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ON THE SOLUBILITIES AND RATES OF SOLUTION OF GASES IN LIQUID METHANE

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ABSTRACT

Curves are given which permit the easy calculation of the solubilities of oxygen, argon, carbon monoxide, nitrogen, neon, hydrogen, and helium in liquid methane at temperatures between 90 and 112 K. The solubilities of these gases decrease in the order in which they are listed above. It was also found that the rates of solution of gases in liquefied natural gas are very high. It appears that only the least soluble gases, neon, hydrogen and helium can be used as fuel system pressurants if liquefied natural gas is to be used in aircraft.

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SUMMARY

Hildebrand's methods were modified and used to estimate the solubilities of oxygen, argon, carbon monoxide, nitrogen, neon, hydrogen, and helium in liquid methane (or liquefied natural gas) at temperatures between 90 and 112 K. This is the temperature range of interest in the possible use of liquid methane in aircraft. Curves are presented which permit the easy calculation of the equilibrium solubilities of these gases. Solubilities for the seven gases decrease in the order in which they are listed above. It is probable that the solubilities of oxygen, argon, carbon monoxide, nitrogen, and air in liquid methane are too high to permit their use as a pressurant in aircraft fuel systems.

It was also found by experiment that the rates of solution of gases in liquefied natural gas are very high. This is confirmed by similar experiments in the literature and by considerations based on kinetic theory.

Therefore, it appears that only neon, hydrogen, and helium can be used as pressurants if liquefied natural gas is to be used in aircraft unless the gases and liquid fuel are separated by a barrier.

INTRODUCTION

Liquid methane promises to give higher performance in supersonic aircraft than can be obtained with conventional liquid hydrocarbon fuels (ref. 1). This is because liquid methane has a much greater capacity as a heat sink and has a higher heat of combustion than the conventional fuels. Liquid methane also promises lower, direct operating costs per seat mile and greater payloads in commercial supersonic transport aircraft because of this better performance and because, as liquefied natural gas, it may cost less per Btu (ref. 2).

However, one of the technical problems that must be resolved before liquid methane or liquefied natural gas finds widespread use in aircraft is that of boiloff losses during climb. In a typical supersonic transport mission these losses may amount to 9.6 percent

of the total fuel load unless pumps are installed to recover the boiloff (ref. 2). Even with these pumps some 2000 pounds, or over 1 percent of the fuel load, will be lost during that portion of the climb when the external pressure is being most rapidly reduced (ref. 2). The loss is prohibitive without boiloff recovery pumps and is undesirable even with pumps. Besides, these pumps represent a weight penalty and added cost and complexity.

Therefore, it would be desirable to eliminate both pumps and boiloff losses through changes in the fuel system or fuel. This can be done, in theory, by making the fuel tanks strong enough to withstand the difference between the vapor pressure of the fuel as loaded (1 atm) and the ambient pressure at cruise altitude (about 0.04 atm). Such tanks may be practical although they will be more complex and heavier than tanks that do not have to withstand this pressure difference (ref. 3). Alternately, the fuel could be cooled to below its normal (1 atm) boiling temperature and thereby reduce the vapor pressure to a level that could be contained in conventional (although insulated) tanks at cruise ambient pressures.

Subcooling the fuel presents a new problem. The vapor pressure will be lower than the external pressure when the aircraft is on the ground or at low altitudes and the tanks may collapse unless a pressurant gas is used. This pressurant is air in normal fuel systems but preliminary estimates indicated that air is quite soluble in subcooled methane. Air might dissolve to the extent of about 10 weight percent and this is not acceptable because of the added weight (ref. 3). There are other approaches to this gas solubility problem but none are ideal. The use of less soluble gases or the separation of gas and fuel by some sort of barrier have been considered (ref. 3).

However, the above estimated solubility of air in liquid methane is only an estimate, and, in general, little has been published on the solubilities of gases in this liquid. There are some data, to be discussed later, on the solubilities of helium, hydrogen, and nitrogen in liquid methane as the results from phase studies at high pressure. We know of no published data on some of the other gases that might be considered, and none of the solubility data are for the conditions contemplated in the use of methane in aircraft.

There is also a need to know the rates of solution of gases in liquid methane. Tanks containing subcooled methane could be opened to the air if the rates of solution were low even though the equilibrium solubility might be prohibitively high. Again, we know of no data in this regard.

Therefore, an analysis has been made of the equilibrium solubilities of several gases in liquid methane under conditions that might be encountered in the use of this fuel in aircraft. These results are compared with literature data where available. Some experimental measurements, in rather simple apparatus, were also made of the rates of solution of gases in subcooled methane. These analytical and experimental results are reported herein.

EQUILIBRIUM SOLUBILITIES

The solubility of a gas is directly proportional to the partial pressure of the gas (Henry's law). This solubility will be zero if the solvent-solute system is at 1 atmosphere total pressure and the solvent is at its normal boiling temperature. The partial pressure of the solvent is then 1 atmosphere and the partial pressure of the solute gas is zero. Therefore no gas will dissolve in methane that is freely boiling in a vented tank. But, when the methane is subcooled to below its normal boiling temperature, its vapor pressure is less than 1 atmosphere. The partial pressure of the solute gas then becomes finite when the total pressure of the system is held at 1 atmosphere and the equilibrium solubility of gas in liquid is also finite.

There are only seven gases that need be considered as pressurants for liquid methane systems. All others except fluorine would condense or freeze at the methane liquefaction temperature. Fluorine cannot be considered because it is far too reactive. The normal (1 atm) boiling temperatures and critical temperatures for these gases and for methane are listed in the following table using data from reference 4.

Substance	Normal boiling temperature		Critical temperature	
	K	°F	K	°F
Helium	4.6	-451.4	5.4	-450.0
Hydrogen	20.7	-422.4	33.2	-399.9
Neon	26.3	-412.4	44.9	-378.9
Nitrogen	77.4	-320.4	126.0	-232.9
Carbon monoxide	81.9	-312.3	134.5	-217.6
Argon	87.6	-302.0	151.2	-187.5
Oxygen	90.1	-297.4	154.3	-181.9
Methane	111.7	-258.5	191.1	-115.7

Solubilities in Ideal Solutions

If liquid methane and any of the above gases formed a completely ideal solution, then the solubility of the gas could be calculated from the following equation.

$$x_2 = \frac{p}{p_2}$$

where

x_2 mole fraction of the solute gas in solution

p   partial pressure of the solute gas, atm

p_2 saturation pressure (vapor pressure) of the solute gas at the temperature of the solution, atm

The pressure p_2 as a function of temperature can be determined from standard vapor pressure data up to the critical temperature. And, as Hildebrand shows on pages 241-242 of reference 5, a fair estimate of solubilities above the critical temperature can be made by using pressures obtained by extrapolation on a log saturation pressure against reciprocal temperature plot. These plots for the seven gases and for methane are given in figures 1(a) and (b), using data from reference 4. The extrapolated portions above the critical temperatures are shown as dashed lines in figure 1(b). The oxygen curve is shown as a dashed line in figure 1(a) to distinguish it from the adjacent curve for argon.

