

DEOXYGENATION, DEAERATION AND DEGASSING : A SURVEY AND EVALUATION OF METHODS

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ABSTRACT

Techniques for the removal of dissolved gases from liquids are reviewed and classified according to their working principles. Consideration of these working principles reveals some inherent limitations of certain techniques and it may be concluded that the different methods complement each other in a number of aspects. Proton spin-lattice relaxation time measurements and polarographic analyses are used for evaluation of different deoxygenation methods. It is concluded that for most purposes the different methods yield satisfactory results if applied properly and within the inherent limitations of the techniques. When the presence of oxygen is very critical and its concentration must be reduced to very small amounts, a combination of methods appears advisable.

INTRODUCTION

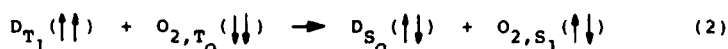
Dry atmospheric air mainly consists of nitrogen and oxygen, with carbon dioxide and argon as minor components. Trace amounts of helium, neon, krypton, xenon, hydrogen, methane and nitrous oxide are also present. These gases dissolve in liquids to concentrations depending on their partial pressure and their Henry coefficient in the respective liquids. Along with water, these gases thus constitute the most common impurities still present in high-purity chemicals. For experimental work in a number of fields some (in most cases oxygen) or all of these gases must be removed. One obvious example where removal of all dissolved gases is required is in vapor pressure measurements. Complete degassing is also required in chemical work, where the presence of unreactive gases such as nitrogen and the rare gases interferes with the reaction process. This is for instance usually the case in studies of radiolytic mechanisms, because of the high energy of the radiation employed, the non-selectivity of energy absorption from ionizing radiation and the high reactivity of the radiolytic intermediates formed. For a lot of experimental work only one or a few particular gases must be removed. From all gases present in air, oxygen poses the greatest interference problems, and this results from both its high concentration in atmospheric air and its particular properties.

Removal of oxygen is quite often required in studies of reaction processes, because of its effect on excited states of molecules and its interference with radical and ionic reactions. Oxygen readily adds to free radicals and if present will almost invariably play a part in photolytic and radiolytic reactions. The product of the reaction



is a (relatively stable) peroxy radical, which will lead to products that differ

considerably from those of the original reacting radicals. Rate constants measured in gas-phase reactions for methyl and other radicals are quite large and may approach values typical of radical recombinations (1a-1e). As a consequence, even small concentrations of oxygen are sufficient in gaseous systems to compete seriously with other usual reactants of free radicals in photolytic and radiolytic studies. Oxygen interference will be important in condensed systems too, since reactions of many carbon-centered radicals with oxygen are found to occur at or near diffusion-controlled rates (1f). Consequently, oxygen must be removed if reactions other than photooxidations are to be studied. The interaction of oxygen with electronically excited molecules may also lead to complications. The energy required to excite oxygen to its lowest excited singlet state is ca. 92 kJ.mol<sup>-1</sup>, a value less than the triplet energy of most organic molecules (2). When oxygen is present, quenching of an excited (donor) triplet state to singlet ground state may occur with formation of oxygen singlet state :



