

Equilibria for mixtures of oxygen with nitrous oxide and carbon dioxide and their relevance to the storage of N₂O/O₂ cylinders for use in analgesia

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Abstract. The liquid-vapour equilibria for the systems nitrous oxide-oxygen and carbon dioxide-oxygen are presented in the form of isotherms on a pressure-composition graph, and isobars on a temperature graph, up to 200 atmospheres ($20.7 \times 10^6 \text{ N m}^{-2}$). In the case of premixed cylinders of a 50/50 nitrous oxide-oxygen mixture used as an analgesic any liquid phase formed as a result of cooling the cylinder to not lower than -40°C can be dispersed by storing the cylinder horizontally for 24 hours at a temperature not less than 5°C .

1. Introduction

The vapour pressure of nitrous oxide is approximately 50 atmospheres ($5.1 \times 10^6 \text{ N m}^{-2}$) at 20°C (Couch and Kobe 1961), so that for a commercial cylinder containing nitrous oxide and oxygen to a total pressure of 136 atmospheres ($13.8 \times 10^6 \text{ N m}^{-2}$) the maximum percentage of nitrous oxide that can be obtained without the condensation of liquid nitrous oxide is 37% by volume if Dalton's Law of Partial Pressures is obeyed. Nitrous oxide is a safe analgesic, a suitable mixture for inhalation being 50% nitrous oxide and 50% oxygen by volume. Particularly for domiciliary administration by midwives to women in labour there is a demand for lightweight cylinders containing a 50/50 nitrous oxide-oxygen mixture. Other developing applications include dental anaesthesia (Bracken *et al.* 1968 a) and in ambulances (Hawkins 1969, Snook 1969). It is essential that at all times the mixture remains in a homogeneous state during the administration. If liquid N₂O were inside the cylinder, then an oxygen-rich mixture would be withdrawn at first, the mixture becoming progressively richer in nitrous oxide until the oxygen concentration fell below 10%. Such a mixture would be dangerous to breathe as it would contain insufficient oxygen to support normal respiration. A prime object of this study was to establish safe procedures for the storage and use of premixed nitrous oxide-oxygen mixtures.

As discussed by Tunstall (1961) and Gale *et al.* (1964) it is in fact possible to produce cylinders filled to 136 atmospheres ($13.8 \times 10^6 \text{ N m}^{-2}$) with a 50/50 mixture of nitrous oxide and oxygen as the sole phase. Basically, the correct amount of liquid nitrous oxide is pumped into the evacuated cylinder, the amount being checked by weight. With the cylinder inverted, oxygen is bubbled up through the liquid nitrous oxide until the total cylinder pressure attains 136 atmospheres. During passage through the liquid, oxygen dissolves in it and also droplets of nitrous oxide are carried up into the gas phase. The net result is that the volume of liquid in the cylinder steadily diminishes until the cylinder is filled only with a homogeneous gas mixture. Condensation of liquid nitrous oxide will occur inside the full cylinder if it is cooled to a temperature less than about -7°C . Temperatures below -7°C can occur in the United Kingdom during winter months and

in many other countries. The following investigation was undertaken to determine the conditions under which condensation occurs and the precautions which could be taken to ensure that no liquid remained in cylinders prior to their use. For comparison purposes a limited study was undertaken with mixtures of carbon dioxide and oxygen, since their physical properties are similar, and some data has already been published (e.g. Zenner and Dana 1963).

2. Experimental details

A static method was used for the study of the liquid-vapour equilibria of the mixtures. The mixture concerned was placed in a high-tensile steel cylinder immersed in a temperature controlled bath of ethylene glycol. When equilibrium was established between the liquid and vapour, the pressure and temperature were measured and samples removed from both phases for analysis.

The gases were of the medical grade supplied by the British Oxygen Company. The nitrous oxide purity is quoted as 99.9%, the impurities being oxygen and nitrogen with a trace moisture content of only 3 to 4 ppm by volume. The purity of the oxygen is quoted as 99.7 to 99.8%, the main impurity being argon. Argon is not liquefiable at room temperature and its critical constants are close to those of oxygen so that the effect of its presence would be negligible.

The cylinders used were mainly of high-tensile steel supplied by the Chesterfield Tube Company and pressure tested to 230 atmospheres ($23.3 \times 10^6 \text{ N m}^{-2}$), the internal volume being approximately 9.4 litres. For high pressure studies four cylinders tested to 340 atmospheres ($34.4 \times 10^6 \text{ N m}^{-2}$) were available, the internal volume of each being 5.7 litres. Dip-tubes were fitted to some cylinders and extended to within $\frac{1}{8}$ in of the bottom of the cylinder so that the liquid phase, if any, could be sampled. One cylinder was fitted with three internal thermocouples, the junctions being respectively at the top, middle and bottom.

