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STABILISATION OF CONCENTRATED OZONE

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The chemical properties of ozone are characterised by two essential features: its chemical instability and its powerful oxidising action. At low concentrations (and in the absence of impurities) ozone decomposes quite slowly under normal conditions. At high concentrations ozone decomposes explosively. Ozone also behaves as a priming explosive in the liquid state (b.p. -111.9°) and in the solid state (m.p. -192.7°).

The applications of ozone in many areas of science and technology are becoming progressively wider: many workers have sought to prepare pure concentrated ozone and have investigated inert solvents which enable the gas to be separated from oxygen and stabilised.

Ozone is prepared, in the form of ozone–oxygen mixtures containing about 8–9 wt.% of ozone, by subjecting oxygen to the action of a silent discharge in ozonisers. The ozone may be concentrated by liquefaction, for example, in the apparatus shown in Fig. 1. Since the explosive propensities of ozone are largely determined by impurities, particularly those of organic origin, the oxygen fed to the ozoniser must be thoroughly purified. Methods of purification have been described in detail in papers [1,2] and also in a patent specification [3]. According to Platz and Hersh [1], if the concentration of organic compounds (expressed as CO_2) in the oxygen is less than 20 parts per million, it is possible to prepare stable 100% liquid ozone by liquefaction. Liquid ozone–oxygen mixtures also can be prepared by liquefaction — for example, by using the apparatus shown in Fig. 2 — because above -180° liquid ozone is miscible in all proportions with liquid oxygen. This is clear from the ozone–oxygen phase diagram [4] given in Fig. 3.

However, the explosion hazards of concentrated ozone depend not only on the presence of impurities, but also on local shock; hence the current interest in the use of inert sorbents or solvents to allow safe storage, transfer, and manipulation of concentrated ozone.

Studies of the adsorption isotherms of ozone on silica gel over a range of temperatures [5,6] have shown that the sensitivity of adsorbed ozone as an explosive is low. This allows ozone to be desorbed almost quantitatively by slightly raising the temperature (say, from -150° to -120°), thus providing a ready means for evolving concentrated ozone from the gas phase by an adsorption–desorption cycle.

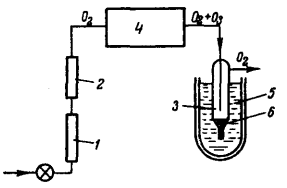


Fig. 1. Liquefaction of ozone:
1) column for oxygen purification; 2) flowmeter; 3) trap; 4) ozoniser; 5) refrigerant; 6) condensed ozone.

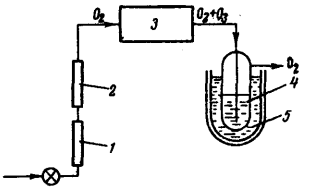


Fig. 2. Liquefaction of ozone–oxygen mixtures:
1) column for oxygen purification; 2) flowmeter; 3) ozoniser; 4) trap; 5) refrigerant.

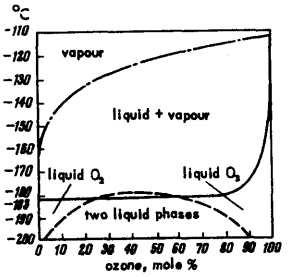


Fig. 3. Phase diagram for the ozone–oxygen system.

Up to 1960, carbon tetrachloride was the only solvent known to be inert towards ozone. However, this solvent has a very low solubility coefficient [7] (4.6 at -12°), and a relatively high melting point (-22.96°). Furthermore, there is a possibility of traces of phosgene being formed after prolonged contact between carbon tetrachloride and ozone. Nevertheless, it has been suggested [8] that liquid ozone can be stabilised by the addition of 0.5–25% of carbon tetrachloride.

A search for a new solvent, made by a group of French workers [9-16], led to the Freons, whose solubility coefficient for ozone at -110° is of the order of 1500–3500. The Freons are inert towards ozone because of the stability of the C–F bond (the bond energy for this class of compounds varies between 90 and 112 kcal mole^{-1}). The presence of traces of free fluorine in Freons has a stabilising effect on ozone. Ozone dissolved in Freons retains its chemical identity, and does not form complexes or solvates. Freons have a low solidification temperature, which assists the dissolution of ozone. Because of the chemical inertness of Freons, apparatus for working with these compounds can be constructed from a wide range of materials.

Ozone can be separated from oxygen at the ozoniser outlet by dissolution in a Freon, whereas oxygen does not dissolve. The solubility of ozone in Freons depends on the nature of the Freon, and is limited by the solidification temperature of the latter. The melting points and boiling points of the Freons used for dissolving ozone are set out in the first two lines of Table 1.