Other mechanisms have also been suggested for the quenching of triplet excited states by oxygen and by NO and certain of the transition metals (3), but no doubt the quenching by oxygen occurs with great efficiency. In fact, bimolecular rate constants for quenching reactions of excited triplet state molecules by oxygen are near the collision number; for acetone triplet with oxygen,  $k = 8.2 \times 10^9 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$  (4a), for instance, whereas for the triplet of N,N,N',N'-tetramethyl-p-phenylene diamine (TMPD) a rate constant of  $1.3 \times 10^{10} \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$  has been reported for its reaction with oxygen in cyclohexane (4b). Quenching of excited singlet species by oxygen is also efficient. However, singlet quenching is much less important than triplet quenching, since equilibrium concentrations of excited singlet species are generally much lower than those of the corresponding triplets as a result of the different lifetimes of these excited states. Quenching of excited species by oxygen may affect reaction processes, because it may result in the removal of excited species before reaction can occur and thus in the suppression of certain reaction paths. In addition to this, singlet oxygen generated by quenching of excited triplet states may react with ground-state substrate molecules. In systems where ions are formed oxygen may also interfere with ionic processes. The electron affinity of oxygen is positive and equal to 0.440 eV.molecule<sup>-1</sup> (5) and electron attachment to oxygen has been observed and studied in both gaseous and condensed systems (6). As a result of this attachment reaction, oxygen may interfere with anionic processes and is thus usually removed when reactions and spectroscopic properties of negative ions are studied. The ionization energy of oxygen, on the other hand, is rather high (12.06 eV.molecule<sup>-1</sup>), many organic radical cations are unreactive towards oxygen and their electronic absorption spectra are not significantly altered by the presence of oxygen (7). The presence of oxygen may even be beneficial since it may result in the complete removal of other intermediates such as triplet states and/or anions and thus in the obtainment of much purer spectra (8). As a consequence, experiments

that are specifically designed to obtain knowledge on such cations have often been performed without oxygen removal. Occasionally, oxygen has even been added in such studies (4b).

The necessity of dissolved oxygen removal is not limited to studies of reaction processes. NMR spin-lattice relaxation for instance is greatly enhanced by the presence of oxygen (9) and removal of dissolved oxygen is thus essential in relaxation time measurements on pure liquids. In high-resolution ESR measurements on free radicals removal of oxygen is required because of its line-broadening effect. The effect arises from a physical interaction involving dipole-dipole coupling between the unpaired electron of the free radicals and those of the oxygen molecules. In addition to this, removal of oxygen may be required in ESR work because many neutral radicals tend to react with oxygen to form peroxy radicals as mentioned above. Removal of oxygen is also generally required in polarographic analyses, since dissolved oxygen is readily reduced at the dropping mercury electrode. An aqueous solution saturated with air exhibits two distinct waves attributable to this element, the first resulting from the reduction of oxygen to hydrogen peroxide and the second corresponding to the further reduction of the hydrogen peroxide to water. While these polarographic waves clearly are convenient for the determination of the concentration of dissolved oxygen, the presence of this element often interferes with the accurate determination of other species and oxygen removal is ordinarily the first step in a polarographic analysis.

Methods have been developed for the removal of dissolved oxygen (deoxygenation), for the removal of all gases dissolved in liquids (degassing) and for the removal of all gases with the exception of one particular gas (usually nitrogen or a noble gas) which is present in large amounts after application of the method; (this technique is usually referred to as deaeration).

#### SURVEY AND PRINCIPLE OF DIFFERENT METHODS

A number of methods based on either physical or chemical principles have been described for the removal of dissolved gases from liquids. In addition to these getters, whose action may be physical and/or chemical in nature, may also be employed for this purpose.

##### A. Physical Methods

Degassing may be considered as merely the removal of highly volatile components from a relatively nonvolatile liquid. This separation should thus easily be accomplishable by skilful rectification. The only difficulty is that the volatile components are initially present in small amount and must be reduced to near zero concentration. A batch rectification procedure has been developed by Van Ness and Abbott (10) using an enriching column operating at almost total reflux, with the enriched volatile components being withdrawn from the top of the column at a very low rate.

A number of other physical methods have been developed that may be classified into two major categories, viz. reduction of the total pressure or of the partial pressure of particular gases above the liquid and crystallization under vacuum. The widely used freeze-pump-thaw procedure has aspects of both

categories and will therefore be treated separately.