As an example of the use of equation (1), consider the solubility of nitrogen in liquid methane at a temperature of 100 K (-279.7° F) and a solvent-solute system pressure of 1.0 atmosphere. From figure 1 the vapor pressures of methane and nitrogen are 0.35 and 7.95 atmospheres, respectively. At 1 atmosphere system pressure, the partial pressure of the nitrogen will be 1.00 - 0.35 = 0.65 atmosphere and the solubility in mole fraction would be

$$x_2 = \frac{0.65}{7.95} = 0.082$$

This is equal to 13.6 weight percent nitrogen in the subcooled methane. These values are for an ideal solution and represent the upper bound; the actual solubilities will always be less in the absence of chemical reaction or hydrogen bonding.

Solubilities in Real (Nonideal) Solutions

Lower, and presumably better, values for solubilities than those obtained from equation (1) can be calculated by correcting for the nonideality of the solutions. Hildebrand (ref. 5) has introduced a solubility parameter δ and differences in the δ value of solvent and solute are a measure of this nonideality. At pressures of 1 atmosphere and for dilute solutions, solubilities can be calculated from the following equation taken from page 244 of reference 5.

$$-\log x_2 = \log p_2 + \frac{V_2(\delta_1 - \delta_2)^2}{4.58\ T} \tag{2a}$$

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where

V_2 molar volume of the solute gas as a liquid, ml

$\delta_1, \delta_2,$ solubility parameters for the solvent and solute

T   absolute temperature of the system, K

At pressures other than 1 atmosphere the equation should be

$$-\log x_2 = \log p_2 + \frac{V_2(\delta_1 - \delta_2)^2}{4.58\,T} - \log p \qquad (2b)$$

It can be seen that any differences in the solubility parameters of solute and solvent introduce a term that reduces the solubility and that the solubility becomes less as these differences increase. For ideal solutions, $\delta_1 = \delta_2$ and the third term in equation (2b) drops out to leave an expression that reduces to the logarithmic form of equation (1).

The solubility parameter is a term based on the latent heat of evaporation per unit volume. Appendix I in reference 5 gives both these values and also the molar volumes for all the compounds considered herein at their normal boiling temperatures. These values are listed in the following table.

Compound	Parameter, δ	Molar volume, V, ml	Temperature, K
Helium	0.5	32	4.2
Hydrogen	2.5	28	20.4
Neon	4.9	17	27
Nitrogen	5.9	35	77
Carbon monoxide	6.1	34	82
Argon	7.0	28	87
Oxygen	7.2	28	90
Methane	6.8	38	112

The solubility parameters decrease in value with increasing temperature and Hildebrand (p. 434 of ref. 5) recommends the following equation for this temperature correction

$$\frac{d \ln \delta}{d \ln V} \cong -1.25 \qquad (3)$$

This requires estimates of the molar volume V at the temperatures of interest which, in turn, requires estimates of density as a function of temperature. These densities were calculated using the following equation taken from page 55 of reference 6.

$$\rho_1 = 2\rho_c + \frac{T_c - T}{T_c - T_b} (\rho_{1,b} - 2\rho_c) - \rho_g \tag{4}$$

where

ρ density, g/ml

$1, c, b, g$ refer to liquid, critical, boiling, and gas, respectively

The molar volumes and the solubility parameters for methane, nitrogen, carbon monoxide, argon, and oxygen were calculated for temperatures between 90 and 112 K and are presented in figures 2 and 3.

Meaningful values of the molar volumes could not be obtained between 90 and 112 K for helium or hydrogen by using equation (4). The critical temperatures for these gases are too far below 90 K to allow reasonable estimates of hypothetical liquid densities. Values were calculated for neon but are suspect for the same reason. However, Hildebrand shows (p. 245 of ref. 5) that the molar volume and solubility parameter calculated for hydrogen at its normal boiling temperature of 20 K can also be used up to 293 K. Therefore in the following calculations for helium, hydrogen, and neon, the normal boiling temperature values for molar volumes and solubility parameters are used at 90 to 112 K. These have already been listed.

Data From Literature

Data on the solubilities of gases in liquid methane were found only for helium, hydrogen, and nitrogen. Those for helium and hydrogen were for very much higher pressures, approximately 20 to 200 atmospheres, than the pressures of interest to this work; nitrogen data was found for more reasonable pressures. For all three gases there were data at several temperatures but, for each, there were only two temperatures appropriate to this study.

In order to estimate solubilities down to pressures of the order of 1 atmosphere, we assumed that Henry's law applied; that is, that the concentration of gas in liquid methane is directly proportional to the partial pressure of that gas in the vapor phase. Therefore, the literature data for the mole fraction of solute gas in liquid methane was divided by the partial pressure (in atmospheres) of the gas in the vapor phase. The quotient is the solubility per atmosphere and is plotted, for helium, hydrogen, and nitrogen in figure 4.

The helium data are from reference 7 and, at temperatures of 90.3 and 106.0 K gave extrapolated solubility values at 1 atmosphere of 5.5×10^{-5} and 8.5×10^{-5} mole fraction, respectively.

The hydrogen data at 116.5 K are from reference 8 and extrapolates to a 1-atmosphere solubility of 10.5×10^{-4} mole fraction. The data at 90.7 K are from reference 9 and are quite scattered (see fig. 4); extrapolation gives a solubility of about 2×10^{-4} mole fraction at 1 atmosphere.

The nitrogen solubility data are from reference 10. These are plotted in figure 4 over a much lower range of pressures than are the helium and hydrogen data. Reasonable extrapolations can be made to 7.7×10^{-2} and 4.3×10^{-2} mole fraction for 99.83 and 110.9 K, respectively.

Calculated Solubilities and Comparison with Literature Data

The solubilities of the various gases in liquid methane can be easily calculated from equation (2) using the vapor pressures, molar volumes, and solubility parameters from figures 1 to 3. As previously mentioned, constant (temperature independent) values for V and δ must be used for hydrogen, helium, and neon. These calculations were made for the six points (two for each gas) extrapolated from the literature and listed above. The results are shown in the following table along with the calculated values for ideal solutions using equation (1).

