

THE MOLLIER DIAGRAM OF NORMAL HYDROGEN AT TEMPERATURES OF  
16 TO 100° K AND PRESSURES UP TO 500 kg/cm<sup>2</sup>

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Inzhenerno-Fizicheskii Zhurnal, Vol. 13, No. 1, pp. 90-97, 1967

UDC 536.2

Experimental data on thermal properties are used to construct the Mollier diagram of normal hydrogen at temperatures of 16-100° K and pressures of 5-500 kg/cm<sup>2</sup>.

The wide employment of normal hydrogen in technology has given rise to the need for a sufficiently accurate Mollier diagram of normal hydrogen for the low-temperature region of state variables, especially for the liquid-phase region at high pressures. The existing diagrams, constructed from experimental low-temperature data are confined to pressures of the order of 200 kg/cm<sup>2</sup>. Recently conducted experimental investigations of the density of normal hydrogen in the liquid phase have extended the range of investigated state variables of liquid hydrogen to 500 kg/cm<sup>2</sup>.

We are now conducting work aimed at deriving an equation of state of hydrogen which will enable the calculation of all the thermodynamic properties of H<sub>2</sub> over a wide range of temperature and pressure.

Since this work requires a great deal of time it is worthwhile calculating a provisional Mollier diagram of hydrogen by a simplified method in the temperature range 16-100° K at pressures up to 500 kg/cm<sup>2</sup>, which is the most important region for technological applications. This paper describes the procedure and the results of this calculation.

For the indicated range of temperature and pressure the amount of experimental data on the caloric properties of normal hydrogen is extremely small, covers a narrow range of state variables, and is very inaccurate in comparison with thermal data. Hence, the calculation of the Mollier diagram in this work was based on the use of thermal data.

Experimental values of the specific volumes of normal hydrogen at temperatures below 100° K are given in many works. An analysis showed that the data of [1-4] are not sufficiently accurate and they were not used in the calculations. Of the other works, only two [5, 6] relate to the liquid phase. In addition, Johnston and White [7] give smoothed experimental pvT values for temperatures above 35° K and pressures up to 200 kg/cm<sup>2</sup>.

In the Scientific Research Institute of High Temperatures, D. L. Timrot and V. E. Lyusternik made measurements of the compressibility of H<sub>2</sub> on the isotherms -195.2° C and -195.55° C up to pressures of 200 kg/cm<sup>2</sup> to verify Johnston and White's smoothed data [7]. Their results agreed within the limits of experimental error. Thus, the data of [7] can be regarded as quite reliable and we used them in the calculations.

Paper [8] gives smoothed pvT data for normal hydrogen at pressures up to 500 kg/cm<sup>2</sup> and low temperatures. To obtain the smoothed data the authors

used their own experimental values, as well as the data of other researchers. A comparison of the data of [8] and [5, 6] showed that at some points there are differences which exceed the over-all experimental error. Our analysis showed that the data of [5, 6] at subcritical temperatures agree better with the results of other researchers than the data of [8].

In view of this, in the construction of interpolation formulas, we gave preference to the data of [5, 6] in the region of state variables for which data were available. At high pressures, where only the data of [8] are available, we obtained the interpolation formulas by using these data.

Experimental values of the saturated vapor pressures of normal hydrogen were obtained in [9] and [10]. The data of [10] cover the temperature range from 13.95-24.59° K and correspond to the formula

$$\lg p(\text{at}) = -44.368/T + 4.5331 + 0.03240 T - 0.0004189 T^2 + 0.00000484 T^3. \quad (1)$$

The data of [9] were obtained at temperatures of 20.90-33.244° K and are interpolated by the equation

$$\lg p(\text{at}) = 3.068281 - 55.25642/T - 3.1282 \cdot 10^{-2} T + 6.6989 \cdot 10^{-4} T^2. \quad (2)$$

The two equations are quite satisfactory as regards accuracy and agree well with one another at temperatures close to the normal boiling point of hydrogen. Hence, Eq. (1) was used to calculate the saturated vapor pressure from the triple point to the normal boiling point and Eq. (2) was used from the normal boiling point to the critical point.

Values for the density of normal hydrogen on the saturation line and given in [10, 11]. They agree well with one another and cover the temperature range from the triple point to the critical point. To interpolate the experimental data we used the equation [11]

$$\frac{(T_c - T)^{0.4}}{\rho - \rho_c} = (A + BT) \cdot 10^3, \quad (3)$$

where

$$A = 0.145985; \quad B = 4.47314 \cdot 10^{-4}.$$

The critical constants of normal hydrogen were taken as:  $T_c = 33.25^\circ \text{K}$ ,  $p_c = 12.568 \text{ kg/cm}^2$ ;  $\rho_c - \rho_0 = 0.03067 \text{ g/cm}^3$ .

The literature at present does not contain an equation of state which can serve as a basis for the analytical treatment of experimental pvT data for normal hydrogen in the entire indicated ranges of tempera-

ture and pressure. The derivation of an equation of state presents some difficulty and did not come within the scope of the present investigation. However, we rejected a purely graphical method of constructing the Mollier diagram since this might reduce its accuracy to some extent, and we used mainly analytical methods. To simplify the analytical treatment of the experimental data we divided the entire range of state variables into three regions: the first includes states of the gas with a subcritical density at all temperatures; the second includes densities and densities above the critical; the third includes temperatures below  $T_c$  and densities greater than  $\rho_c$ .

