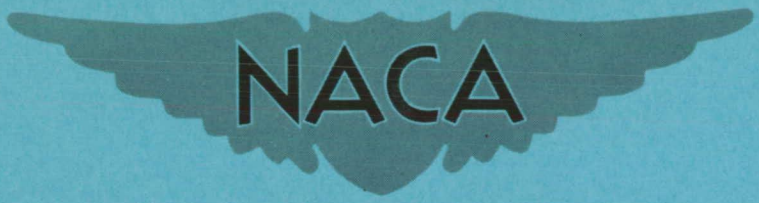

RESEARCH MEMORANDUM

DILUTION OF LIQUID OXYGEN WHEN NITROGEN IS USED FOR PRESSURIZATION

By Thomas J. Walsh, R. R. Hibbard, and Paul M. Ordin

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NATIONAL ADVISORY COMMITTEE
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SUMMARY

A graphic method for determining the composition and phases existing within a propellant tank when liquid oxygen is pressurized with nitrogen gas is presented, and an example of the calculations involved is included. The assumed limiting conditions are that the pressurizing gas flows adiabatically from the pressure tank and that the equilibrium state exists in the oxygen-nitrogen system. Enthalpy-concentration plots for the oxygen-nitrogen mixtures at constant pressures from 100 to 600 pounds per square inch absolute are presented. Both the equilibrium considerations and a small amount of experimental testing show that gaseous nitrogen is unsuited for pressurizing liquid-oxygen systems.

INTRODUCTION

Gas-pressurization systems provide a simple and commonly used means for feeding propellants into rocket combustion chambers. Nitrogen and helium are often so used. Ideally, the pressurizing gas should neither dissolve in the propellants nor condense in the tanks; helium is preferred on both counts.

Nitrogen is considerably cheaper than helium and is widely used, especially with systems operated at ambient temperatures. However, for use at the low temperatures required with liquid oxygen, nitrogen is far less attractive than helium. At these low temperatures and at the pressures of interest, the nitrogen can dissolve in the oxygen to the extent that the propellant is seriously diluted. The dilution may vary from negligible amounts to equilibrium concentrations, depending on the elapsed time between pressurizing the tank and discharging its contents and on the rate at which equilibrium is approached. Therefore, both the equilibrium state of the oxygen-nitrogen system and the rate of solution are factors in considering the feasibility of using nitrogen as a pressurizing gas.

This report considers the vapor-liquid equilibrium for the oxygen-nitrogen system with the assumption that the pressurization is an

adiabatic process. The extent to which liquid oxygen must be diluted to attain a given equilibrium pressure then can be determined by using enthalpy-concentration diagrams, which are presented herein for pressures from 100 to 600 pounds per square inch absolute. Also presented is a limited amount of experimental data that roughly indicate the amount of dilution experienced in one propellant system. The rate at which equilibrium is approached may be expected to be influenced both by system design and by method of operation. Therefore, the experimental results will not be directly applicable to other systems.

PROCEDURE

An enthalpy-concentration diagram for oxygen-nitrogen mixtures at 1 atmosphere is given by Dodge in reference 1. This diagram is based on the enthalpy-temperature data of Millar and Sullivan for pure oxygen and nitrogen (ref. 2), where the zero enthalpy base for both components is taken at the normal boiling point of nitrogen (139.3° R). Similar diagrams were prepared for higher pressures by the following method (enthalpy data from ref. 2 were used throughout).

In evaluating vapor-liquid equilibriums, the experimental data of Dodge (ref. 3) at low pressures were combined with the calculated data of Koch and Williams (ref. 4) at high pressures by preparing a plot of pressure against the mole percent oxygen in the vapor with constant mole percent oxygen in the liquid as a parameter. Smooth curves were drawn through the two sets of data and are shown as figure 1.

The methods used for determining the enthalpy of oxygen-nitrogen mixtures at various temperatures can be shown by referring to figure 2, where curves for the pure components were first drawn.

The enthalpy-temperature relations for saturated liquids are shown as solid lines in this figure. Below the critical temperature for nitrogen the enthalpy of mixtures is simply a linear function of composition, and curves were so drawn. Next, the critical conditions for the pure components were connected by a straight line (shown by dot-dash in fig. 2), and it was assumed that the enthalpies of mixtures at their critical temperature lie on this line and are directly proportional to molar composition. This fixed the critical-point condition for any mixture and permitted the saturated-liquid curves to be extended from the lower temperature region by fairing through the critical points.

The enthalpies of mixtures in the saturated-vapor state (dashed lines in fig. 2) were estimated by adding the latent heats of vaporization to the enthalpies of the saturated liquids. Latent heats of vaporization were estimated by using the relation between latent heat and reduced temperature developed by Watson (ref. 5) to determine the latent

heat of the mixture. This relation indicates that the ratio of the latent heat at a given temperature to the latent heat at the normal boiling point is a unique function of the reduced temperature. The particular relation for this system was developed by plotting the latent-heat ratio against reduced temperature for oxygen and for nitrogen on a common plot and drawing the best smooth curve through the combined data. The single curve was used for all mixtures and was read in reverse to determine latent heat as a function of temperature for the various mixtures of nitrogen and oxygen. The latent heat thus determined was added to the enthalpy curves for the liquid state to produce a smooth loop for each 10-percent increment of oxygen in the mixture, as shown in figure 2.

Figure 2 was used to determine the enthalpy for the enthalpy-concentration plots at various pressures. The assumption of no heat of mixing is implied by this method. Dalton's and Raoult's laws were used to calculate the equilibrium composition for the liquid existing at a given temperature and at a predetermined total pressure. The enthalpy was read, and a point was marked on the saturated-liquid (bubble-point) line. The equilibrium vapor composition was read from figure 1, and the vapor enthalpy was determined; this fixed a point on the saturated-vapor (dewpoint) line. Several such points determined both lines. The resulting enthalpy-concentration charts are presented for several pressures ranging from 100 to 600 pounds per square inch absolute in figure 3.

APPLICATION

The use of figure 3 to estimate equilibrium compositions is shown by the following example. The enthalpies of gaseous nitrogen and liquid oxygen are required, and figure 4 gives the enthalpy for nitrogen over the region of interest; that for liquid oxygen can be taken from figure 2.

Assume that liquid oxygen at 1 atmosphere pressure and at its normal boiling point (162° R) is contained in a tank with negligible ullage, and must be pressurized to 200 pounds per square inch absolute with gaseous nitrogen at 1000 pounds per square inch absolute (68 atm) and 520° R. The molar enthalpy of the liquid oxygen is 280 Btu (fig. 2) and for the gaseous nitrogen is estimated to be 4885 Btu (fig. 4). These points are located on figure 3(c) (for 200 lb/sq in. abs, with the nitrogen point obtained by extrapolation). A straight line is then drawn between the points; the intercept of this line with the saturated-liquid curve (point x on fig. 3(c)) gives the composition of the liquid phase at adiabatic equilibrium. In this case, sufficient nitrogen would have to be added to give a liquid phase which is 83 mole percent oxygen and 17 percent nitrogen. The temperature would then be 218° R, and the vapor phase would be 42 mole percent oxygen and 58 percent nitrogen.

EXPERIMENTAL RESULTS

The preceding example shows that the use of nitrogen to pressurize liquid-oxygen tanks can result in a substantial dilution of the propellant. At higher pressures the dilution would have been more severe.