1. Reduction of the total pressure or of the partial pressure of particular gases above the liquid.

According to Henry's law, the concentration at constant temperature of a gas in a liquid is directly proportional to the pressure of the gas above the liquid. When several gases are being dissolved simultaneously in a solvent, Henry's law is valid for each gas independently; the concentration of each gas from a mixture of gases is directly proportional to the partial pressure of the gas in the mixture. It is evident therefore that reducing the total pressure above a liquid will result in degassing and that reducing the partial pressure of particular gases above a liquid will result in specific removal of these gases.

a. Reduction of the total pressure above the liquid.

According to Henry's law, reduction of the total pressure above the liquid with regular vacuum pumps will result in degassing. A cold finger or condenser may be introduced into the degassing chamber in order to minimize loss of product. The process will be far from instantaneous, however, especially when the ratio of surface to volume is small and agitation of the liquid may speed up the process considerably. Battino *et al.* (11-13) describe three different apparatuses, which enable circulation or stirring of the liquid while pumping in order to present a continuously renewed large surface area for outgassing. Newton (14) describes a method of refluxing the product under vacuum while pumping on it either with a regular vacuum pump for degassing or with a Toepler pump for collecting dissolved gases. Circulation, stirring and boiling may be replaced by subjecting the liquid to ultrasonic vibrations and a practical method based on this principle has been described by Barbee and Brown (15).

b. Reduction of the partial pressure of particular gases above the liquid.

The partial pressure of particular gases above the liquid may be reduced to virtually zero by chasing these gases with another gas. Nitrogen or rare gases are usually employed but other gases (e.g.  $N_2O$ ) may also be used when their presence is required for specific purposes (16,17). Quite in general, a high molecular weight gas is to be preferred in order to make the process most efficient. Bubbling of the gas through the liquid results in agitation and thus in a continuously renewed surface area. Evaporation of liquid and change of solution composition may be eliminated by cooling the sample and/or by passing the bubbler gas first through a prebubbler containing the same solution. Accidental intake of oxygen or other interfering gases after bubbling poses the greatest threat to the effectiveness of the method. An efficient technique for sealing samples after deaeration by argon bubbling has been described by Freeman and co-workers (18). If the sample may not be sealed, a stream of the purging gas must be passed over the surface during the measurement to prevent reabsorption of oxygen or other interfering gases.

The method has been used widely in polarographic studies and different methods have been described for the continuous removal of oxygen in flow systems. Intimate contact between the liquid and the gas can be achieved in flow-

through columns with particulate packings (19) or in columns consisting of a narrow tube (20), where turbulent flow is ensured at relatively low flow rates. In a different type of apparatus, the gas is bubbled through a sintered glass disc to ensure contact between the chaser gas and the thin layer of flowing liquid (21) whereas another method is based on diffusion of gases through a semipermeable membrane into a space with a low partial pressure of the particular gases (22). Static methods may be expected to yield better results than flow methods, however, since gas bubbling may be continued over a much more extended period of time.

## 2. Crystallization under vacuum.

During crystallization, gases dissolved in liquids are not likely to be included in the crystal lattice and, especially when crystallization occurs under vacuum, will separate from these materials. The method will be most efficient when the solid is deposited as a thin film. Bell *et al.* describe a method that consists in the sublimation of the product onto a cold glass surface, while non-condensable gases are continuously pumped away (23). Rondeau, on the other hand, has described a technique that consists in the evaporation of the liquid sample under vacuum and condensation as a thin layer along the bottom of a spherical cold wall, followed by pumping on the thin exposed layer of the sample (24).

## 3. The freeze-pump-thaw procedure.

The freeze-pump-thaw method is quite frequently used for degassing in a number of chemical disciplines. The technique is well known and will therefore not be described in detail. It consists essentially in freezing the sample at low temperature, pumping on it with a high vacuum pump and then allowing it to thaw under vacuum (without pumping). This cycle must be repeated a number of times. Though based on the above two principles, the method is not necessarily better than the other methods described, since little emphasis is on the rate of dissolved gas removal. No stirring or other agitation is generally applied to the liquid and crystallization is in bulk instead of as a thin exposed layer of sample. Also, for glassy samples the aspect of crystallization is absent and the procedure may then be expected to be quite slow and less effective because the solubility of most gases in liquids increases with decrease in temperature. Consequently, for glassy samples other degassing methods are to be preferred.