With a rotary pump and oil diffusion pump the cylinder to be filled was first evacuated to less than 0.01 torr. The evacuated cylinder was weighed to the nearest 25 g on a spring balance. The required gases could then be pumped one at a time into the cylinder. The cylinder valves and gland, together with all the clearances were filled with distilled water to ensure that every stroke of the pump delivered exactly a pump cylinder full of gas. The gas leaving the pump passed through a drying train consisting of a water separator and silica gel dryer. A by-pass line permitted gas to be decanted directly from supply cylinders into the cylinder to be filled. Three Bourdon-type gauges were available to measure the cylinder pressure. Each was calibrated against a dead-weight tester. As a result of pressurizing, the cylinder normally became quite warm (up to 40 °C) and time was allowed for it to cool to ambient temperature. Nitrous oxide was added first then oxygen. As the oxygen dissolved the pressure fell and more oxygen was added to compensate for this until the required filling pressure was obtained at ambient temperature. The weight of the filled cylinder was checked with the spring balance. The addition of a gas such as oxygen to a cylinder containing some liquid nitrous oxide or carbon dioxide gives rise to a 'ram' effect by which condensation of more nitrous oxide or carbon dioxide causes an intense local heating, sufficient to blister the paint on the cylinder. In order to avoid admitting the oxygen too slowly, the cylinder was periodically disconnected from the compressor and inverted to reduce the local heating. If liquid nitrous oxide had first been introduced, a knowledge of the masses of the gases introduced together with their molecular weights enabled the overall molar composition to be calculated. When no condensation had occurred the change in weight was too small for this method to be used. Recourse was then made to the results of Din and Burn (1965) which give the departures from ideal behaviour of mixtures of nitrous oxide-oxygen and carbon dioxide-oxygen. All filled cylinders were left horizontal for at least 24 hours after filling before use in any cooling experiments, and vigorously rolled to mix the contents.

The temperature-controlled bath contained a total of 32 litres of an equal mixture of water and ethylene glycol. It was fitted with a 1.5kW electric heater and a refrigeration coil

whose rate of cooling was $4000 \text{ cal min}^{-1}$. Stirring was by means of a circulating pump assisted by blowing a stream of air through the fluid. A thermistor held the bath temperature constant to within $\pm 0.1^\circ\text{C}$ over the range from ambient to -20°C . When the set temperature had been attained it was held at this for at least one hour, this being twice the time for the temperature to become constant throughout the cylinder.

The analysis of the gaseous binary gas-liquid (after evaporation) phase was made by analysing the oxygen concentrations using a null-balance paramagnetic oxygen analyser type DCL 101 by Servomex Instruments Ltd. The performance of this analyser has been assessed by Nunn *et al.* (1964). The overall sampling and analysis technique was accurate to within $\pm 0.1\%$ oxygen.

In order to determine the variation of equilibria with temperature, the composition of the vapour phase was checked at 5°C intervals and that of the liquid phase at 10°C intervals. The sampling line and associated pressure gauge were first evacuated and then filled with the gas sample from the cylinder. After the pressure had been read, a portion of the sample was fed into a gas-tight syringe and from this to the oxygen analyser. The volume withdrawn was only $1/2500$ of the cylinder volume.

In the case of liquid samples, the pressure was first measured separately, and then the sampling valve was immersed in the coolant bath so that it attained the same temperature as the cylinder mixture. By this technique the sample could be expanded to atmospheric pressure at its equilibrium temperature. Care had still to be taken to avoid local temperature changes leading to a separation of the sample into two phases at a different temperature. When a phase separation had been detected the cylinder was re-warmed in order to determine how best it could be ensured that the contents had returned to a homogeneous mixture before use.