However, in the practical case, nitrogen might be used without significant dilution, because the nitrogen would condense only at the surface of the oxygen and would be transferred into the body of the liquid by diffusion or mixing. If these diffusion or mixing processes were sufficiently slow, much of the oxygen could be drawn off as substantially undiluted liquid.

To test this possibility, an insulated tank having a volume of about $1\frac{1}{2}$ cubic feet was fitted with a dip tube to the bottom to take off liquid phase and with a pressure line to the top (fig. 5). This tank was 60 to 80 percent filled with liquid oxygen and was pressurized from a nitrogen supply at 1500 pounds per square inch absolute and 520° R. After holding for varying times, the liquid oxygen was released at rates of 0.1 to 0.2 pound per second, and samples were taken from the product line at times corresponding to varying percentages of liquid withdrawn. These samples were analyzed for oxygen content.

While no consistent data were obtained, the results from two such runs are shown in figure 6, where the percent of oxygen found in the liquid product is plotted against the percent of liquid taken from the tank. Data from runs made at 450 and 900 pounds per square inch absolute and with different holding times are shown. The calculated composition for the equilibrium liquid is 72 mole percent oxygen and 28 percent nitrogen at 450 pounds per square inch absolute. At 900 pounds per square inch absolute the adiabatic model predicts that there would be no liquid phase at equilibrium, since 900 pounds per square inch absolute is well above the critical pressure and cannot be generated from a simple vapor-pressure effect. It may be assumed, however, that equilibrium conditions were not obtained for any of the tests. In both cases the first portions of the liquid taken from the tank were undiluted oxygen; this shows that nitrogen had not diffused to the bottom of the tank in the holding times used. However, only a part of the tank contents could be withdrawn as substantially undiluted oxygen, and this amount differed between these two runs in an unexplainable manner. These data are contrary to expectations, since more undiluted oxygen was available for the higher pressure - longer holding time run. However, variations in the degree of mixing, heat input, temperature stratification, and solubility may account for these initial results. Nevertheless, in both cases the liquid withdrawn during the later portions of these runs was seriously diluted. Rocket performance would be appreciably reduced with such a propellant. Pressurization with helium gas under the same conditions and at a pressure of 900 pounds per square inch indicated no contamination of the oxygen.

CONCLUSIONS

With an adiabatic process assumed, enthalpy-concentration diagrams are developed herein that can be used to estimate the equilibrium composition of the liquid phase after liquid oxygen is pressurized with gaseous nitrogen. At equilibrium the liquid contains substantial quantities of nitrogen. Limited experimental work also indicates a serious dilution of the oxidant when nitrogen is used as the pressurizing gas. However, a barrier at the liquid-gas interface would permit the use of nitrogen. A float might be used, or possibly small amounts of helium added to the oxidant tank prior to pressurization would serve as an adequate barrier to diffusion.

Lewis Flight Propulsion Laboratory
National Advisory Committee for Aeronautics
Cleveland, Ohio, January 9, 1958

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2. Millar, Russell W., and Sullivan, John D.: Thermodynamic Properties of Oxygen and Nitrogen. Tech. Paper No. 424, Bur. Mines, 1928.

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4. Koch, H. A., Jr., and Williams, V. C.: Graphical Residual, Its Application to Phase Relations of Oxygen and Nitrogen. Chem. Eng. Prog., vol. 43, no. 11, 1947, pp. 623-632.

5. Watson, K. M.: Prediction of Critical Temperatures and Heats of Vaporization. Ind. and Eng. Chem., vol. 23, 1931, pp. 360-364.

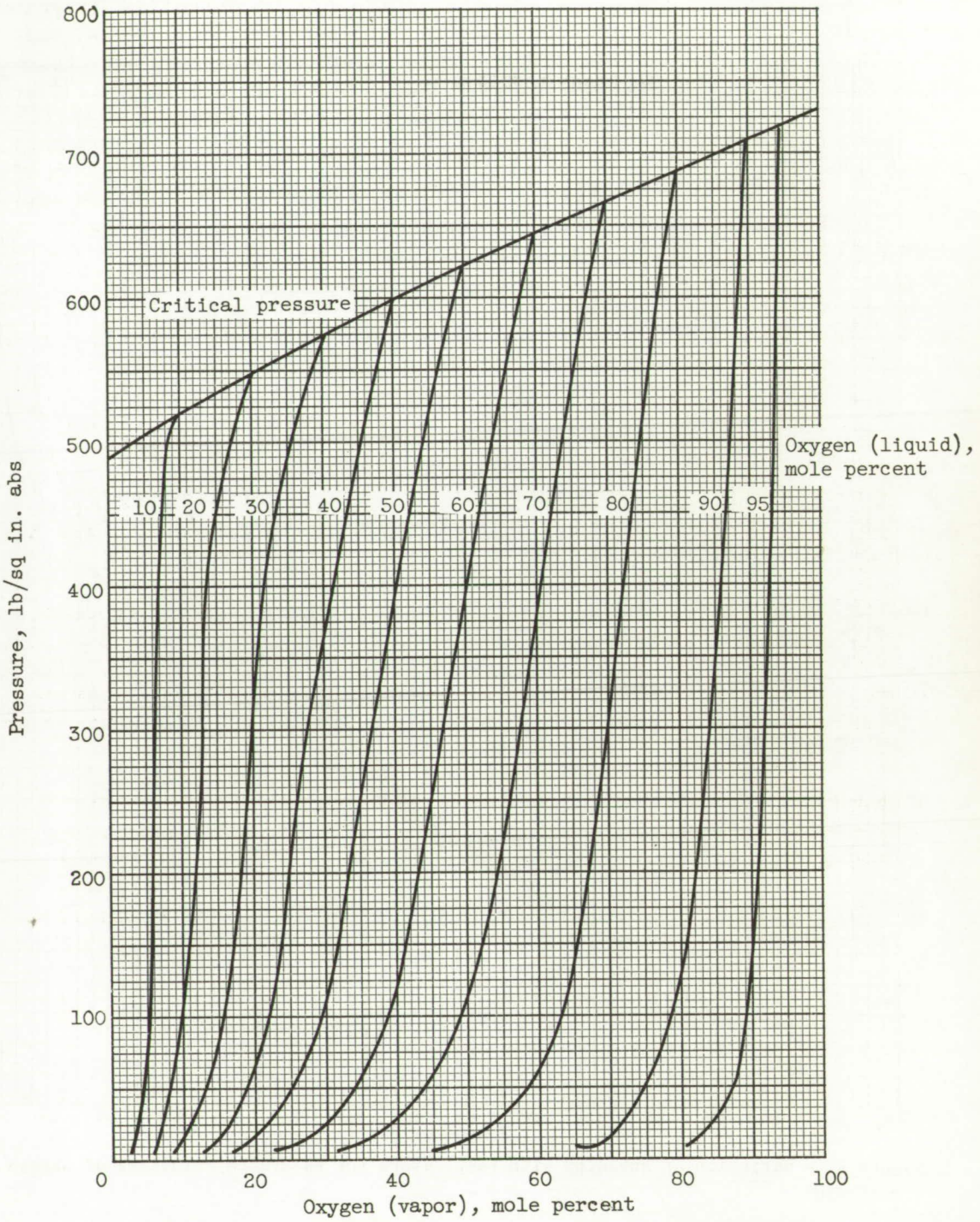


Figure 1. - Vapor-liquid equilibrium data for oxygen-nitrogen mixtures.