Degassing by freeze-pump-thaw cycling always is rather time-consuming, but it may become extremely tedious if the liquid sample is contained in a narrow tube such as those used in NMR and ESR spectroscopy, because of the unfavorably small surface area to volume ratio. The liquid sample should then be degassed elsewhere in the vacuum system and eventually returned to the tube by distillation. This procedure may become impractical if the liquid has too low a vapor pressure to permit liquid nitrogen pumping and a different transfer method must then be applied. A quick and easy method of degassing liquid samples with low volatility has been described by Rondeau (25).

Liquid nitrogen is generally used as the coolant in freeze-pump-thaw cy-

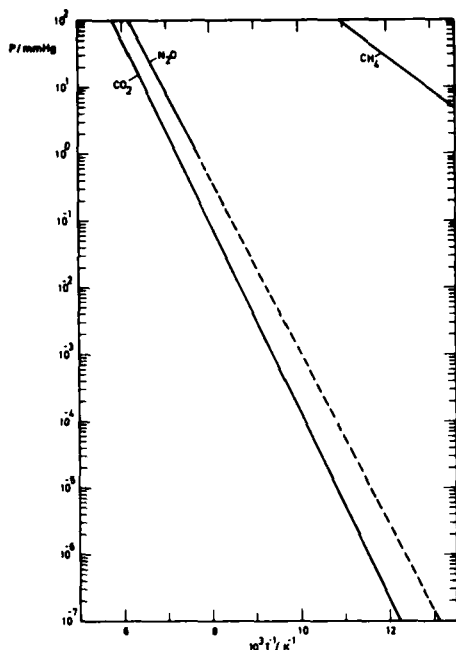


FIG. 1. Dependence on temperature of the vapor pressure of some compounds present in atmospheric air. Graph constructed with data from reference 24 ( $\text{CO}_2$ ) and 35 ( $\text{CH}_4$  and  $\text{N}_2\text{O}$ ).

cling. This poses problems in the case of heavier dissolved gases, such as carbon dioxide. The vapor pressure of carbon dioxide is quite low at liquid nitrogen temperature (see Figure 1) and thus beyond reach of most conventional pumping systems. A similar situation exists for nitrous oxide, though this gas is only present in minute amounts in atmospheric air. If such gases are to be removed from the sample a different coolant has to be used, the choice depending on the capabilities of the pumping system and the vapor pressure and melting characteristics of the sample.

#### B. Chemical Methods

Chemicals that react quantitatively with dissolved gases may be employed for removal of these gases. The method is especially interesting for the removal of oxygen because of the high reactivity of this element. Procedures have been described for the deoxygenation of pure liquids, liquid mixtures and solutions of solids in liquids using tris(2,2'-bipyridyl)cobalt(II)perchlorate and sodium tetrahydridoborate in a color-indicating reaction (26,27). A deep blue color is obtained when all of the free oxygen has been removed, whereas the presence of oxygen is indicated by a brown color.

#### C. The Use of Getters

Alkali and alkaline earth metals as well as other metals have been applied as getters to effect a number of functions, such as the removal of residual gases for the production of very high vacuum and the purification of rare gases as well as a variety of functions in electron tubes. The gettering mechanism may be essentially physical involving adsorption or absorption of the gas and/or essentially chemical involving formation of quite stable chemical compounds. Oxygen may be removed with very high efficiency by the gettering technique.