Solute gas	Temperature, K	Solubility, mole fraction		
		Literature extrapolation	Nonideal solution	Ideal solution
Helium	106	8.5×10^{-5}	1.9×10^{-5}	1.0×10^{-2}
Helium	90.3	5.5×10^{-5}	$.25 \times 10^{-5}$	1.0×10^{-2}
Hydrogen	116.5	10.5×10^{-4}	3.5×10^{-4}	2.9×10^{-3}
Hydrogen	90.7	2×10^{-4}	1.1×10^{-4}	4.1×10^{-3}
Nitrogen	99.8	7.7×10^{-2}	6.0×10^{-2}	12.9×10^{-2}
Hydrogen	110.9	4.3×10^{-2}	2.9×10^{-2}	6.3×10^{-2}

It can be seen that, in all six cases, the nonideal calculation using equation (2) gives values that are less than the literature indicates they should be. These range from 0.78 (nitrogen at 99.8 K) to 0.045 (helium at 90.3 K) of those estimated by extrapolating the literature data. Nevertheless, the values calculated from equation (2) are very much

closer than those obtained from the ideal equation (1). The latter very seriously over-estimates the gas solubilities and especially for helium where the predicted solubilities are over 100 times too high.

It appears that the Hildebrand correction for nonideality is too large. Considerably better agreement with the data can be achieved by multiplying this term by a factor less than 1.0. The factors required to fit the data are:

Solute gas	Temperature, K	Factor
Helium	106	0.76
Helium	90.3	.63
Hydrogen	116.5	.48
Hydrogen	90.7	.83
Nitrogen	99.8	.66
Nitrogen	110.9	.48

However, the use of adjustable constants for each gas and temperature or even for just each gas is obviously of little value. There would be no way of predicting solubilities in the absence of data and no need to predict solubilities if data are available. Nevertheless, the above comparison does indicate that much better results can be obtained by applying a single correction factor to Hildebrand's last term. This factor is about 0.65 based on the data presented herein. Therefore, the following equation is recommended for the prediction of the solubility of any gas in liquid methane over the temperature range of 90 to 112 K.

$$-\log x_2 = \log p_2 + \frac{0.65\, V_2 (\delta_1 - \delta_2)^2}{4.58\, T} - \log p \qquad (5)$$

The constants can be combined and rounded off to give

$$-\log x_2 = \log p_2 + \frac{V_2 (\delta_1 - \delta_2)^2}{7.0\, T} - \log p \qquad (5a)$$

Equation (5a) was used to predict the solubilities, at 1 atmosphere solute gas pressure, shown in figure 5(a) and (b).

Figure 5(a) presents the curves for oxygen, argon, carbon monoxide, and nitrogen. Also shown are the two experimental values for nitrogen. Agreement is excellent at

99. 83 K and good at 110. 9 K. The curves for these gases show that solubility should decrease with increasing temperature and the nitrogen data confirm this. This figure shows the mole fraction solubility of oxygen to be 1.0 at 90 K. This means that oxygen, which has a normal boiling temperature of 90.1 K would continuously condense in, and be miscible in all proportions, with liquid methane at 90 K. This is confirmed by reference 11 where, in a study of the solubility of methane in liquid oxygen, it was concluded that these formed a near-ideal solution at -297° F (90 K).

Figure 5(a) should not be used where the predicted solubilities are very high. Equation (5) only applies to systems where the solute concentration is much less than that of the solvent (ref. 5). The curves on figure 5(a) can be safely used when the partial pressure of the solute gas is well below 1 atmosphere and where the mole fraction of the gas would be small. For example, consider a liquid methane system at 100 K and 1 atmosphere total pressure with air freely circulating above the liquid. At this temperature the partial pressure of the methane would be 0.35 atmosphere (fig. 1) and of the air would be 0.65 atmosphere. Assuming air to be 21 percent oxygen, 78 percent nitrogen, and 1 percent argon, the partial pressures of these three gases would be 0.137, 0.507, and 0.0065 atmosphere, respectively. Their solubilities would then be, using figure 5(a):

Oxygen - 0.137 × 0.40 = 0.055 mole fraction

Nitrogen - 0.507 × 0.08 = 0.041 mole fraction

Argon - 0.0065 × 0.30 = 0.002 mole fraction

These solubilities are all low enough to allow figure 5(a) to be used.

The calculated solubilities for neon, hydrogen, and helium are shown in figure 5(b). Equation (5a) was used along with the extrapolated vapor pressures taken from figure 1(b) and with the normal boiling temperature values for molar volumes and solubility parameters.

For neon, the calculated solubilities are substantially independent of temperature and about 2×10^{-3} mole fraction over the temperature range (fig. 5(b)).

The hydrogen and helium curves in figure 5(b) both show solubilities increasing with increasing temperature. This temperature effect is just opposite that found with oxygen, argon, carbon monoxide, and nitrogen but the limited amount of extrapolated experimental data appears to confirm this analytical trend. The agreement between data and calculation is only fair as seen in figure 5(b). However, the experimental data are quite scattered in one case and the extrapolation of the effect of pressure is long in all cases. All that can be said is that the agreement between calculation and data is within a factor of 2.

In summary, it appears that equation (5a) gives reasonably accurate predictions for the solubilities of gases in liquid methane and should be good enough for the early evaluation of the potential problems in using liquefied natural gas in aircraft.

RATES OF SOLUTION

Reference 3 suggests that liquefied natural gas (LNG) might be subcooled 25° R (13.9 K) for aircraft use but that the solubilities of air or nitrogen would be excessive; the solution of about 10 weight percent nitrogen would be expected. For this amount of subcooling, calculations from figure 5(a) gives the nitrogen and air solubilities as 11.3 and 21.8 weight percent. This study confirms the earlier estimates that equilibrium solubilities are high but does not prove that the rates of solution are so great that equilibrium is likely to be approached. Therefore, some relatively simple experiments were run to get an indication of the rates of solution of gas into LNG.

Apparatus

This is shown in figure 6. The Dewar flask had a capacity of 1.74 liters and was connected, through the use of a silicone-greased rubber stopper to a 1/4-inch outside diameter steel tubing manifold, a Heise 0 to 1.0 atmosphere absolute pressure gage, a vacuum pump, and to either of two sources of solute gas. One was a 19.7-liter glass carboy that was filled to 1 atmosphere. The other was a 16.27-liter steel tank that had its own gage and could be filled to higher pressures. Two copper-constantan bare junction thermocouples were led through the stopper. One had its junction in the liquid and the other measured the temperature of the ullage space in the neck of the flask.

