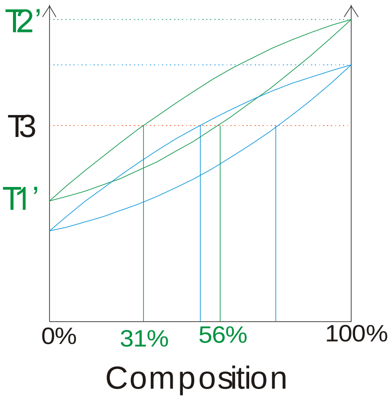
[2] The diagram actually assumes the two liquids are miscible, which may not be the case, and that perfluorohexane is a liquid at –196°C, which is not the case. Nevertheless, the argument sill holds.

The effect of temperature is sometimes measured in another way, and the RTZ manual has both. Figures E9-4/3 and E9-4/4 in the manual are as described above; as the temperature rises, the total pressure remains constant, and the partial pressure of the air falls to allow for the perfluorocarbon pressure (at the boiling point, the lines stop; heat the perfluorocarbon any more and the vapour pressure will go over 1 bar, the total allowed pressure). In figures E9-4/1 and E9-4/2 the partial pressure of the air is constant, and as the temperature rises the total pressure increases, being the sum of the air partial pressure plus the increasing perfluorocarbon pressure (so the perfluorocarbon can be heated above the boiling point).

How Solubility Changes With Pressure

Gas solubility increases with pressure, approximately linearly, in accordance with Henry's law.

What is the effect of changing the pressure? Let us suppose the pressure is doubled. At this higher pressure, the boiling point of the perfluorohexane is 79°C (23°C higher; T2'), while nitrogen boils at –189°C (7°C higher; T1'). And the two curves move up accordingly (the green data on the diagram below).



However, if you increase the pressure of the gas, the composition in the vapour phase will change as the partial pressure of the perfluorocarbon remains the same if the temperature is constant. At the temperature T3, the composition has changed from 50% perfluorohexane to 31%. This change is reflected in the liquid; before there was 75% perfluorohexane, now there is 56%, and while the perfluorohexane has decreased, the nitrogen has increased, from 25% to 44%. Increasing the pressure of the gas will increase the amount of gas dissolved. According to Henry's law, the amount of gas dissolved will be approximately proportional to the pressure of the gas (though I have been unable to find or devise any explanation for why this might be so).

Effect of Different Liquids

Gas solubility is highest for those liquids with lower intermolecular bonds and perfluorocarbon have the lowest intermolecular bonds of any liquids.

Water and oil do not mix because the intermolecular bonding between water molecules is very strong. Ethanol, however, will mix with water, because ethanol also has strong intermolecular bonds – not as strong as water, but comparable. When the ethanol mixes, it breaks strong intermolecular bonds in the water, but makes new strong bonds between the water and the ethanol (with a little help from entropy). We can conceptualise this by considering pulling apart the water molecules, pulling apart the ethanol molecules, then putting them all together. As long as the energy you get back when you put them together is not too much less than the total amount for pulling them apart, the liquids mix.

For gases, it is much the same, but you get very little energy back when you put the gas and the liquid together – because there is very little bonding between the liquid and gas molecules. However, the more bonding that there is, the more the gas will dissolve.

There is a list that can be compiled with each liquid ordered by the strength of its intermolecular bonds. Water is right at the top, ethanol slightly lower, and oil rather lower than that. Most people are familiar with the "like dissolves like" rule; what this is saying is that two liquids near each other on the list will be miscible, so water and ethanol mix, but oil and water do not.

Perfluorocarbons are further on down the list, so much lower that they do not mix with oils even. Gases will dissolve better in liquids lower down the list (the situation is somewhat complicated by the various ways to express gas solubility).

Liquid	ml per 100 ml	ml per 100 g	mole fraction x10^5
Water	1.6	1.6	1.2
Ethanol	14.6	18.6	35.7
Acetone	17.7	22.4	54.2
Toluene	12.2	14.1	54.1
Cyclohexane	18.5	23.8	77.3
Flutec PP1	44.2	26.3	370.3

Effect of Different Perfluorocarbons

There are two points to consider. The first is the different boiling point, which will in effect move the curves up and down; the reverse of changing the temperature. The second effect is due to different molecule weights (and associated physical properties, such as viscosity).