Sandhu *et al.* have used misch metal for the removal of oxygen from methane (28). The technique was subsequently modified by Lees *et al.* in order to be applicable to liquids (29). In this method, a diffuse layer of misch metal is deposited on a spherical surface at the top of the tube by flashing the misch metal in an argon atmosphere at a pressure of a few millimeters, with the sample kept frozen in the bottom part of the sample tube. Before and after flashing, the tube is pumped to  $10^{-5}$  or  $10^{-6}$  mmHg and the tube is subsequently sealed off with the sample still frozen. It is not necessary to vaporize the liquid in this method; by action of the getter the partial pressure of oxygen is reduced to near zero, resulting in a thorough removal of oxygen from the liquid.

#### EVALUATION OF DIFFERENT METHODS

Different described methods will be evaluated by their efficiency for oxygen removal, which may be assessed by nuclear spin-lattice relaxation time measurements. The nuclear magnetic resonance spin-lattice relaxation time ( $T_1$ ) in diamagnetic compounds is very sensitive to small amounts of oxygen in the sample, because of the fact that the  $O_2$  molecule is paramagnetic. The presence of even small concentrations of oxygen in such samples results in considerably lower spin-lattice relaxation times (30,31). Similar effects are observed for other paramagnetic species such as nitric oxide (31), diphenyl picryl hydrazyl (32) and di-tert-butyl nitroxide (33).

The mechanism of the nuclear spin-lattice relaxation process can be considered, at a molecular level, to be due to a net transfer of energy from the nuclei to their environment, i.e. to the lattice, which transfer is brought about by time-dependent magnetic fields that thus enhance the relaxation process and significantly reduce the value of  $T_1$ . Because of the high sensitivity of  $T_1$  to the presence of oxygen, this property can be used to measure the concentration of small amounts of oxygen in solution. For this reason,  $T_1$  values are used here for evaluation of described deoxygenation, deaeration and degassing methods.

Proton spin-lattice relaxation times obtained for benzene after removal of oxygen (and other gases) by various methods are given in Table I. The data can not be compared as such, however, because of the temperature dependence of nuclear spin-lattice relaxation times. Nuclear spin-lattice relaxation times of organic liquids generally increase with increasing temperature. Plots of  $\log T_1$  versus  $1/T$  are usually linear over a more or less restricted temperature range and the temperature dependence may thus approximately be represented by an equation of the type :

$$T_1 = T_{1,inf} \cdot \exp(-E_a/RT) \quad (3)$$

where  $T_{1,inf}$  is the nuclear spin-lattice relaxation time at infinite temperature. The parameter  $E_a$  is generally referred to as the "activation energy" (43,44); in order to avoid confusion this notation will be followed here.

TABLE I  
Spin-lattice relaxation times of benzene after removal of oxygen by various methods.

Method	$T_1, T/s$	T/K	$T_{1,298}/s^a$	Ref. & Notes
No deoxygenation	4.2	305	3.9	b
	4.6	309	4.0	c
	4.8	309	4.2	d
	2.7	293	2.9	e
Prolonged boiling in vacuo	19	293	20.2	e
Freeze-pump-thaw				
at ca. $10^{-3}$ mmHg; 4 cycles	5.5	309	4.8	d,o
at ca. $10^{-5}$ mmHg; 4 cycles	20.8	309	18.2	d
unspecified	18	295	18.7	f
	19.3	298	19.3	g
	19.9	297	20.1	h
	19.6	298	19.6	i
	20.6	300	20.1	j
	20.0	303	18.8	k
Bubbling oxygen-free nitrogen for 15 min.	20.9	309	18.3	d
Chemical deoxygenation	23.6	309	20.7	c
	23.3	309	20.4	d,n
	20.6	305.8	18.7	l
	18.4	305	16.9	b,m,o