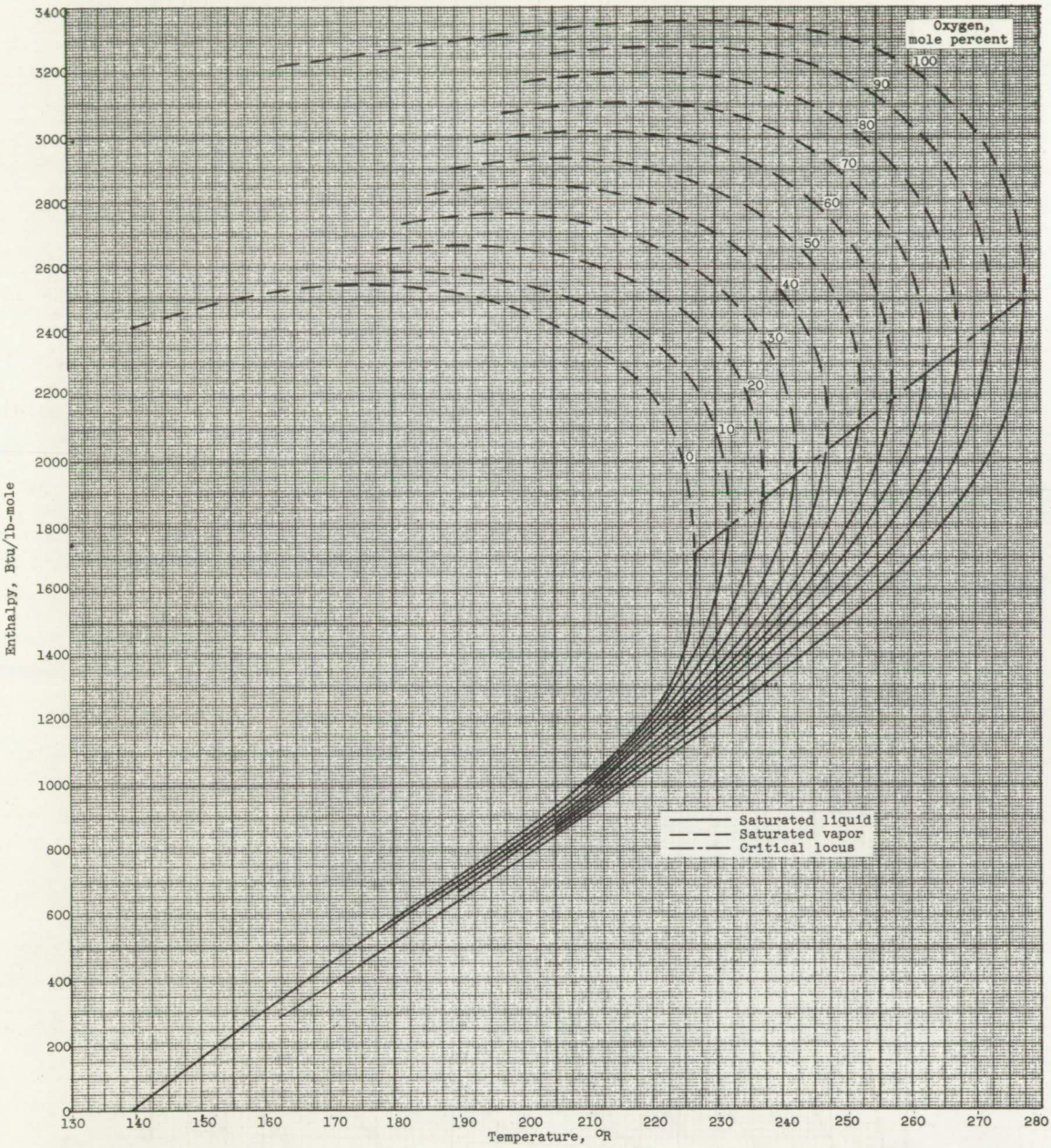
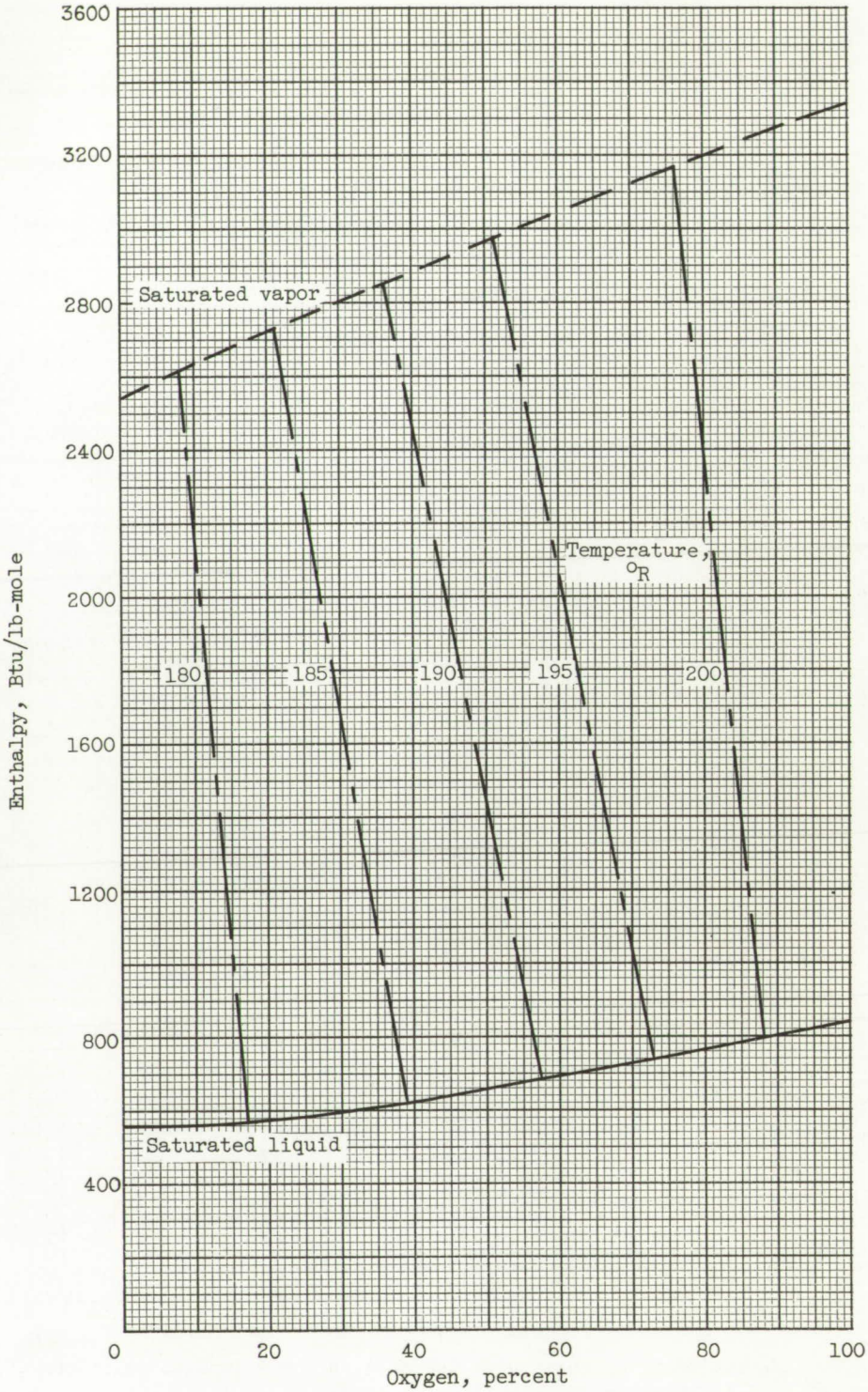
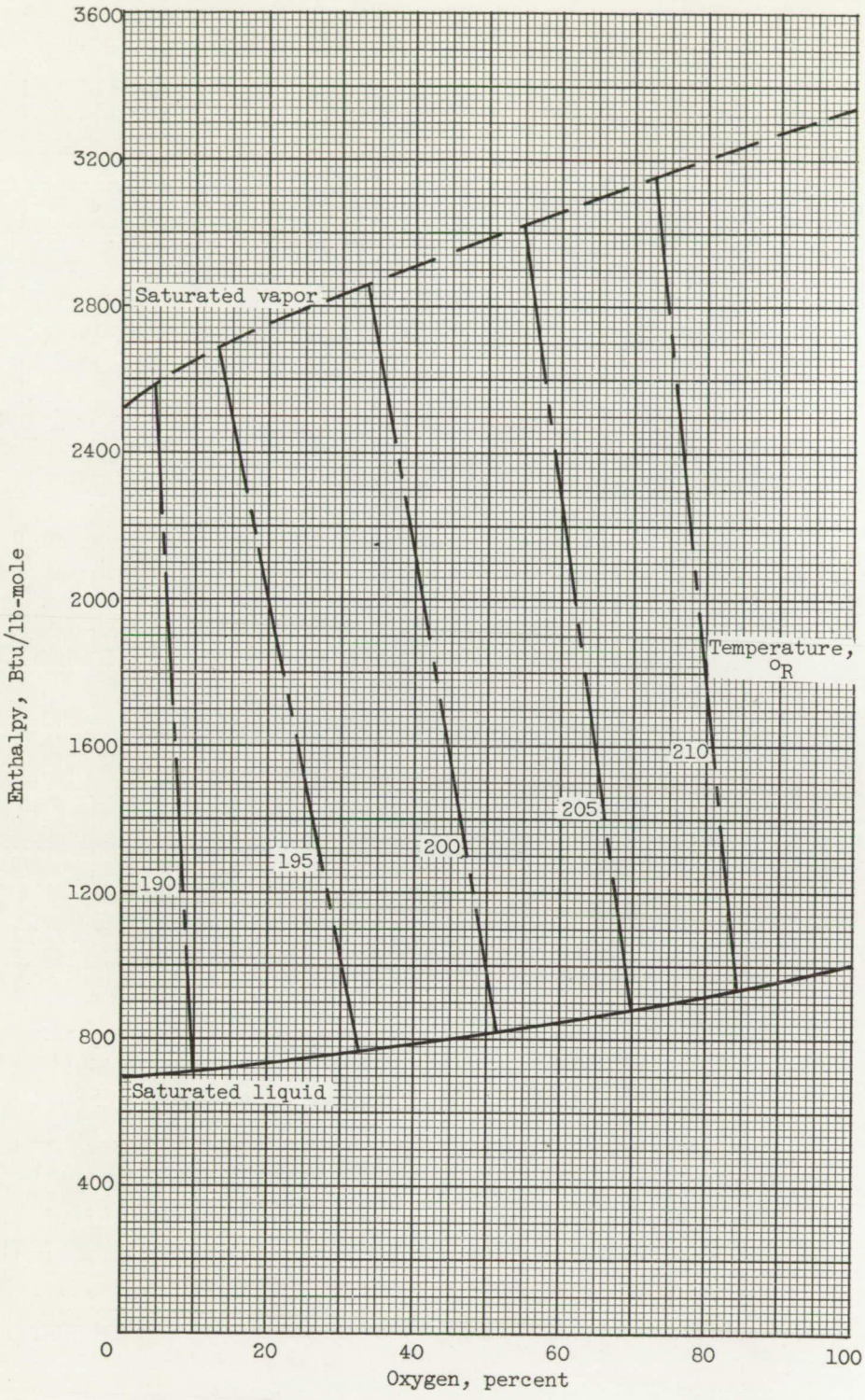