3. Results

The results obtained on nitrous oxide-oxygen and carbon dioxide-oxygen mixtures are presented in figures 1 and 2 in the form of isotherms on a pressure-composition graph, and also in tabular form (table 1). Above the critical temperature of pure nitrous oxide or carbon dioxide no two-phase region exists and hence there are no equilibrium isotherms above this temperature. The 0°C isotherm for the nitrous oxide-oxygen mixture is shown in figure 3. The curve obtained by joining the points of known vapour composition, the

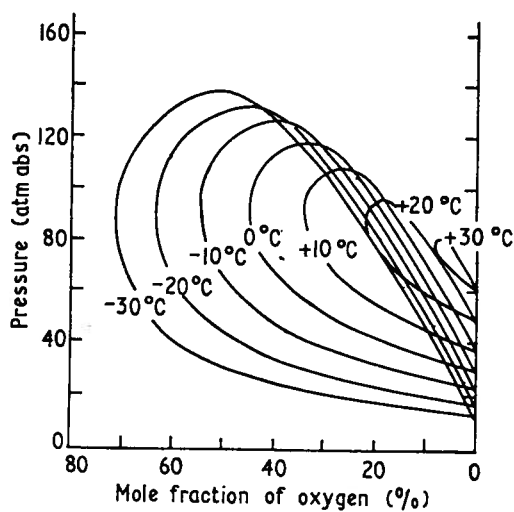


Figure 1. Liquid-vapour equilibrium isotherms for nitrous oxide-oxygen mixtures.

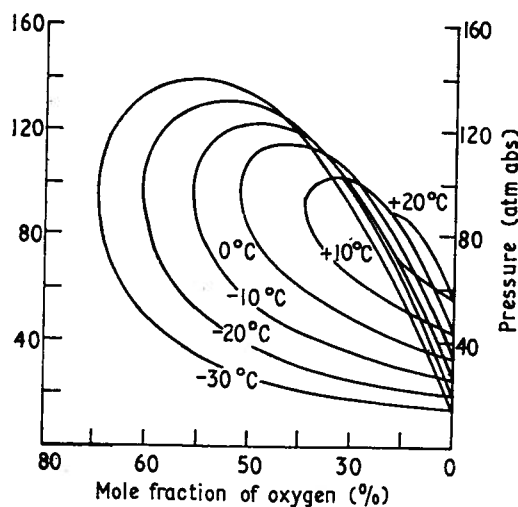


Figure 2. Liquid-vapour equilibrium isotherms for carbon dioxide-oxygen mixtures.

Table 1. Nitrous oxide-oxygen equilibrium data

Vapour curve		Liquid curve	
Pressure (atm)	Composition % oxygen	Pressure (atm)	Composition % oxygen
-30°C		N ₂ O vapour pressure=13.04 atm	
19.6	26.1	29.2	4.3
29.2	46.1	43.7	8.5
33.5	52.6	59.4	13.2
37.7	56.9	72.0	17.2
51.7	64.1	82.0	20.6
59.5	67.2	106.4	29.9
59.9	67.1		
62.2	67.8		
73.1	69.9		
78.3	70.5		
85.3	71.0		
96.8	70.8		
107.0	69.7		
113.1	68.2		
-25°C		N ₂ O vapour pressure=15.27 atm	
22.0	23.2		
31.8	42.6		
38.1	50.4		
42.3	54.2		
45.2	55.8		
51.2	59.3		
62.8	63.6		
76.7	65.3		
89.9	66.8		
102.3	66.1		
113.8	64.0		
-20°C		N ₂ O vapour pressure=17.78 atm	
25.1	21.3	34.4	4.5
34.6	38.7	49.1	8.6
41.1	46.7	66.8	14.0
45.5	50.5	79.8	18.2
54.0	55.7	91.8	22.5
66.7	60.2	117.5	32.8
81.3	62.1		
86.9	62.7		
88.4	62.9		
89.2	63.4		
90.4	63.2		
91.4	62.7		
95.6	63.2		
107.2	61.6		
123.1	56.0		
-15°C		N ₂ O vapour pressure=20.57 atm	
28.1	19.3		
35.9	32.6		
38.6	36.7		
44.4	42.8		
48.6	46.7		
51.6	48.2		
58.1	51.9		

Vapour curve		Liquid curve	
Pressure (atm)	Composition % oxygen	Pressure (atm)	Composition % oxygen
-15°C		N ₂ O vapour pressure=20.57 atm	
70.5	56.3		
85.0	57.9		
91.0	58.7		
99.1	58.3		
113.7	55.2		
-10°C		N ₂ O vapour pressure=23.67 atm	
32.2	17.5	41.0	4.6
41.5	31.7	56.2	9.1
46.4	37.9	75.6	15.3
52.5	43.1	89.3	19.7
62.2	48.3	106.9	26.1
75.1	52.4		
89.5	54.1		
96.1	54.4		
103.3	53.6		
118.5	47.6		
-5°C		N ₂ O vapour pressure=30.87 atm	
35.3	15.6		
45.2	29.2		
49.7	34.1		
54.3	38.3		
56.7	39.0		
16.9	44.5		
79.6	48.4		
94.0	49.4		
108.1	47.7		
0°C		N ₂ O vapour pressure=30.87 atm	
39.4	14.2	49.1	5.0
49.2	26.4	64.0	9.4
53.9	30.7	84.9	16.4
58.7	34.7	98.3	22.0
61.2	35.9	114.1	29.2
71.4	40.7		
84.5	44.0		
99.3	44.5		
113.2	39.3		
+5°C		N ₂ O vapour pressure=35.01 atm	
44.0	12.5		
53.8	23.5		
63.5	31.0		
66.1	32.2		
75.8	36.4		
89.6	39.4		
104.3	37.4		