TABLE 1. Solubility coefficients for 100% ozone in various fluorochloromethanes and fluorochloroethanes.

Freon	CF-11	CF-12	CF-13	CF-22	CF-113	CF-114	CF-14
Formula	CCl_3F	CCl_2F_2	$CClF_3$	$CHClF_2$	$C_2Cl_3F_3$	$C_2Cl_2F_4$	CF_4
M.p., °C	−111	−158	−181	−160	−35	−94	−183.8
B.p., °C	+23.8	−29.8	−81.4	−40.8	+47.6	+3.5	−128.8
Temperature, °C	Solubility coefficient S_B^T (pressure dependent)						
−110±1	8.3—9	12—14	13—15	21—22			
−94±1	4.1—4.4	4.4—4.5					
−63±1	1.2—1.3					1.2—1.4	
−23±1	0.3—0.35				0.485—0.495		
	Solubility coefficient S_B^T (100%)						
−110±1	1610±80	2090±80	2180±80	3490±80			
−94±1	132±5	136±5				35±1	
−63±1	25.4±0.2				9.4±0.2		
−23±1	6.6±0.3						

The best solvent and stabiliser for liquid ozone is Freon-14. The phase diagram[17] for the liquid ozone–liquid Freon-14 system is reproduced in Fig. 4.

Two types of apparatus are used to dissolve ozone in Freons, depending on whether the melting point of the Freon is higher or lower than the boiling point of ozone (-111.9°). In the former case dissolution is obtained by bubbling the gas through liquified Freon to saturation. In the latter case the ozone and Freon are liquified simultaneously in a small distillation column to which the two gases are admitted in countercurrent. Fig. 5 shows the general layout of the apparatus; Fig. 6 is a more detailed sketch of the cell used for dissolution. The Freons are previously purified (to the 99.99% level) by distillation followed by drying with activated gels, 5 A zeolite, and phosphorus pentoxide. They are then condensed in a graduated vessel which has been carefully dried. A predetermined volume of Freon is distilled into the ozone saturator cell, also carefully dried. The saturation time depends on the temperature, pressure, and nature of the Freon. The saturation limit for a number of Freons was reached at -110°. The longest duration of the experiments was 6 h. When calculating the solubility, allowance was made for the "dead volume" of the cell (the space above the liquid phase) and for the mass of solvent lost by evaporation whilst bubbling the ozone–oxygen mixture. The solubility data, expressed as the Bunsen coefficient

$$S_B^T = \frac{V_{O_3}}{V_F}\frac{760}{P},$$

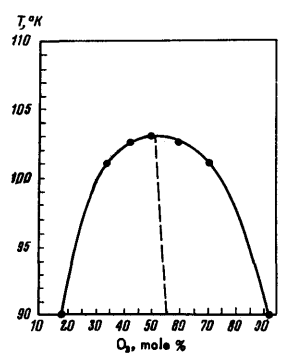


Fig. 4. Phase diagram for the liquid ozone–liquid Freon-14 system.

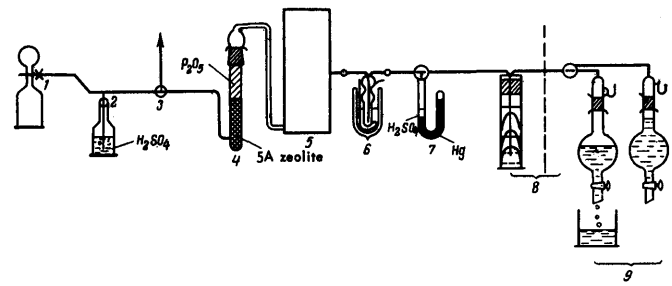


Fig. 5. Apparatus for dissolving ozone in Freons: 1) oxygen cylinder; 2) manostat; 3) oxygen discharge; 4) drying tube; 5) ozoniser; 6) dissolution cell; 7) manometer; 8) absorption towers; 9) volume meters.

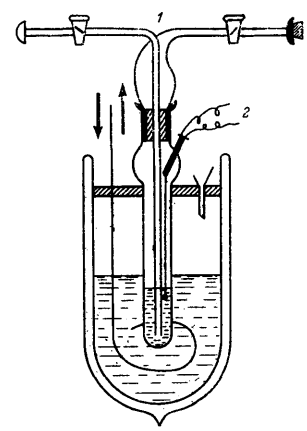


Fig. 6. Cell for ozone dissolution: 1) ozone inlet tube; 2) thermocouple.

where V_{O_3} is the volume of dissolved ozone under normal conditions, V_F is the volume of Freon at temperature T, and P is the effective total pressure in mmHg, are tabulated in lines 3–6 of Table 1. The remaining lines of the table list the solubility data expressed as the Bunsen coefficient, S_B^T(100%), for one atmosphere.