Figure 2. - Variation of enthalpy with temperature for saturated solutions of oxygen and nitrogen.



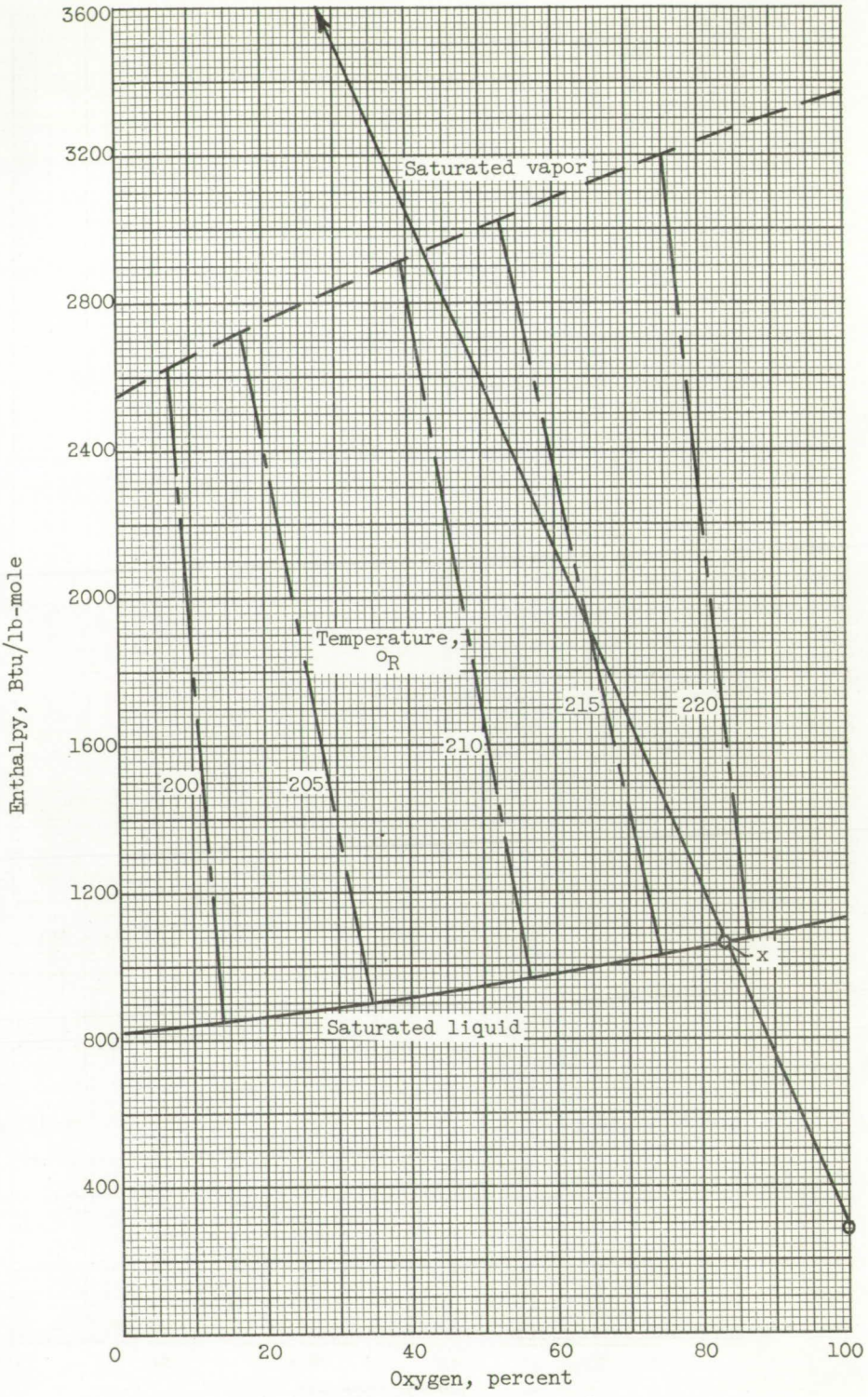
(a) Pressure, 100 pounds per square inch absolute.