Vapour curve		Liquid curve	
Pressure (atm)	Composition % oxygen	Pressure (atm)	Composition % oxygen
+10°C		N ₂ O vapour pressure=39.55 atm	
48.8	11.1	58.2	5.2
59.0	20.8	74.3	10.2
68.6	27.6	94.5	18.0
68.7	27.75	104.4	21.65
71.3	28.7		
80.5	32.2		
94.9	33.9		
+15°C		N ₂ O vapour pressure=44.51 atm	
49.8	6.3		
53.6	9.6		
61.4	16.5		
64.1	18.2		
76.7	25.2		
90.6	27.9		
93.4	28.0		
+20°C		N ₂ O vapour pressure=49.93 atm	
55.4	5.4	69.7	5.5
58.9	8.5	92.1	13.9
67.1	14.5		
69.7	15.8		
82.5	21.0		
93.7	21.3		
+25°C		N ₂ O vapour pressure=58.9 atm	
61.3	4.7		
65.5	7.4		
72.6	11.2		
76.7	11.3		
84.4	15.1		
+30°C		N ₂ O vapour pressure=63.32 atm	
68.2	3.7	73.0	2.8
72.4	6.4	80.4	5.7
78.3	8.1		
79.2	8.3		
81.0	7.7		

Vapour pressure values for pure nitrous oxide are taken from Couch and Kobe (1961).

Accuracy: Over the whole range of this study, the accuracy of the measurements was pressure ± 0.1 atm; temperature ± 0.1 °C; composition ± 0.1 % v/v.

'vapour curve' or dew-point curve, gives the point at which the first drop of liquid condenses. Similarly, the points of known liquid composition give the 'liquid curve' or bubble-point curve. If one of these points is approached from outside the loop it gives the point where the first bubble appears. When the mole fraction of oxygen is zero, the bubble-point and dew-point curves meet at the vapour pressure for pure nitrous oxide at the temperature of the isotherm. The broken line in figure 3 adjacent to the vapour curve represents the ideal vapour phase composition assuming that the vapour phase is a mixture of perfect gases obeying Dalton's Law. This assumes that the vapour pressure of nitrous oxide remains

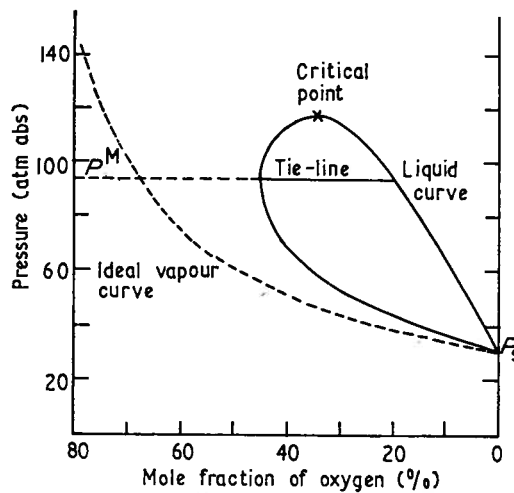


Figure 3. The 0°C isotherm for nitrous oxide-oxygen mixtures.

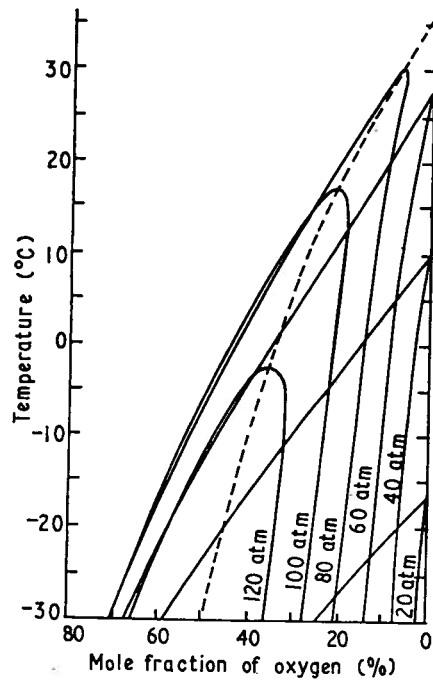


Figure 4. Liquid-vapour equilibrium isobars for nitrous oxide-oxygen mixtures.