The table below is reproduced from the RTZ manual, with one or two additions. Solubility is measured as ml of gas per 100 g of liquid at 25ºC, 1 atm.

Gas	FLUTEC™ liquid				
	PP1	PP2	PP3	PP6	PP9
Helium	6.6	5.5	4.6	3.9	3.4
Hydrogen	10.7	9.0	7.4	6.3	5.6
Nitrogen	26.3	22.0	18.3	15.6	13.8
Carbon monoxide	26.3	24.2	20.0	17.1	15
Argon	39.8	33.5	27.7	23.7	20
Oxygen	41.0	34.6	28.6	24.4	22
Carbon dioxide	156	132	109	93	82
Sulphur hexafluoride	167	140	116	99	87
Ethane	263	221	183	156	138
Propane	5.90				
Chlorine	781	657	542	463	408
Fluorine	44				
Ozone*	7.8	7.4		6.3	6.3

Note that the values for ozone are for a small concentration (6% w/w) in oxygen.

An alternative table is below, showing the molar proportion (x1000). The carbon monoxide values are not included as they do not fit the pattern. It seems likely that the true value for carbon monoxide in PP1 is about 27.5; this would then give good agreement with the other FLUTEC liquids and other gases.

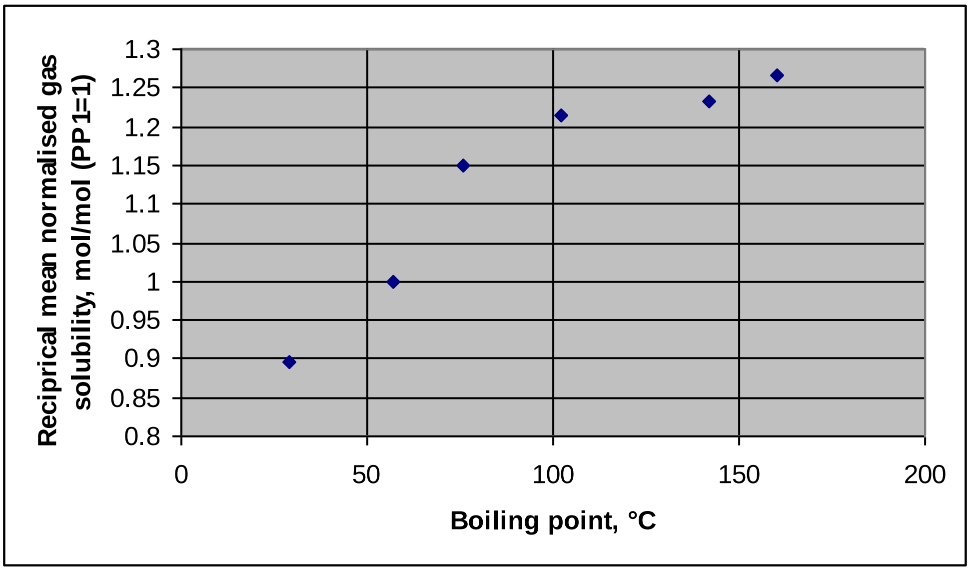
	PP50	PP1	PP2	PP3	PP6	PP9
Helium	1.11	1.00	0.86	0.82	0.80	0.78
Hydrogen	1.80	1.61	1.41	1.32	1.30	1.28
Nitrogen	4.42	3.97	3.44	3.27	3.22	3.15
Argon	6.69	6.01	5.23	4.95	4.89	4.57
Oxygen	6.94	6.19	5.41	5.11	5.03	5.03
Carbon dioxide	26.36	23.54	20.63	19.46	19.18	18.74
Sulphur hexafluoride	28.03	25.20	21.88	20.71	20.42	19.89
Ethane	44.23	39.68	34.53	32.68	32.18	31.54
Chlorine	131.14	117.85	102.66	96.79	95.49	93.26

It is then possible to compare the different FLUTECs; the table below shows each solubility normalised to PP1 (i.e., the molar solubility for one gas in a FLUTEC divided by the molar solubility of the gas in PP1.