A preliminary experiment on the boiloff rate of LNG showed the heat leak rate into the Dewar to be 232 calories per hour. This heat leak would raise the temperature of confined LNG less than 0.4° C per hour when the flask is full. This small heat leak was included in subsequent calculations.

The volumes of all lines, vessels, and the gage were determined for use in the calculations.

Procedure

The gas reservoirs were pumped down to less than 1 torr and then filled with the solute gas under investigation.

The natural gas was condensed from the laboratory supply lines. A mass spectrometric analysis of the condensed liquid gave

Component	Concentration, mole percent
Methane	90.9
Ethane	3.5
Propane	1.4
Carbon dioxide	.9
Nitrogen	2.7
Oxygen	.6
Total	100.0

The nitrogen, oxygen, and carbon dioxide were probably contaminants introduced during liquefaction. There were also trace amounts of less volatile components that showed up as a residue when a flask of LNG had evaporated nearly to dryness. The Dewar flask was weighed prior to each experiment to get the weight of LNG.

The flask was connected to the system and the LNG subcooled by pumping off a part of the charge. There were some slugging losses in preliminary experiments. These were avoided later by adding a few porous ceramic chips as boiling aids and by throttling the pump inlet during the early part of the pump down. The LNG was so subcooled about 15° C (27° F) in 30 to 45 minutes and then closed off for about 1/2 hour to come to temperature equilibrium and to insure that there were no leaks. The liquid temperature as measured by the thermocouple always corresponded to that calculated from the measured system pressure within the accuracy of the temperature measurement (about 2^O C) using pure methane vapor pressure data.

After subcooling and when the 19.7-liter, 1-atmosphere reservoir (supply system A in fig. 6) was used, the connecting stopcock was fully opened so that all parts of the system were at the same pressure. This resulted in an initial increase in system pressure to near 1 atmosphere followed by a decrease in pressure as the gas dissolved in the LNG. System pressure was recorded as a function of time.

When the pressurized tank gas supply (system B in fig. 6) was used, the valve on this tank was manually controlled to keep the Dewar at near 1 atmosphere pressure. The pressure in this supply tank was then recorded as a function of time.

With either system the rates of solution were observed for 5 to 35 minutes with the LNG flask undisturbed. These rates were quite high initially but slowed down very much by the end of this time. The experiment was continued by gently swirling the LNG flask by hand. There was sufficient flexibility in the connecting line to allow a swirling motion, in the horizontal plane, with an amplitude of 1 to 2 centimeters and a rate of 2 to 4 cycles per second. This is a very mild agitation but the rate of solution increased markedly and then again became very slow after another 5 to 15 minutes. At the end of this time, the

flask was disconnected and reweighed.

Calculations were made of the rates of solution from a knowledge of the pressures, volumes, and temperatures of the various parts of the system. The perfect gas law was used along with enthalpy charts and the previously determined heat-leak rate into the Dewar.

Results

The data were calculated to mole fraction dissolved and were plotted as a function of time. Typical results aie shown in figure 7. The equilibrium solubilities calculated for nonideal solutions are also shown.

A result for nitrogen using the 19.7-liter gas reservoir is shown by the dotted line in figure 7. In this experiment the total pressure in the system was almost 1 atmosphere immediately after opening the stopcock (time zero on these plots) but decreased, in this experiment, to 368 torr by the end of the run. Therefore, the equilibrium concentration decreased with time. It can be seen that the rate was quite high in quiescent LNG for 2 to 3 minutes but leveled off after 6 to 8 minutes. The rate increased again when the flask was swirled but again quickly leveled off.

Figure 7 shows as a solid line similar data taken with the pressurized supply tank where the solution rates were at about 1 atmosphere total pressure. The two curves in figures 8 are much the same.

Other experiments were run but their results are not shown, partly because of a defect in the experiment but most important, because a truly quantitative description of solution rates was not possible in this type of experiment.

As shown in figure 7, the amounts of nitrogen dissolved by the end of the experiment were less than that calculated for equilibrium. This might be because saturation was not reached but, more probably, was due to oxygen and nitrogen left in the LNG after subcooling and prior to the solution rate experiments. The LNG was condensed at below its normal boiling temperature in a separate system and was poured into the Dewar flask. Air dissolved during this transfer but this air was expected to be completely removed during pump down. However, a mass spectrometric analysis made near the end of the project showed that there was considerable nitrogen and oxygen present after subcooling by pump down and before the solute gas was intentionally added. Therefore, the LNG was already partly saturated prior to the solution experiment.

This air contamination problem could have been overcome but we realized that the rate of solution is critically dependent on the degree of agitation of the liquid and we know of no criteria for describing liquid phase agitation. Therefore, there is no way of expressing, quantitatively, solution rates as a function of agitation.

Mass transfer and thermal conduction are certainly the rate-limiting processes in the quiescent experiments. When a solute gas is admitted over a liquid, the very uppermost surface must quickly become both saturated by the gas and heated by the enthalpy contribution of this gas. Concentration and temperature gradients are set up which limit the rate for further gas additions. These gradients and subsequent rates would be amenable to purely analytic solutions for a completely quiet liquid. However, natural convective mixing would complicate the analysis. The results would be of little practical importance anyway since any aircraft application would have liquid motion in the fuel tanks.

These experiments showed only that the rate of solution is quite fast and that appreciable amounts of nitrogen are dissolved in 2 to 3 minutes in a system where the motion of the liquid is much less than that in any sort of a mobile fuel system. Therefore, LNG cannot be exposed to gases with high equilibrium solubilities with the hope that little will dissolve because the rate of solution might be low.

This conclusion from simple experiments is confirmed by a study of the rates of solution and evolution of air into vigorously shaken petroleum fluids (ref. 12). Rates were determined for fluids ranging from heavy lubricating oil to aviation gasoline and it was found that the rate of solution increased with decreasing fluid viscosity. The gasoline was least viscous (0.635 centistoke) and, in two experiments, had a half-life solution time of only 1.21 and 1.34 seconds with strong shaking. Liquid methane has an even lower viscosity (0.33 centistoke at its normal boiling temperature) so it can be assumed that the rate of solution of gases into LNG would be even higher. This suggests that LNG would be substantially saturated in a few seconds if a liquid-gas system were agitated strongly.