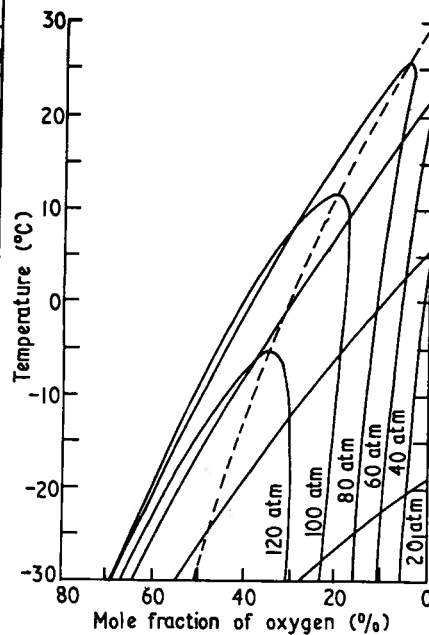


Figure 5. Liquid-vapour equilibrium isobars for carbon dioxide-oxygen mixtures.

constant and independent of the total pressure in the cylinder. In practice the partial pressure of nitrous oxide found in the vapour phase of these mixtures always exceeds that of pure nitrous oxide. Above a certain pressure, P^M (approximately 94 atmospheres, $9.5 \times 10^6 \text{ N m}^{-2}$ in figure 3), the percentage of nitrous oxide increases rather than decreases as the pressure is raised. This results in the liquid and vapour phase compositions becoming equal at a critical point. A horizontal line drawn on the pressure-composition diagram connects positions of equilibrium and is therefore a tie-line. The isotherms of figures 1 and 2 have been transformed into isobars on a temperature-composition diagram as shown in figures 4 and 5.

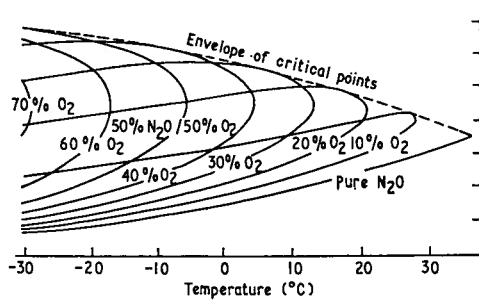


Figure 6. Pressure-temperature curves for nitrous oxide-oxygen mixtures of constant composition.

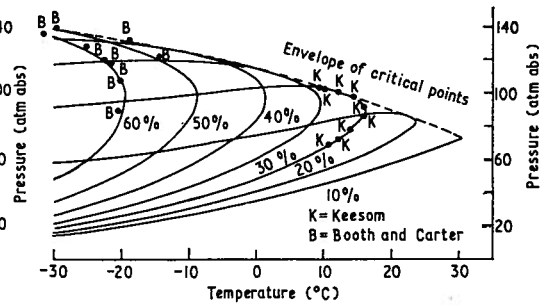


Figure 7. Pressure-temperature curves for carbon dioxide mixtures of constant composition.

When a full cylinder of a 50/50 nitrous oxide-oxygen mixture is cooled, the variation in temperature occurs with the mixture in the cylinder at a constant overall specific volume and there is a corresponding pressure drop, as shown by the broken line AB in figure 10. Point A represents a full commercial cylinder at 136 atmospheres and 20°C. Point B is a dew point and liquid starts to form there. The liquid composition is given by the bubble curve passing through B, i.e. 26% oxygen, 74% nitrous oxide (see figure 1). As cooling is continued the liquid gradually becomes richer in nitrous oxide, the gas phase becoming correspondingly richer in oxygen, figure 11. The case for a mixture of 81.5% nitrous oxide-18.5% oxygen is shown in figure 12. For this mixture the filling density is greater than critical and thus the cylinder is full of liquid at this temperature, and during cooling a bubble point is crossed. Bubbles of vapour now form in the liquid, the composition of the first bubble being 29.2% oxygen, 70.8% nitrous oxide.