<sup>a</sup> Calculated using a value of  $9.2 \text{ kJ.mol}^{-1}$  for the so-called "activation energy" as determined by Powles (45). <sup>b</sup> Reference 36. <sup>c</sup> Reference 26. <sup>d</sup> Reference 27. <sup>e</sup> Reference 31. <sup>f</sup> Reference 37. <sup>g</sup> Reference 38. <sup>h</sup> Reference 39. <sup>i</sup> Reference 40; extrapolation from measurements on binary  $\text{CD}_3\text{OH}/\text{C}_6\text{H}_6$  systems. <sup>j</sup> Reference 41. <sup>k</sup> Reference 42. <sup>l</sup> Reference 52. <sup>m</sup> Magnesium filings were added for deoxygenation, the runs being made after a wait of one or more days during which  $T_1$  increased. <sup>n</sup> Average of different reported values. <sup>o</sup> Method appears unreliable or less reliable than other methods.

Activation energies of  $8.0 \text{ kJ.mol}^{-1}$  and  $9.2 \text{ kJ.mol}^{-1}$  are reported for benzene by respectively Bonera and Rigamonti (37) and Powles (45). An activation energy of  $9.8 \text{ kJ.mol}^{-1}$  may, on the other hand, be calculated for benzene from data reported by Green and Powles (46a). Using a value of  $9.2 \text{ kJ.mol}^{-1}$ , data in Table I may be adapted to a temperature of 298 K. Examination of these data reveals no systematic differences between the different methods, except for the very low value for the freeze-pump-thaw technique at  $10^{-3}$  Torr and the value of Nolle and Mahendroo (36) obtained by adding magnesium filings, which also appears significantly below other reported values. Quite in line



with this, Mitchell and Eisner removed oxygen by vacuum distillation and/or by a series of freeze-pump-thaw cycles for measurements of spin-lattice relaxation times for protons in benzene, chlorobenzene and cyclohexane in solution in  $\text{CS}_2$  and  $\text{CCl}_4$  and found that both methods were equally effective (41,42). Results from other fields also point in the same direction. In pulse radiolysis studies on solvated electrons in methanol and ethanol, for instance, freeze-pump-thaw degassing and argon bubbling result in the same electron lifetime for a given type of sample at room temperature (18).

Information on the quantitative aspect of oxygen removal may also be deduced from nuclear spin-lattice relaxation time measurements. When different entities and/or mechanisms contribute to the spin-lattice relaxation, reciprocals of spin-lattice relaxation times of the various contributions are additive. Thus, when a paramagnetic impurity contributes to the relaxation :

$$1/T_1 = 1/T_1' + 1/T_1'' \quad (4)$$

where  $T_1$  is the relaxation time of the liquid containing the impurity,  $T_1'$  that of the pure liquid and  $1/T_1''$  reflects the contribution of the paramagnetic impurity. The additional contribution to the relaxation rate resulting from the presence of a paramagnetic entity is proportional to the concentration of this paramagnetic entity. Thus, for liquids containing dissolved oxygen :

$$1/T_1 = 1/T_1' + R.O_2 \quad (5)$$

From results presented by Chiarotti *et al.* (31), it may be deduced that the value of the slope,  $R$ , is equal to  $213 \text{ dm}^3 \cdot \text{mol}^{-1} \cdot \text{s}^{-1}$  for oxygen in benzene; (for measurements at  $20^\circ\text{C}$  and a frequency of 7 MHz). The resulting dependence of the proton spin-lattice relaxation time of benzene on dissolved oxygen concentration is shown in Figure 2. From this figure and the data in Table I, it may be concluded that the oxygen concentration in benzene is at least reduced to about  $2 \cdot 10^{-5} \text{ mol} \cdot \text{dm}^{-3}$  or about  $1.8 \times 10^{-4} \text{ mole } \%$ . An upper limit of  $2.5 \times 10^{-4} \%$ , on the other hand, has been placed by Sandhu *et al.* on the concentration of oxygen present in methane after treatment with a getter made of misch metal (28). The effectiveness of the different deoxygenation methods may be higher but the sensitivity of nuclear spin-lattice relaxation time measurements is inadequate to measure lower oxygen concentrations.