Figure 3. - Variation of enthalpy with concentration for oxygen-nitrogen mixtures at constant pressures.



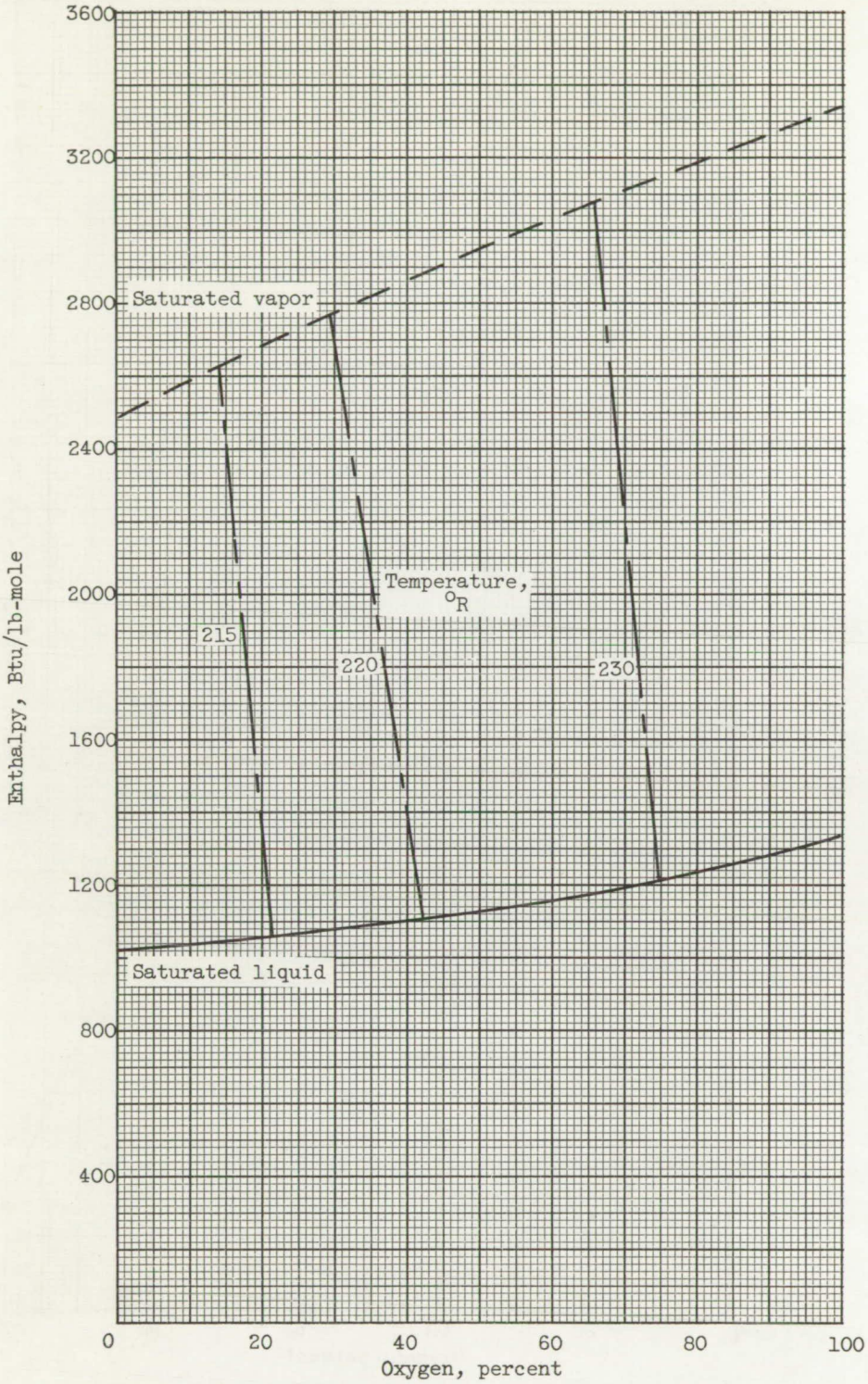
(b) Pressure, 150 pounds per square inch absolute.

Figure 3. - Continued. Variation of enthalpy with concentration for oxygen-nitrogen mixtures at constant pressures.



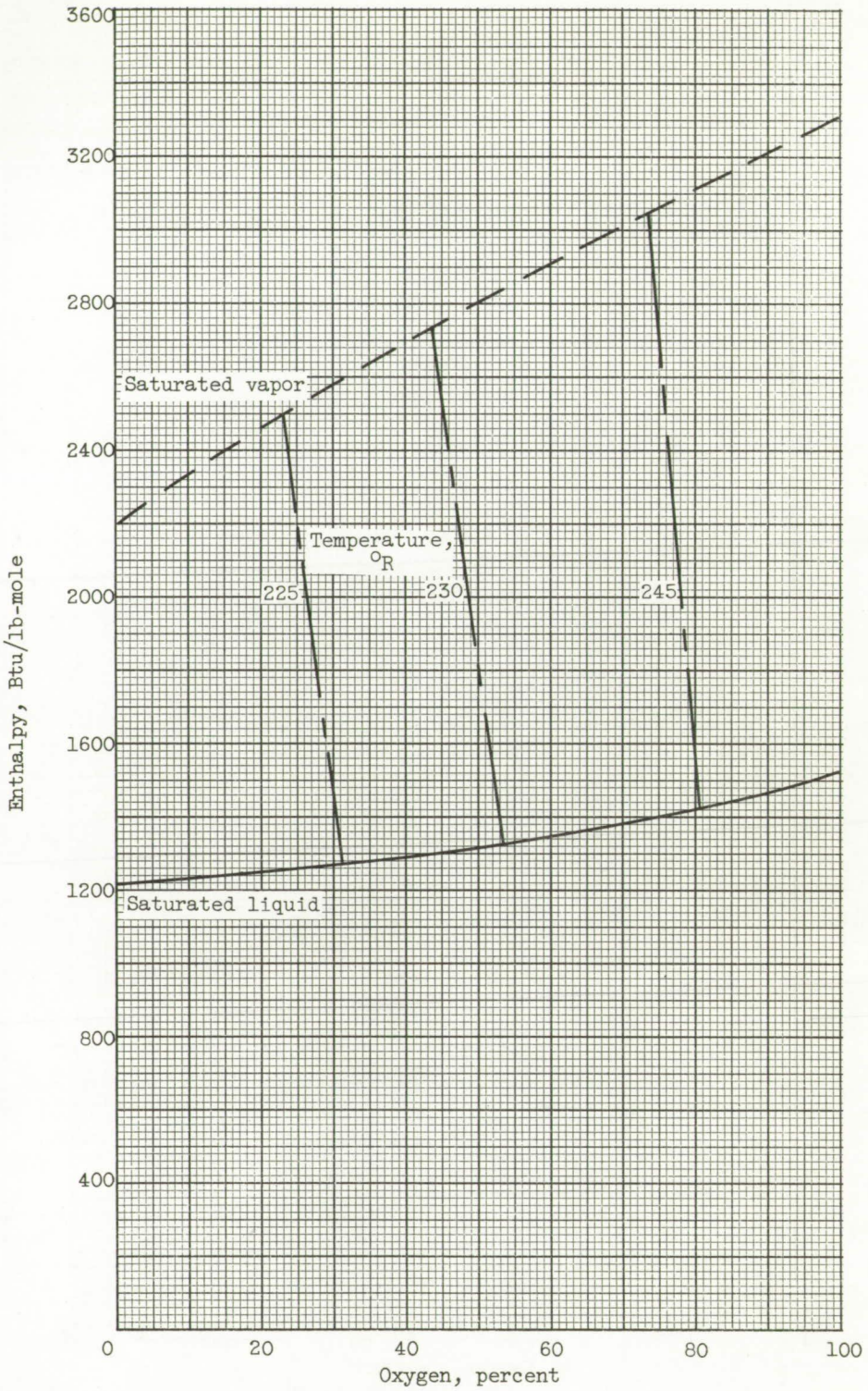
(c) Pressure, 200 pounds per square inch absolute.