The best solvent for gaseous ozone is Freon-22, monochlorodifluoromethane $CHClF_2$, because it has a low molar volume.

Some mixtures of the Freons, for example a 50% mixture of CF-114 and CF-11, offer a higher solubility than the pure components. An increase in solubility with decrease in molar volume is observed on going from Freon-11 to Freon-12 and -13, in which ozone exhibits virtually ideal solubility.

For very low ozone concentrations at -63° and -23° the solubility of ozone calculated by the formula $S_B^T(100\%) = S_B^T\frac{P_0 - P}{P(P_0 - 1)}$ is very close to the value calculated by the direct proportionality law $S_B^T(100\%) = SP\frac{1}{P}$, as Table 2 shows.

This is evidence that dilute solutions of ozone in Freons obey Henry's law. The solubility coefficients for ozone

TABLE 2. Calculated solubility values for ozone.

	$S_B^T(100\%) = S_B^T \frac{P_0 - P}{P(P_0 - 1)}$			$S_B^T(100\%) = S_P \frac{1}{P}$		
T, °C	CF-11	CF-113	CF-114	CF-11	CF-113	CF-114
—63	25.8	—	35	23.6	—	32
—23	6.6	9.4	—	6.6	9	—

TABLE 3. Solubility coefficient expressed in mole fraction.

T, °C	$X^{100\%}$			
	CCl_3F	CCl_2F_2	$CClF_3$	$CHClF_2$
—110	0.850	0.867	0.862	0.895
— 94	0.317	0.323		
— 63	0.084			
— 23	0.024			
	Ratio $\frac{X^{100\%}}{Xi}$			
—110	0.95	0.97	0.97	1.00
— 94	0.93	0.95		
— 63	1.01			
— 23	1.00			

($X^{100\%}$), expressed in mole fractions, are given in Table 3, together with the ratio of the real solubility to the ideal solubility Xi. It is clear that this ratio is close to unity, a rare occurrence in gas solubility.

From the data of Table 3, Chrétien and coworkers[9] have calculated the molar latent heat of dissolution of ozone in CCl_3F and CCl_2F_2, which turned out to be 3290 ± ± 50 and 3590 cal mole^{-1} respectively. The latent heat of evaporation of ozone is 3410 ± 100 cal mole^{-1} at the boiling point. These values are of the same magnitude, which suggests that no chemical reactions occur when ozone is dissolved in Freons, and that neither complexes nor solvates are formed.

Mahieux[10] also examined the possibility of obtaining mixtures of liquid and solid ozone with Freons, and measured the stability of these mixtures. The ozone was condensed in vessels of two types. One of the vessels (Fig. 7) is an ordinary spiral tube, fitted with a reservoir. The ozone–oxygen mixture obtained from the ozoniser is passed through the spiral cooled to about -140°. Only the ozone is liquified, and collects in drops in the reservoir, which already contains a known volume of condensed Freon. The alternative vessel (Fig. 8) includes a capillary through which the ozone–oxygen mixture is led into the condensed Freon, where the ozone condenses. It is best to use Freons CF-12 and CF-22 to condense the ozone. Freons having a boiling point lower than that of ozone are not recommended (for example, Freon-14). Freon-13 evaporates very rapidly under reduced pressure, entraining the ozone. The advantage of Freons CF-12 and CF-22 is that, because of their relatively high boiling point, the ozone evaporates first from the mixture. Also, the low melting point of these Freons (-158° and -181°) enables mixtures with solid ozone to be obtained at temperatures above the freezing point of ozone (-192.7°).

When ozone is condensed in Freon it forms a blue liquid which solidifies as the temperature is reduced to -192°, acquiring a transparent black colour if the molar concentration of ozone is ~60%. At lower ozone concentrations, liquid ozone and liquid Freon are miscible in all proportions without separating into layers. Layering occurs in

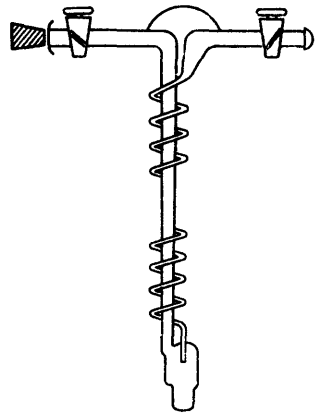


Fig. 7. Tube for liquefaction of ozone (with spiral).