This same conclusion can be reached from arguments based on kinetic theory when mass and heat transfer are not limiting. There would be no concentration or temperature gradients in a well-stirred system and the solution rate would be controlled by the arrival rate of gas at the gas-liquid interface. This arrival rate per unit area, W, is given by

$$W = \frac{1}{4} n \bar{c}$$

where n is the number density and $\bar{c}$ the mean molecular velocity. At 100 K and 1.0 atmosphere, the arrival rate for nitrogen is 0.84 gram mole per second per square centimeter. In the experiments with the quiet liquid there were about 40 gram moles of LNG, about 50 square centimeters of liquid to gas surface, and about 2/3 atmosphere nitrogen pressure. The arrival rate of nitrogen would then be $0.84 \times 50/40 \times 2/3 = 0.70$ mole nitrogen per second per mole of LNG. Since the equilibrium solubility is of the order of 0.04 mole per mole, saturation should be achieved in less than 0.1 second in

the absence of concentration and temperature gradients. The rate would be even higher if the area of the surface to gas interface were increased by shaking.

Rates of Gas Evolution

There is the related question as to how easily a gas contaminated solution of LNG could be degassed. Nothing was done in this regard except the observation that oxygen and nitrogen were still present in LNG that had been subcooled about 15° C by evacuation; 8 to 10 percent of the LNG was so removed. This should have been expected since the removal of the more volatile components (oxygen and nitrogen) from an only moderately less volatile liquid (LNG) cannot be accomplished by a simple flash evaporation. An efficient separation of these components would require a fractional distillation. Consideration of this aspect is beyond the scope of this report.

CONCLUDING REMARKS

A study of the equilibrium solubilities and the rates of solution of gases into sub-cooled liquid methane (or liquefied natural gas) was prompted by an interest in this hydro-carbon as a possible fuel for the Supersonic Transport or other supersonic aircraft.

Calculations were based on Hildebrand's treatment of nonideal (real gas) solutions. These showed that the solubilities of nitrogen, carbon monoxide, argon, and oxygen would all be quite high in subcooled methane. For example, when subcooled 25° F (13.9 K) below its normal boiling point, this calculated value was 11.3 weight percent for nitrogen. Carbon monoxide, argon, and oxygen would be even more soluble. On the other hand, neon, hydrogen, and helium are much less soluble. Calculations for these three gases are probably less exact. Nevertheless, it appears that the solubilities of neon, hydrogen, and helium in 25° F (13.9 K) subcooled methane will be about 2×10^{-3}, 5×10^{-4}, and 1×10^{-4} mole fraction, respectively.

Curves are presented which allow the easy calculation of the solubilities of all these gases in methane or LNG between 90 and 112 K.

A few experiments were run on the rates of solution of gas into LNG. These showed that the rates were quite high in completely quiet LNG with an indication that equilibrium solubility would be approached in a few minutes with only modest agitation. Other evidence suggests that equilibrium solubility would be attained in the order of a second if the liquid-gas system were shaken vigorously.

Therefore, it seems that one of the less soluble gases, neon, hydrogen, or helium, must be used as a pressurant in a LNG system unless the gas and liquid phases are separated by a physical barrier such as a membrane or some floating material. Otherwise there will be a considerable dilution of the fuel which probably would not be acceptable for aircraft operations.

Lewis Research Center,
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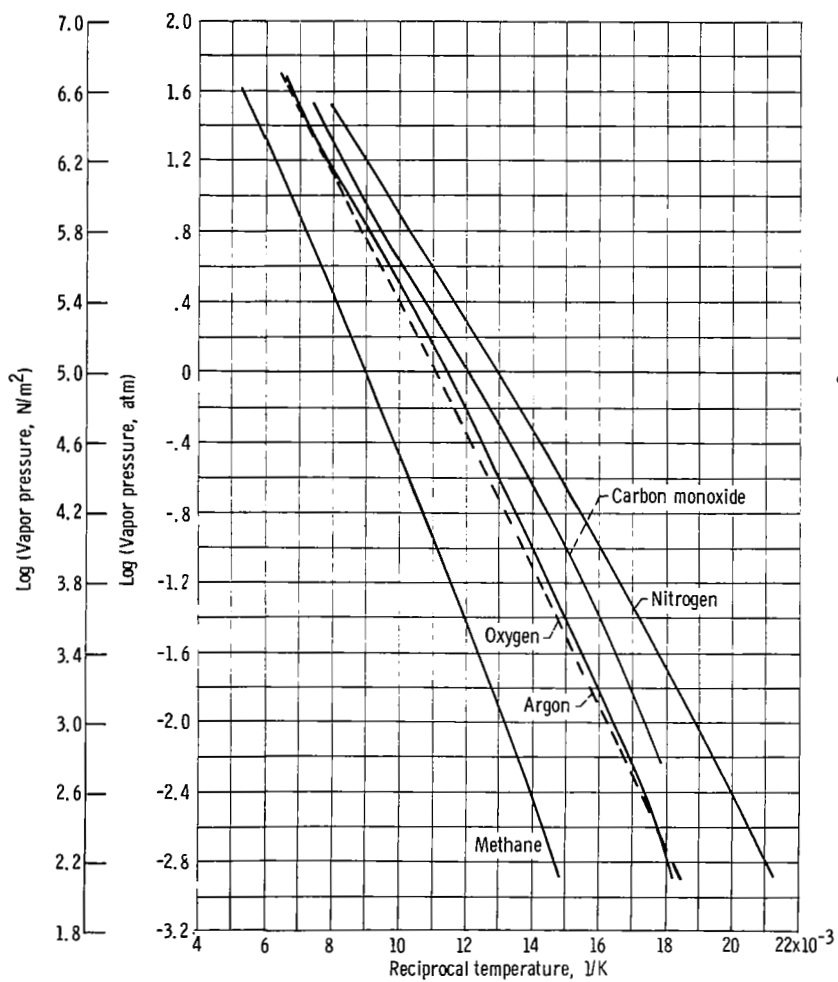
(a) Methane, oxygen, argon, carbon monoxide, and nitrogen.
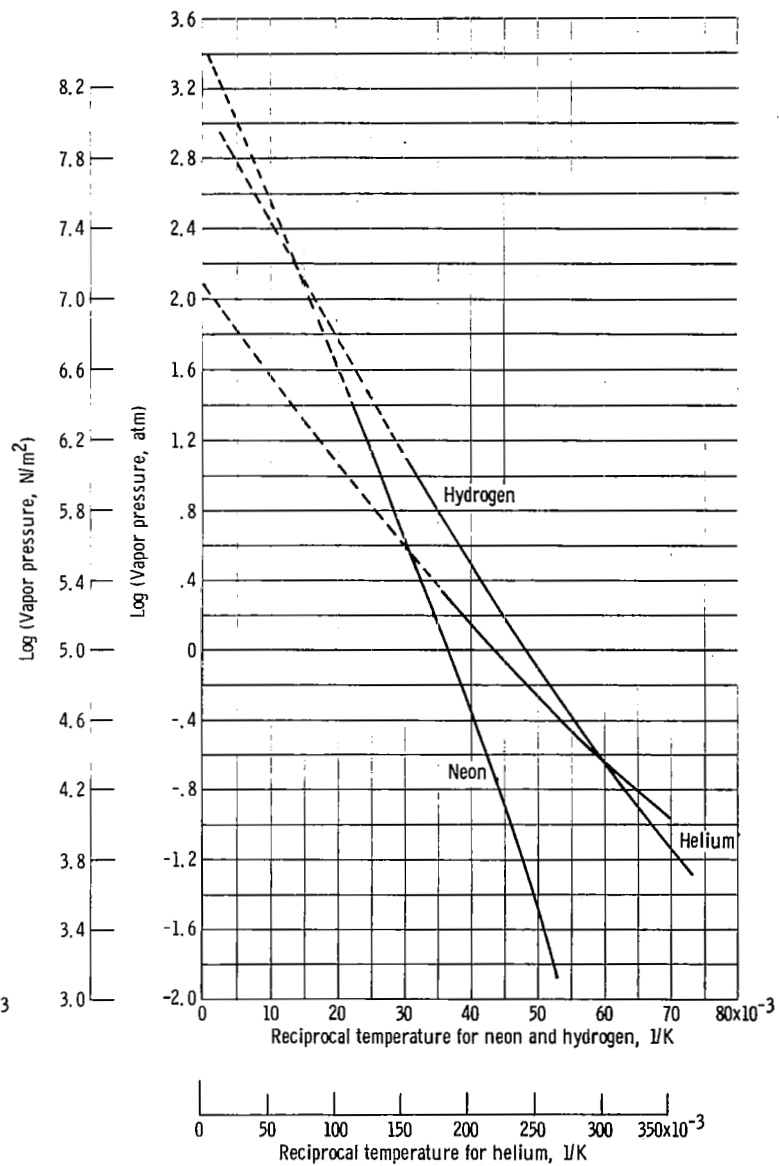
(b) Neon, hydrogen, and helium.