The maximum temperature at which liquid will form for the 50/50 nitrous oxide-oxygen mixture is -5.5°C and this is equivalent to a cylinder filled to 115 atmospheres ($11.7 \times 10^6 \text{ N m}^{-2}$) at 20°C. For filling pressures above or below this value the onset of condensation will take place at a lower temperature, i.e. -7°C for a 136 atmosphere filling

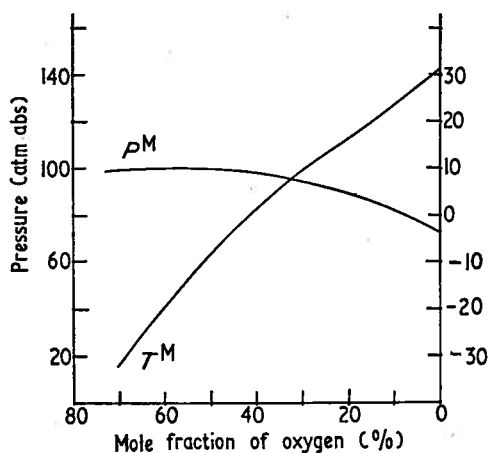


Figure 8. Variation of the maximum condensation temperature T^M and the corresponding pressure P^M with the composition of a nitrous oxide-oxygen mixture.

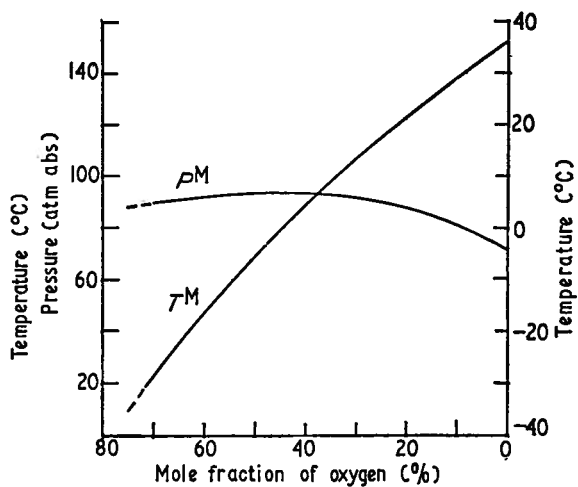


Figure 9. Variation of the maximum condensation temperature T^M and the corresponding pressure P^M with the composition of a carbon dioxide-oxygen mixture.

pressure at 20°C. It can be seen from figure 10 that raising the filling pressure to 204 atmospheres ($20.7 \times 10^6 \text{ N m}^{-2}$) will reduce the condensation temperature to -17°C .

For pressures up to the critical pressure, P_2^c of the less volatile component, i.e. the condensable gas, the two branches of each isobar meet at the temperature corresponding to the vapour pressure of the pure condensable gas for that isobar. For pressures greater than P_2^c the pure nitrous oxide or carbon dioxide cannot exist as a liquid and a vapour phase in equilibrium and so the isobars for these pressures cease to meet the ordinate. In figures 4 and 5 the right-hand portion of each isobar represents the liquid equilibrium, the steep slope indicating that at a constant pressure the rate of change of temperature with liquid composition is rapid. The broken line on each diagram gives the locus of the critical points. Curves of constant composition for the two systems are plotted on the respective pressure-temperature diagrams in figures 6 and 7. Referring to the nitrous oxide-oxygen system, the curve representing pure nitrous oxide reduces to the vapour pressure curve, terminating at the critical point for nitrous oxide. As the oxygen fraction in the mixture is increased so loops are formed, each passing through a temperature maximum, whilst some pass through a critical point and a pressure maximum. All the points of maximum temperature lie on the vapour or dew-point curves, and each critical point lies between the points of maximum temperature and maximum pressure. Figures 8 and 9 illustrate the variation of the critical temperature and pressure with the mixture composition.

4. Discussion

For figures 1 to 7, all the measurements of temperature, pressure and composition producing points lying inside the appropriate loop or curve indicate the existence of two phases, whereas for points lying outside the loop or curve only one phase exists. From figures 8 and 9, it can be seen that an increase in the proportion of the condensable gas contained in the mixture reduces the critical temperature and raises the critical pressure. Figure 6 shows clearly that a liquid phase will form in the 50/50 nitrous oxide-oxygen mixture when the temperature falls below -7°C , thus confirming the results of Crawford *et al.* (1967).