Figure 3. - Continued. Variation of enthalpy with concentration for oxygen-nitrogen mixtures at constant pressures.



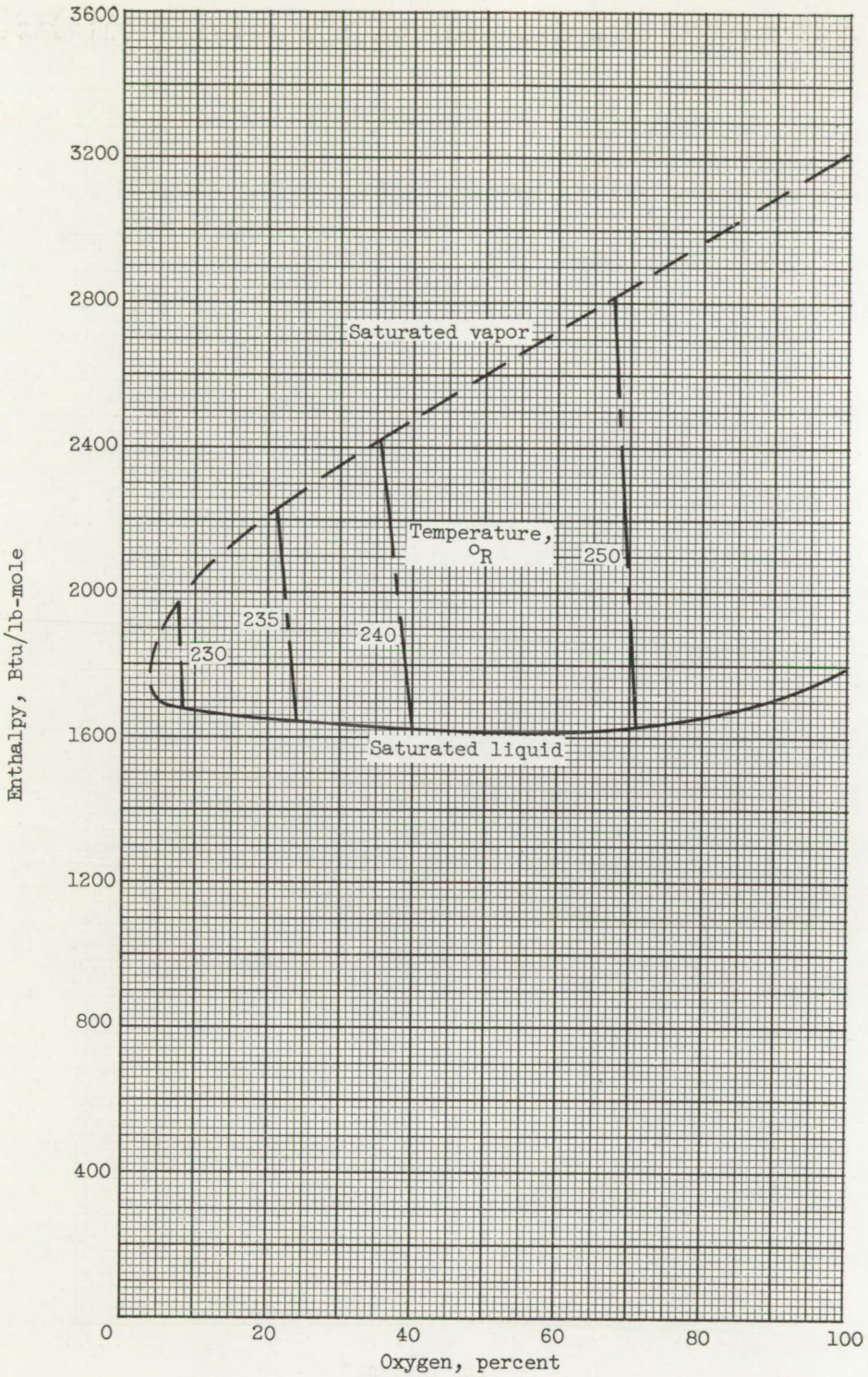
(d) Pressure, 300 pounds per square inch absolute.

Figure 3. - Continued. Variation of enthalpy with concentration for oxygen-nitrogen mixtures at constant pressures.