Kishore *et al.* conclude from polarographic measurements that aqueous solutions flushed with argon contain less than  $10^{-6} \text{ mol} \cdot \text{dm}^{-3}$  dissolved oxygen (47). In the flow method of Trojanek and Holub (22), based on diffusion of gases through a semipermeable membrane into a space with a low partial pressure of the particular gas, the efficiency of oxygen removal is strongly dependent on the ratio of the length of flow through the separation unit ( $L$ ) to the average flow rate of the solution ( $\bar{V}$ ). Under suitable conditions, the value of the oxygen limiting current may be decreased more than 500-fold, which amounts to an oxygen concentration of less than  $5.4 \times 10^{-7} \text{ mol} \cdot \text{dm}^{-3}$ . The semi-logarithmic dependence of the efficiency of oxygen removal on  $L/\bar{V}$  shows no sign of leveling off even at this value. In the apparatus of Blaedel

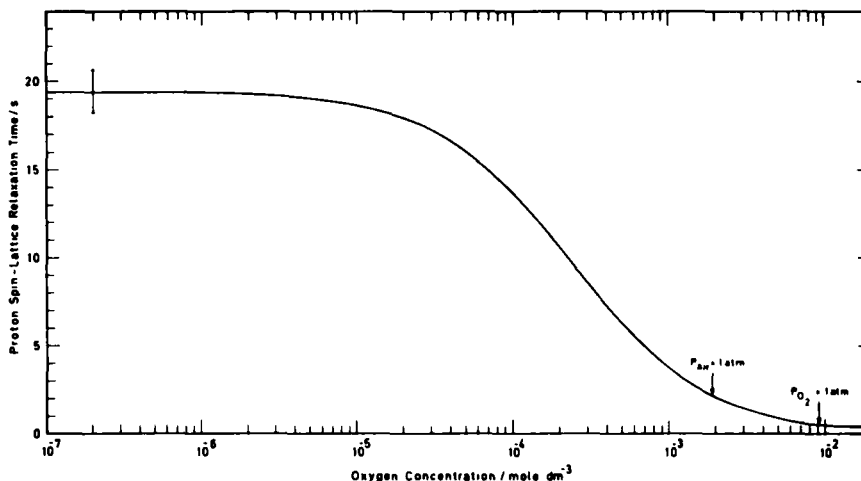


FIG. 2. Dependence of the proton spin-lattice relaxation time of benzene on dissolved oxygen concentration. Graph based on results presented in reference 31. The range of experimental  $T_1$  data for benzene deoxygenated by different reliable methods is indicated with a bar, whereas oxygen concentrations at 1 atm. air pressure and 1 atm. oxygen pressure are indicated by arrows. For data on the solubility of oxygen in benzene see references 93 to 95.

and Todd (20), in which the deaerator is simply a capillary tube, oxygen removal becomes more effective at lower solution and higher gas flow rates. Under suitable conditions, less than 0.1% of the oxygen originally present in the influent solution could be detected, which amounts to an oxygen concentration of  $2.7 \times 10^{-7} \text{ mol. dm}^{-3}$ . This is a flow method and better results may be expected for static methods. Barbooy and Feitelson (48) state that solutions can be freed from oxygen down to about  $10^{-9} \text{ mol. dm}^{-3}$  by a method which essentially consists in a combination of reducing the total pressure of gases above the solution and the degassing method described by Rondeau (24). Combination of methods may in general be expected to be superior to application of one of these methods alone. Ganjoo *et al.*, for instance, first flush with nitrogen and subsequently degas using freeze-pump-thaw cycles (49). This has the clear advantage that the oxygen concentration in the gas that has to be pumped away is very low.