	PP50	PP1	PP2	PP3	PP6	PP9
Helium	1.1103	1.0000	0.8629	0.8248	0.8077	0.7803
Hydrogen	1.1149	1.0000	0.8710	0.8184	0.8048	0.7928
Nitrogen	1.1145	1.0000	0.8662	0.8235	0.8108	0.7948
Argon	1.1133	1.0000	0.8716	0.8236	0.8139	0.7612
Oxygen	1.1222	1.0000	0.8739	0.8255	0.8135	0.8128
Carbon dioxide	1.1197	1.0000	0.8762	0.8269	0.8149	0.7962
Sulphur hexafluoride	1.1123	1.0000	0.8681	0.8220	0.8103	0.7891
Ethane	1.1145	1.0000	0.8701	0.8235	0.8108	0.7948
Chlorine	1.1128	1.0000	0.8711	0.8213	0.8103	0.7913
Mean	1.1149	1.0000	0.8701	0.8233	0.8108	0.7904
Std. Dev.	0.0038		0.0040	0.0025	0.0032	0.0139

There would seem to be a good correlation. The ratio of gas solubilities for different gases is the same for all perfluorocarbons.

Although there is this clear trend that the normalisation value decreases with increasing molecular weight, no simple equation could be found relating the value to molecular weight, boiling point or density, so it would not be possible to give more than a rough estimate for other FLUTEC liquids.



So if we have the solubility for one of these six FLUTEC liquids, we can predict the solubility for the other five with a fair degree of confidence. For other FLUTECs, rather more guesswork is required.

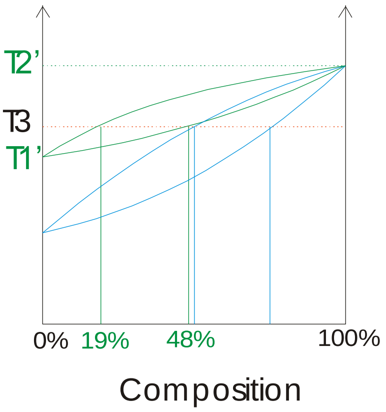
Wesseler et al. have studied this to some degree, looking at the correlation between gas

solubility and boiling point, density, molecular weight, kinematic viscosity. They claimed to have found that there is often one trend for cyclic perfluorocarbon and another for acyclic.
They also noted a correlation between oxygen solubility and other properties, but there is one relationship for cyclic PFCs and another for acyclic. I am unconvinced, but different people get different solubility values, so maybe it fits their data and not ours (but then, which is right?).

Effect of Different Gases

Gases with higher intermolecular bonds and higher boiling points tend to have higher solubility in perfluorocarbons.

There are two effects that must be considered when considering the difference between two gases. The first is the boiling point of the gas. Considering the diagrams earlier, if we change to a gas with a higher boiling point, then effectively we are squashing the curves up to the boiling point of the perfluorocarbon, while keeping the temperature, T3, constant.



As can be seen, the composition of the perfluorocarbon will decrease, corresponding to an increase in solubility.

The second effect is due to changes in the intermolecular forces in the gas, and between the gas and the liquid. A useful measure of the intermolecular bonding is the solubility parameter (so-called because of its application for liquid-liquid mixing). The solubility parameter is equal to the square root of the heat of vaporisation divided by the molar volume (the molar volume is the volume of one mole, i.e., the molecular weight divided by the density).

A rough estimate of the solubility of a gas in PP1 can be obtained by taking the solubility parameter at the boiling point in units of kg and ml, multiplying that by the boiling point of the gas. Solubility in other FLUTEC liquids will be proportionally less.

References and Notes

Some data for gases came from:

www.uigi.com (CO2, O2, N2, H2, Ar)

www.spectra-gases.com (CO, F2, SF6)

www.airliquide.com (C2H6)

Fluorine solubility in PP1: KV Scherer, jr, K Yamanouchi and T Ono, J. Fluorine Chem., 50, 1990, 47-65.

Ozone solubility: R Brabets, D Clark and A Snelson, J. Fluorine Chem., 41, 1988, 311-320.

Serratrice et al claim a good correlation between isothermal compressibility (the reciprocal of the bulk modulus) and oxygen solubility. The paper is in French with an English abstract: G Serratrice and J-J Drlpuech, Nouveau J. de Chimie, 6 (10), 1982, 489-493

AKJ
10 May, 2005