When a full cylinder of a 50/50 nitrous oxide-oxygen mixture is cooled, the variation in temperature occurs with the mixture in the cylinder at a constant overall specific volume and there is thus a corresponding pressure drop, as shown by the broken line in figure 10. Point A represents a full commercial cylinder at 136 atmospheres, and 20°C . Point B is a dew point and liquid starts to form there. The liquid composition is given by the bubble

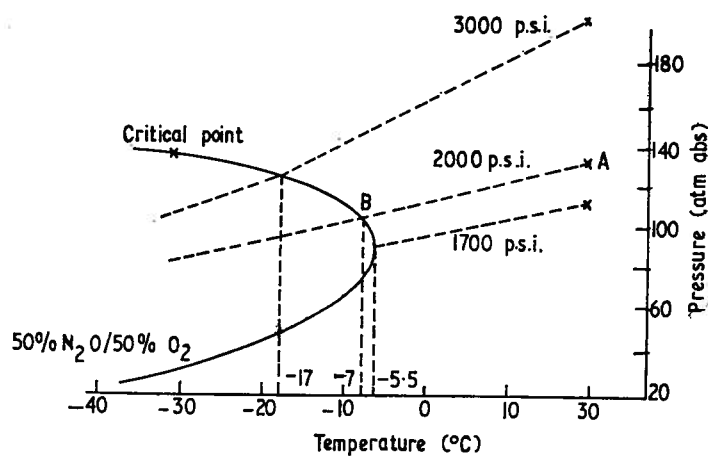


Figure 10. Variation of the pressure with temperature for cylinders of 50/50 nitrous oxide-oxygen mixture.

curve passing through B, i.e. 26% oxygen, 74% nitrous oxide, see figure 1. As cooling is continued the liquid gradually becomes richer in nitrous oxide, the gas phase becoming correspondingly richer in oxygen, figure 11. The case for a mixture of 81.5% nitrous oxide–18.5% oxygen is shown in figure 12. For this mixture the filling density is greater than critical and thus the cylinder is full of liquid at this temperature and during cooling a bubble point is crossed. Bubbles of vapour now form in the liquid, the composition of the first bubble being 29.2% oxygen, 70.8% nitrous oxide.

The maximum temperature at which liquid will form for the 50/50 nitrous oxide–oxygen mixture is -5.5°C and this is equivalent to a cylinder filled to 115 atmospheres ($11.7 \times 10^6 \text{ N m}^{-2}$) at 20°C . For filling pressures above or below this value the onset of

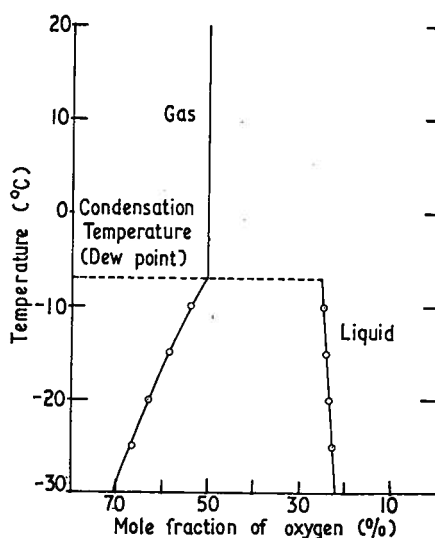


Figure 11. Variation of the composition of the gas and liquid phases during cooling at a constant overall specific volume of a 50/50 nitrous oxide–oxygen mixture when the filling density is less than critical

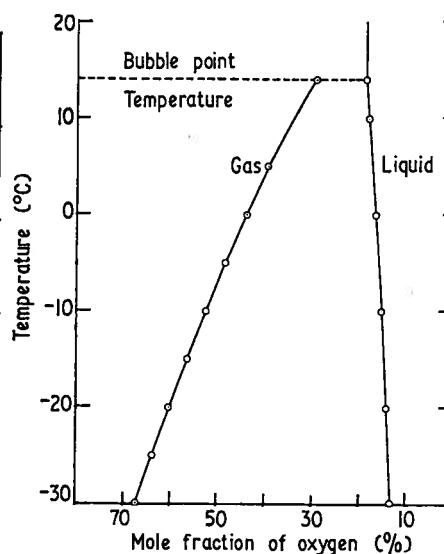


Figure 12. Variation of the composition of the gas and liquid phases during cooling at a constant overall specific volume of a mixture of 18.5% oxygen, 81.5% nitrous oxide when the filling density is less than critical.