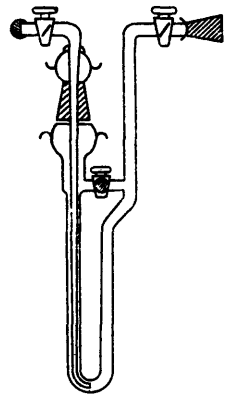


Fig. 8. Tube for liquefaction of ozone (with capillary).

the region from -230° to -270° for Freons CF-13, CF-12, and CF-22, but in practice the limiting temperature is that of liquid nitrogen (-196°), and therefore layering is not observed.

Streng and Grosse[18] have reported that ozone is unstable in the neighbourhood of its freezing point. Mahieux[10] showed that solutions of ozone in Freons are thermally stable, and that no explosive decomposition takes place when ozone is solidified in a Freon medium.

The condensation of ozone is more efficient than the dissolution process, since from 70 to 90% of the ozone passing through the Freon is retained by liquefaction as compared with 10–15% during dissolution. The concentration of ozone in ozone–Freon mixtures can reach 50%.

The preparation of solutions of ozone in Freons has practical importance[11]. The solubility of ozone in Freons enables ozone to be separated from oxygen and to be stored safely and for long times in a concentrated form: it offers a portable source of ozone which can always be handled and conveyed over any distance.

By evaporating ozone from these solutions we can obtain pure ozone or ozone mixed with oxygen or with inert gases

at a known concentration[12]. Various substances can be made to react directly with the ozone in an inert solvent medium[13].

Solutions of ozone may be stored in stainless steel bottles[11] of 5, 10, and 15 l capacity (calculated as 100% ozone). Below -50° these solutions may be stored indefinitely. At room temperature the decomposition time of the ozone (time for 50% decomposition of the stored ozone) is of the order of weeks. As a rule, vessels containing dissolved ozone are stored at -30° and transported at -15°. At the latter temperature the solutions can be kept for one month. The rate of decomposition of the ozone depends on the nature of the Freon and on the shape of the vessel. Solutions of ozone in Freon-12 have been examined for sensitivity towards mechanical, electrical, and explosive shocks, and for temperature resistance[19]. The sensitivity of both the vapour phase and the liquid phase of a 10% solution of ozone in Freon-12 towards a high-voltage electrical discharge and towards detonation at high pressures was tested. No detonation took place when explosion was initiated in the gas or the liquid phase of a 12% solution of ozone in Freon-12 at -78° and 105 atm (of helium). The gas and the liquid phase were tested for shock resistance by dropping a 5.6 kg weight from 35 cm, but it was found that solutions containing 10 wt.% of ozone in Freon-12 are completely safe at -78°. Experiments on the effect of temperature showed that increase in temperature does not produce an explosion, or even appreciable decomposition of the ozone.

We have recently confirmed[20] that solutions of pure ozone in Freon-12 and -113 can be prepared, and handled with safety during liquid-phase reactions with alkalis and peroxidic compounds.

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APPLICATION OF ELECTRON SPIN RESONANCE IN POLYMER CHEMISTRY

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Electron spin resonance (ESR) is the name given to the resonance absorption of the energy of an oscillating magnetic field by a paramagnetic substance in which the field induces transitions of unpaired electrons between split Zeeman levels. The ESR phenomenon was discovered by Zavoiskii[1] and interpreted theoretically for the first time by Frenkel'[2]. The ESR method is of particular value for the study of free radicals, because of its high sensitivity, the possibility of investigating free radicals directly in the course of reactions, and also the completeness and uniqueness of the information about their structure thus obtained. The number of ESR studies on free radicals is extremely large. In this review we shall confine ourselves to certain results relevant to the physics and chemistry of polymers.

I. THEORETICAL FOUNDATIONS OF THE ESR METHOD

1. The Basic Features of the Phenomenon

Consider a specimen containing unpaired electrons, for example a reaction mixture with free radicals. In the absence of an external magnetic field, all orientations of the spins and magnetic moments of the electrons have the same energies. An external magnetic field removes the degeneracy: only two orientations of the spins and magnetic moments of the electrons are now possible, along and against the field, since the electron spin is $S = 1/2$ and according to quantisation rules only $2S + 1 = 2$ states are possible. This means that the zero energy level splits into