Figure 1. – Vapor pressure as function of temperature.
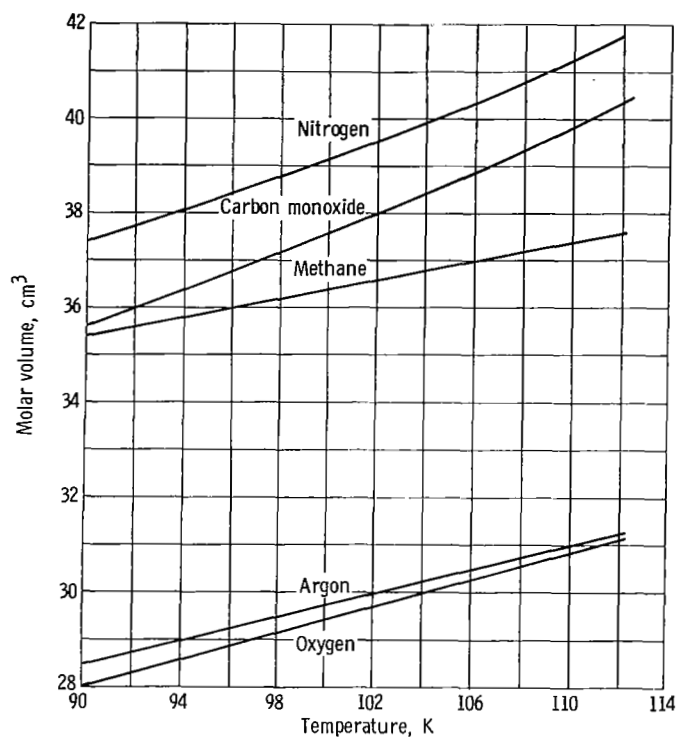
Figure 2. - Molar volume as function of temperature.
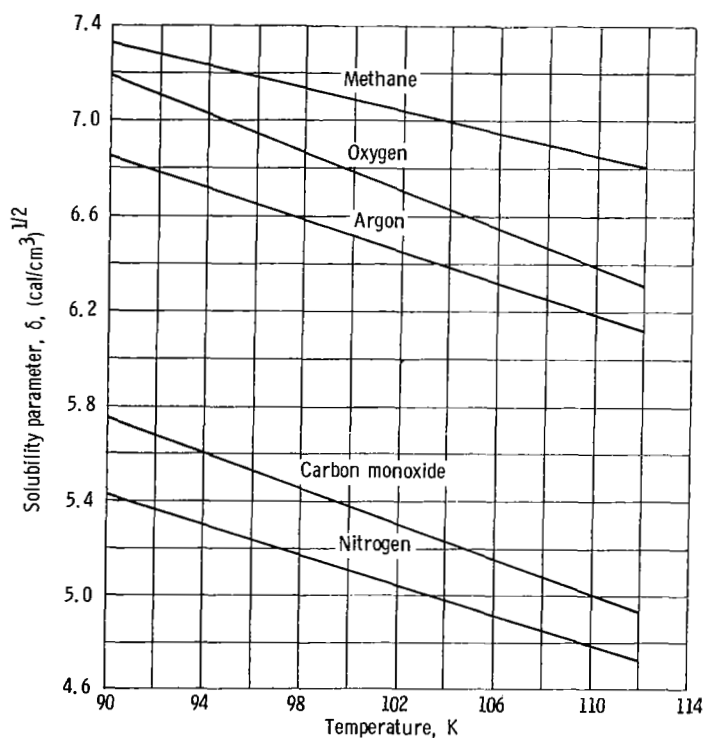
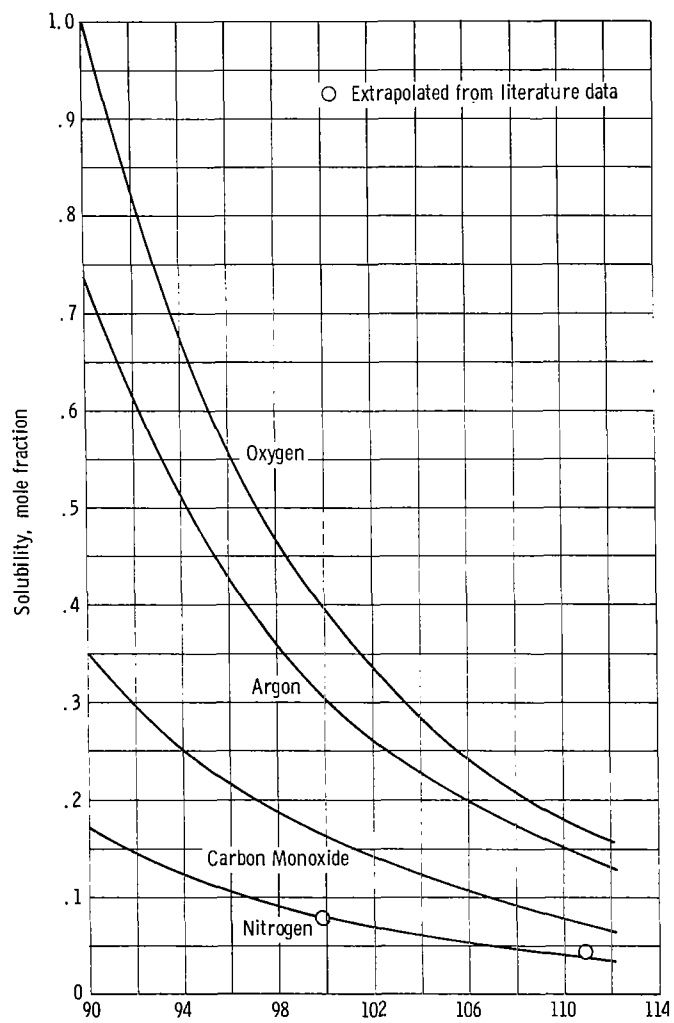Figure 