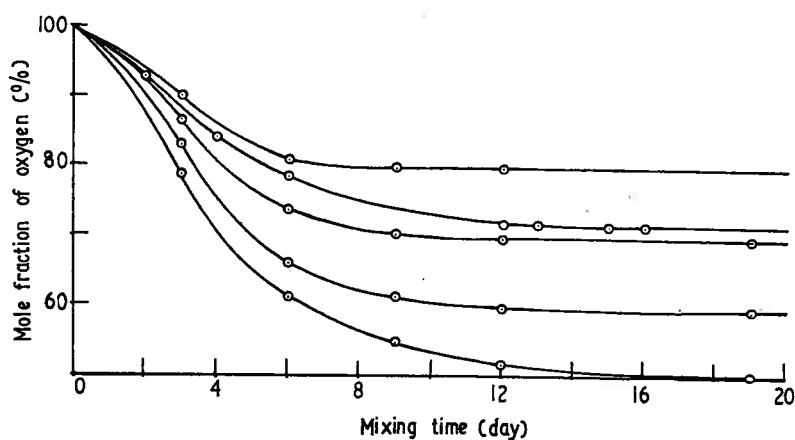


Figure 13. The variation of composition with mixing time for cylinder mixtures of nitrous oxide–oxygen when stored in a vertical position at 20°C , cylinder filling pressure 68 atmospheres ($6.9 \times 10^6 \text{ N m}^{-2}$).

condensation will take place at a lower temperature, i.e. -7°C for a 136 atmosphere filling pressure at 20°C . It can be seen from figure 10 that raising the filling pressure to 204 atmospheres ($20.7 \times 10^6 \text{ N m}^{-2}$) will reduce the condensation temperature to -17°C .

Subsidiary experiments revealed that for an oxygen percentage of 80%, mixtures required a period of 7 days to become homogeneous when stored vertically in cylinders with a filling pressure of 68 atmospheres ($6.9 \times 10^6 \text{ N m}^{-2}$). For a 50% mixture the time increased to 2 weeks, figure 13. By rolling the cylinders horizontally the time could be reduced to 15 minutes. When cylinders containing a 50% mixture were stored vertically at 20°C after an initial cooling to -20°C the time to re-mix increased to several days, figure 14. The filling pressure was 136 atmospheres ($13.8 \times 10^6 \text{ N m}^{-2}$).

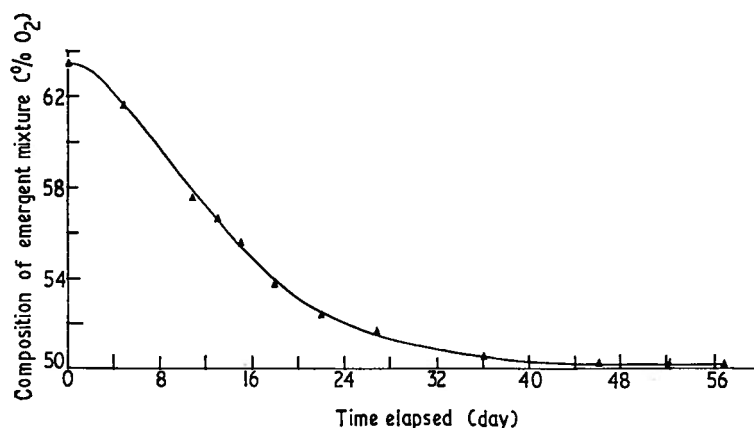


Figure 14. The variation of composition with mixing time for a cylinder mixture of 50/50 nitrous oxide-oxygen when stored in a vertical position at 20°C after an initial cooling to -20°C , cylinder filling pressure 136 atmospheres ($13.8 \times 10^6 \text{ N m}^{-2}$).

When a homogeneous gas mixture is cooled and then rewarmed, if in the process a liquid phase forms, then the mixture is no longer in a state of equilibrium. Mechanical agitation of the cylinder will almost instantaneously re-mix the contents. This can result in a drop in temperature of the mixture of as much as 10 or 12 degC which can lead to a renewal of the liquid phase if the cylinder pressure is sufficiently high. From a large number of experiments it became evident that any cylinder containing a 50/50 nitrous oxide-oxygen mixture at a total pressure of 136 atmospheres ($13.8 \times 10^6 \text{ N m}^{-2}$) and cooled to not lower than -40°C would have a composition of within $\pm 2\%$ by volume of its original value if stored horizontally for 24 hours at a temperature not less than $+5^{\circ}\text{C}$, Bracken *et al.* (1968 b). The adoption of this simple procedure will effectively remove any possibility that cooling of 50/50 nitrous oxide-oxygen mixtures will give rise to a patient breathing a dangerously oxygen-deficient mixture.

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