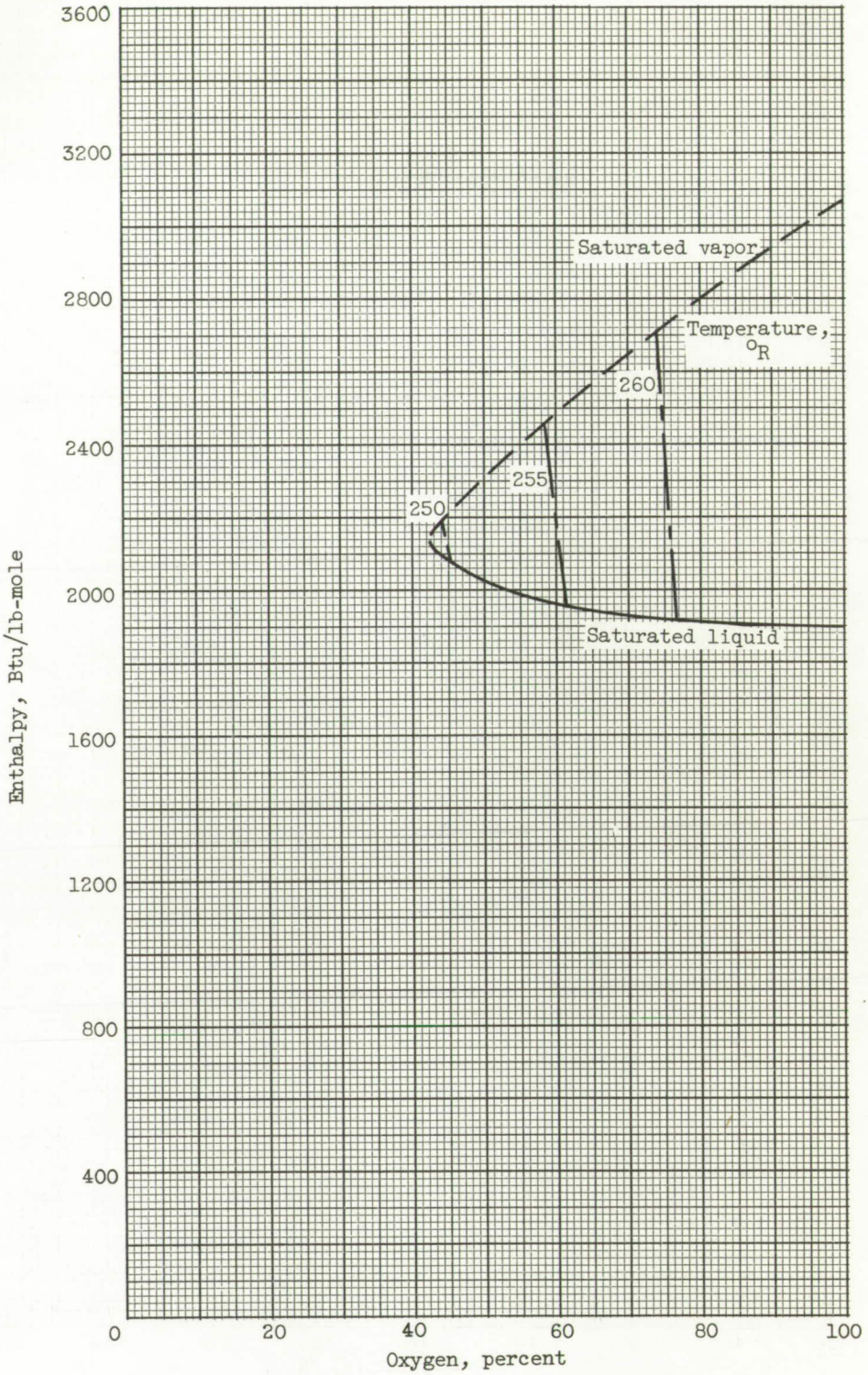
(e) Pressure, 400 pounds per square inch absolute.

Figure 3. - Continued. Variation of enthalpy with concentration for oxygen-nitrogen mixtures at constant pressures.



(f) Pressure, 500 pounds per square inch absolute.

Figure 3. - Continued. Variation of enthalpy with concentration for oxygen-nitrogen mixtures at constant pressures.



(g) Pressure, 600 pounds per square inch absolute.

Figure 3. - Concluded. Variation of enthalpy with concentration for oxygen-nitrogen mixtures at constant pressures.

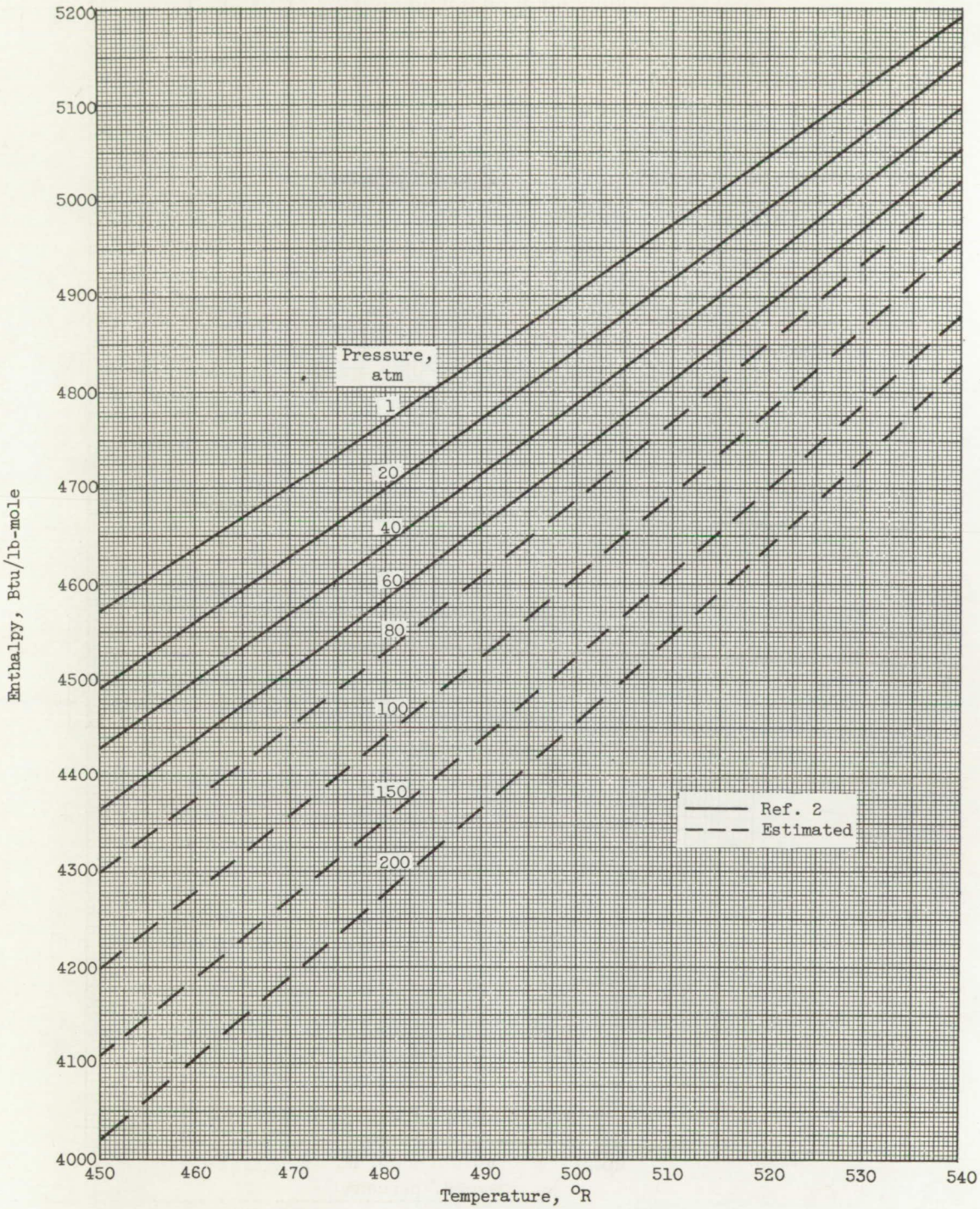


Figure 4. - Enthalpy of gaseous nitrogen.