Homer and Coupland, who developed a method of chemical deoxygenation, state that spin-lattice relaxation times for benzene, toluene, p-xylene, mesitylene, acetone, dichloromethane and cyclohexane obtained after chemical deoxygenation are significantly higher than those obtained after the application of other deoxygenation techniques (27). Their measurements were performed at rather high temperature as compared to other nuclear spin-lattice relaxation time measurements and the effect of temperature must therefore be taken into

account. The temperature dependence of the nuclear spin-lattice relaxation time for the compounds mentioned has been studied by various workers. From data reported by Green and Powles on the spin-lattice relaxation time for ring protons in toluene (46a), which are approximately linear against  $1/T$  on a logarithmic scale from  $-90^{\circ}\text{C}$  to  $100^{\circ}\text{C}$ , an activation energy of  $10.5 \text{ kJ.mol}^{-1}$  may be calculated. The same authors report spin-lattice relaxation times for ring protons in p-xylene and mesitylene over a somewhat more restricted temperature range. From these data, which are also fairly well linear with respect to  $1/T$  on a logarithmic scale, activation energies of respectively  $10.9$  and  $11.2 \text{ kJ.mol}^{-1}$  may be calculated. Data on spin-lattice relaxation times for methyl protons in toluene, p-xylene and mesitylene of these authors are not linear with respect to  $1/T$  on a logarithmic scale, which precludes the calculation of activation energies, but they all increase with temperature in the  $0^{\circ}\text{C}$  to  $50^{\circ}\text{C}$  temperature range. From data in the  $-50^{\circ}\text{C}$  to  $50^{\circ}\text{C}$  temperature range of Powles and Neale on the spin-lattice relaxation times for the ring and methyl protons in toluene (46b) activation energies of respectively  $9.9$  and  $7.3 \text{ kJ.mol}^{-1}$  may be calculated. Temperature dependences were also studied for the other compounds mentioned. An activation energy of  $6.3 \text{ kJ.mol}^{-1}$  has been reported for acetone by Bonera and Rigamonti (37). O'Reilly *et al.* have measured proton, deuterium and chlorine-35 relaxation rates in dichloromethane and report that the activation energy for relaxation is essentially the same for H, D and Cl and equal to  $7.6 \text{ kJ.mol}^{-1}$  (50a). Proton spin-lattice relaxation times have also been measured at various temperatures in a solution of 10 mole % cyclohexane in cyclohexane- $\text{d}_{12}$  by O'Reilly *et al.* yielding an activation energy of  $7.15 \text{ kJ.mol}^{-1}$  (50b). The temperature dependence of the spin-lattice relaxation time of protons has also been studied in a number

of compounds not mentioned above, including acetyl chloride, dibromomethane, 1,2-dibromomethane, methyl acetate and nitromethane by Köksal and Çağlayan (43) and hexane and nitrobenzene by Powles and Pajak (51). Activation energies are situated between  $6.3$  and  $13.5 \text{ kJ.mol}^{-1}$  in these studies. Such activation energies bring the  $T_1$  values reported by Homer and Coupland much more in line with other measurements. Also, in a subsequent and more extensive study in which oxygen was also removed by chemical deoxygenation, a considerably lower proton spin-lattice relaxation time is reported for benzene (52). This study also showed that additives (for instance  $\text{CDCl}_3$ ) may considerably increase the proton spin-lattice relaxation time in benzene. It appears reasonable therefore to conclude that the chemical deoxygenation method described by Homer and Coupland is not superior to other deoxygenation methods. This also appears to be the general opinion of workers in the field of nuclear spin-lattice relaxation, where removal of oxygen is of considerable importance. Indeed, in recent studies of nuclear spin-lattice relaxation, deoxygenation is quite generally performed either by the freeze-pump-thaw technique (53-62) or by bubbling with nitrogen or argon (63-65). Degassing by repeated freeze-pump-thaw cycling (66-70) and deaeration by inert gas bubbling (71-81) are also quite generally preferred in current photochemical studies. The same can be said about recent radiation-chemical work (82-92).

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