3. - Solubility parameter as function of temperature.
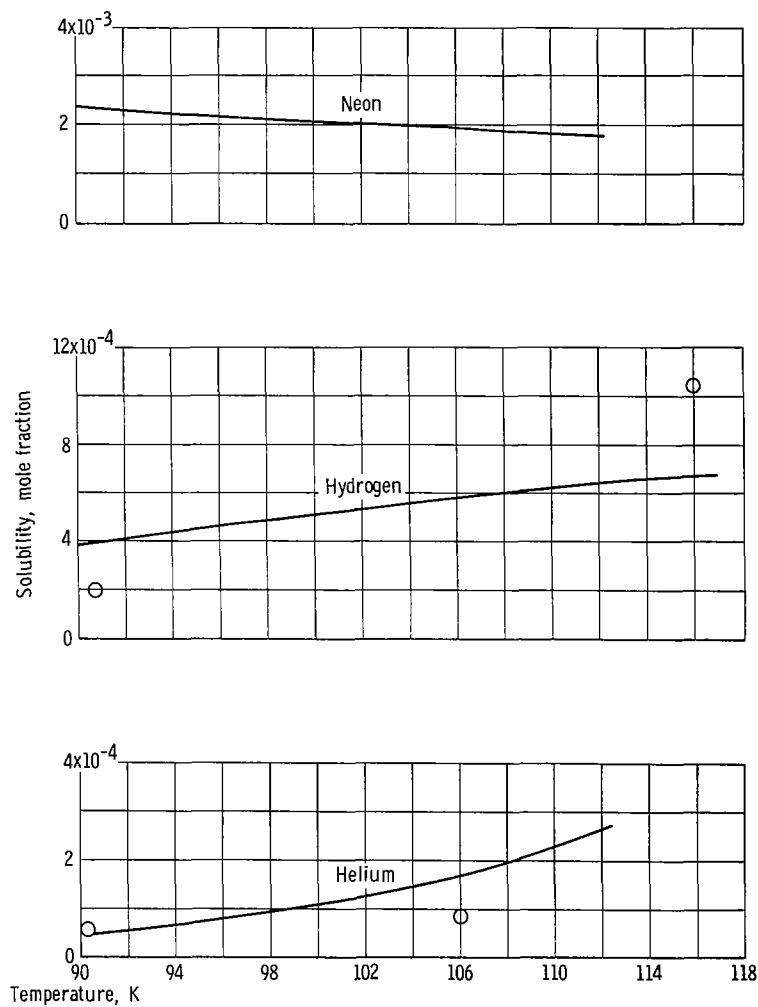
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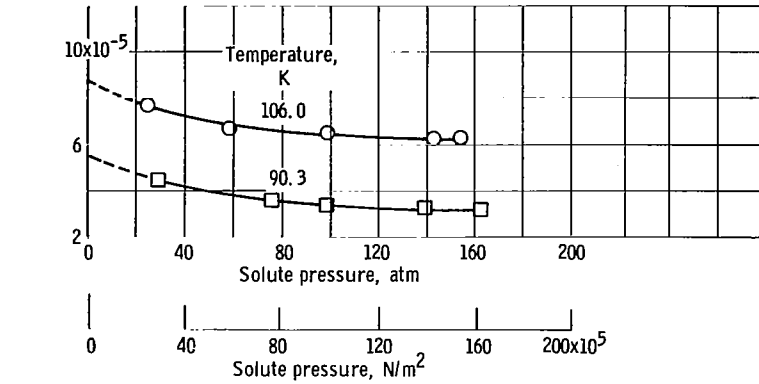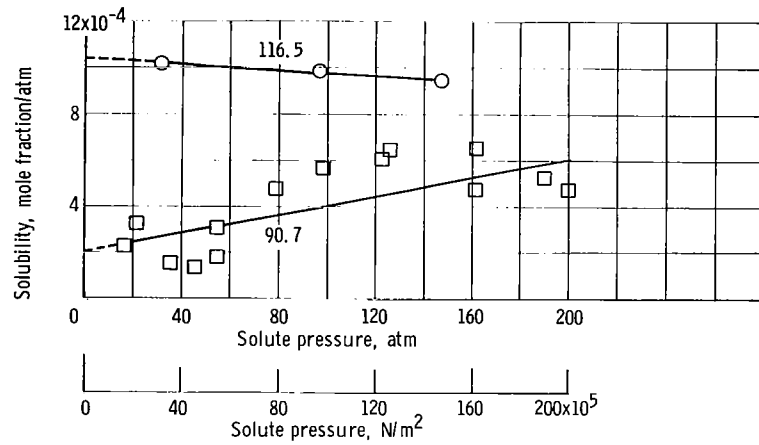
(a) Helium.