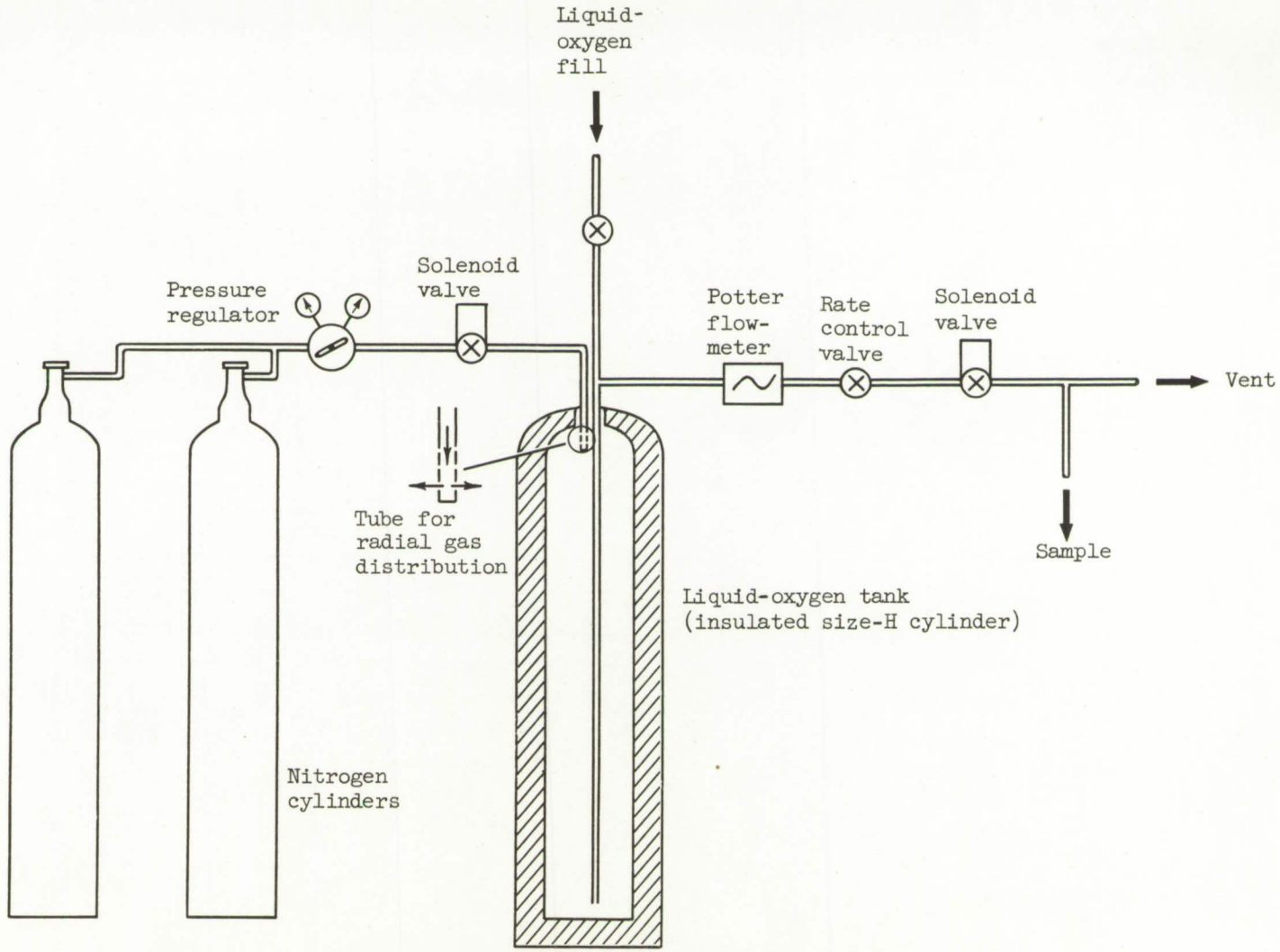


Figure 5. - Rig for testing liquid-oxygen dilution.

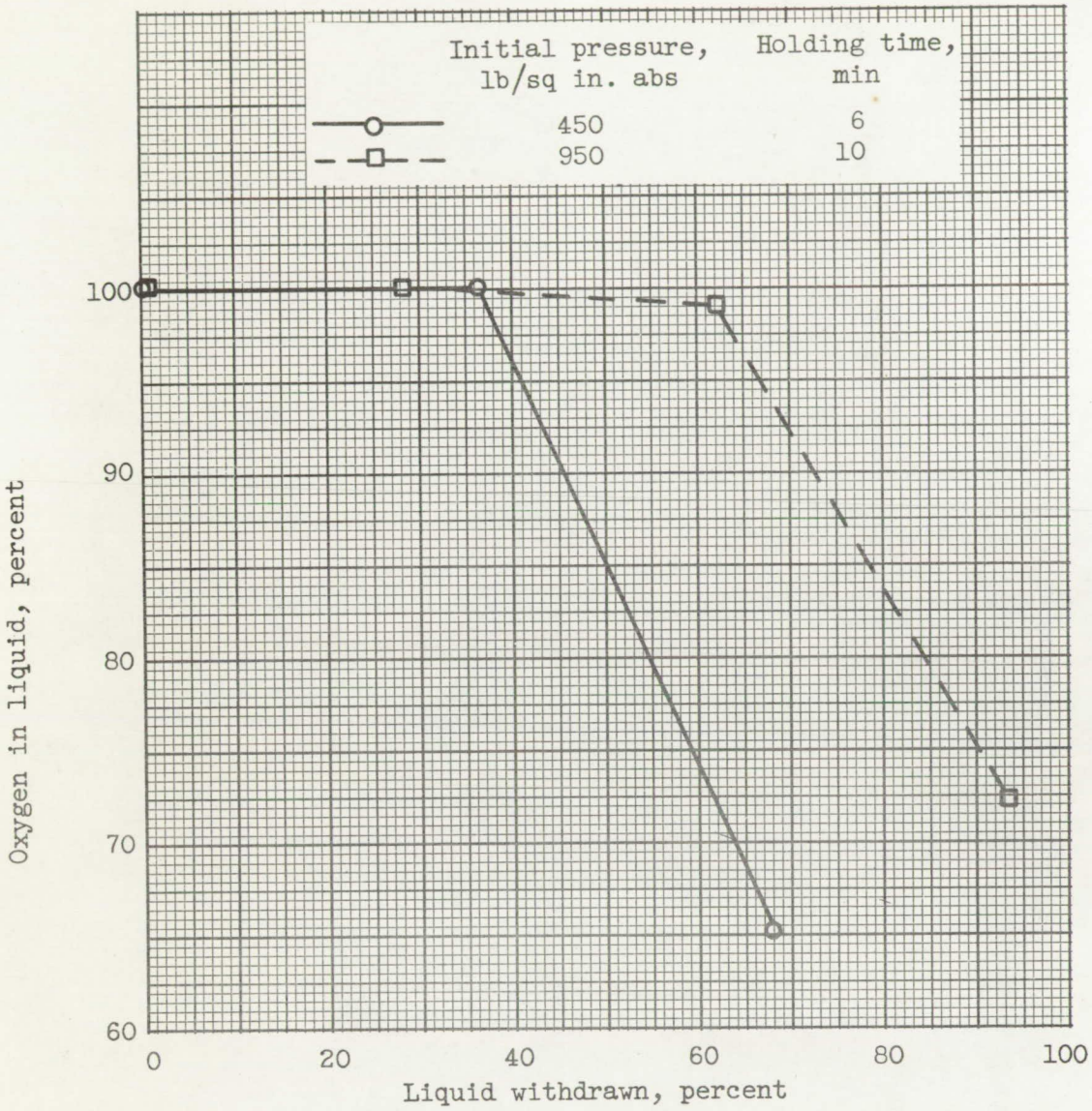


Figure 6. - Composition of oxygen product from nitrogen-pressurized system.