(b) Hydrogen.
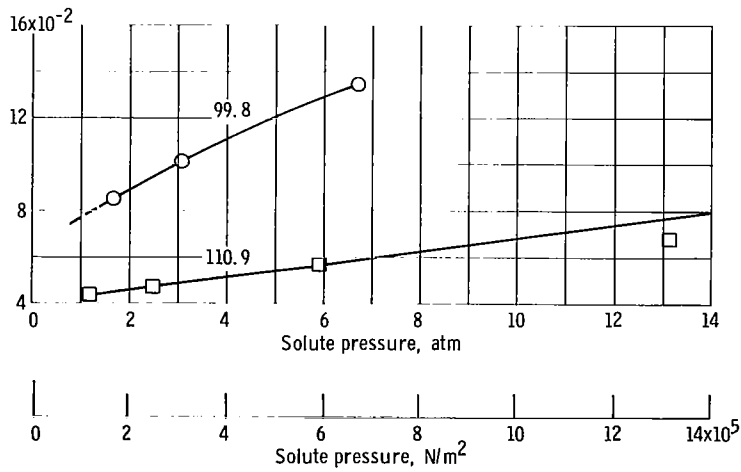
(c) Nitrogen.

Figure 4. – Literature values for solubilities of Helium, Hydrogen, and Nitrogen.

(a) For Oxygen, Argon, Carbon Monoxide, and Nitrogen.

(b) For Neon, Hydrogen, and Helium.

Figure 5. - Calculated solubilities of gases in liquid methane at solute partial pressure of 1.0 atmosphere (1.013x10^5 N/m^2).
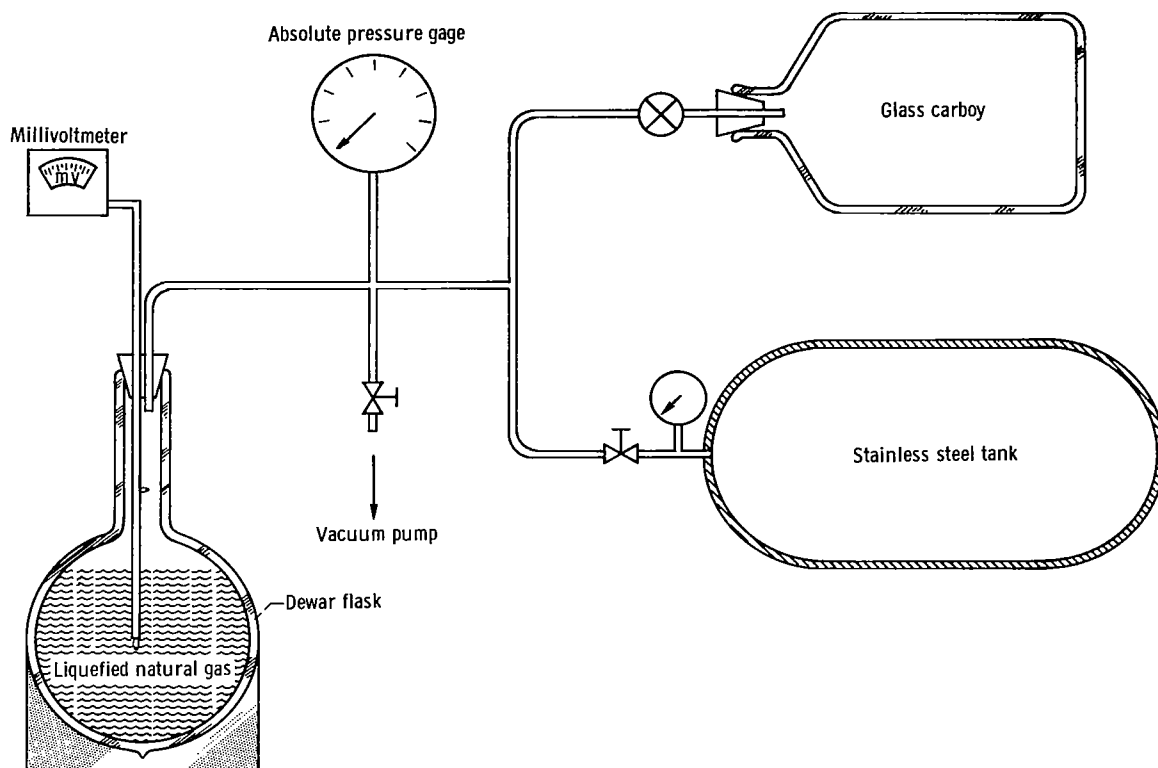
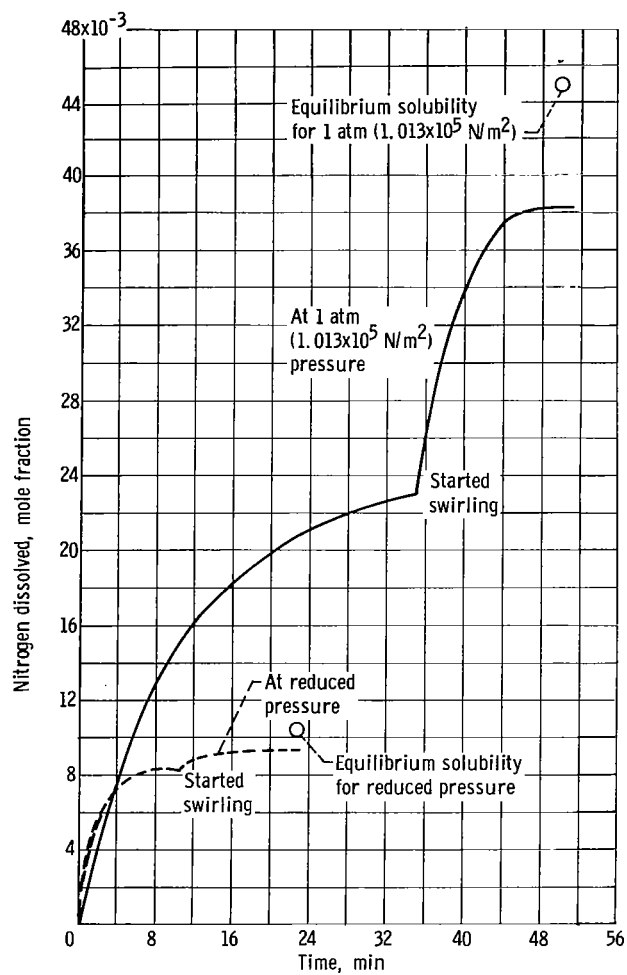Figure 6. – Apparatus for measuring rates of solution.

Figure 7. – Rates of nitrogen solution In liquefied natural gas.