In the first region, i. e.,  $\rho \leq \rho_s$ , we used the equation of [12] for the specific volumes. It is one of the most accurate equations, valid for a wide range of temperature and pressure, and suitable for calculations of caloric properties.

In this work we made an additional comparison of the equation of [12] with the experimental data in the low-temperature region of variables and confirmed the high accuracy of this equation.

At supercritical densities and temperatures below  $100^\circ \text{K}$  the published equations of state for normal hydrogen are based on the assumption of linearity of the isochors and usually have the form

$$\rho(v, T) = A(v) + B(v)T. \quad (4)$$

An example of such a relationship is the equation of [5], proposed for specific volumes of  $13\text{--}19 \text{ cm}^3/\text{g}$  at pressures up to  $110 \text{ kg}/\text{cm}^2$ . This equation was compared with the experimental data for the liquid state in wider ranges of specific volume and pressure. The discrepancies were found to increase sharply even when the values of the state variables were only a little outside the range recommended in [5]. Within the recommended range the equation on the average was satisfactorily accurate as regards thermal properties, but did not predict the actual behavior of the isochors of normal hydrogen, which have a very pro-

nounced curvature. Hence, equations of state based on the assumption of linearity of the isochors are not satisfactory for the prediction of the properties of normal hydrogen in a wide pressure range.

The interpolation formula which we used for subcritical temperatures has the form

$$\rho(v, T) = \rho(T_c, v) + \rho[T_c, v'(T)] + p_s(T) + \delta\rho(v, T). \quad (5)$$

The meaning of the terms contained in this equation is illustrated in Fig. 1a.

For supercritical temperatures and  $\rho \geq \rho_c$  the interpolation formula has the form

$$\rho(v, T) = \rho(v_c, T) + \rho(T_c, v) - \rho_c + \delta\rho(v, T). \quad (6)$$

The meaning of the terms contained in the equation is illustrated in Fig. 1b. The pressure on the critical isochor  $p(v_c; T)$  was calculated from the equation of [12]. We obtained analytical relationships for all the terms contained in Eqs. (5) and (6).

Formulas (5) and (6) agree well with one another on the critical isotherm and with the equation obtained in [12] on the critical isochor (from the first derivative of the thermal quantities). A comparison of the experimental and calculated pressures is shown in Figs. 2 and 3.

The absolute differences between the calculated and experimental pressures at some points are extremely high. It should be borne in mind, however, that in the liquid-phase region the derivative  $(\partial p/\partial v)_T$  is large and, hence, an appreciable difference in pressure has hardly any effect on the specific volume. In addition, the differences between the calculated values and the data of [5] and [6] are of opposite signs in most cases.

The structure of the interpolation formulas (5) and (6) is such that the main curvature of the isotherms in the  $p$ - $v$ -diagram is due to the term  $p(T_c, v)$ . The term  $\delta\rho(v, T)$  has an insignificant curvature on the isotherms. Hence, having an expression for  $p(T_c, v)$  valid up to high pressures, we can obtain the pressures at high densities by extrapolation of the term  $\delta\rho(v, T)$  to the

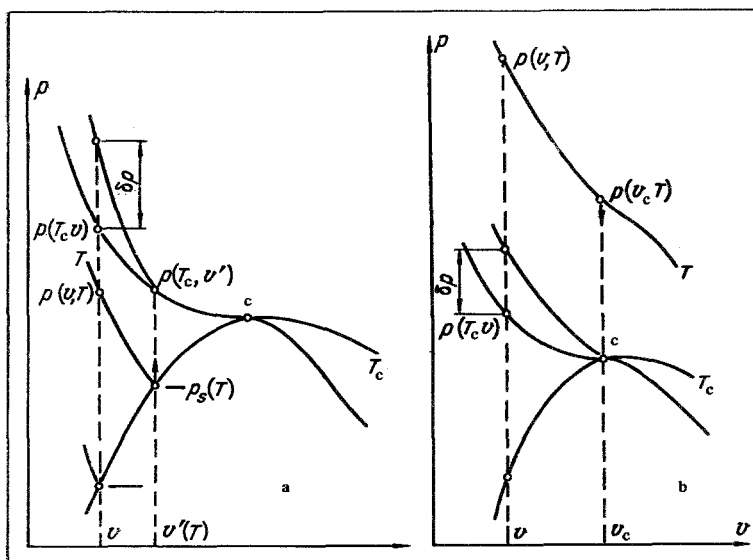


Fig. 1. Diagram illustrating interpolation of experimental  $p$ - $v$ - $T$  data for  $T \leq T_c$  (a) and  $T \geq T_c$  (b).

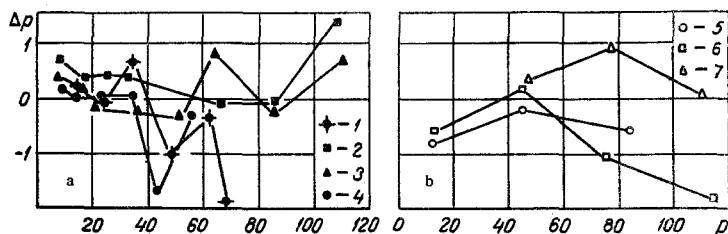


Fig. 2. Comparison of experimental  $p$  $v$  $T$  data with data calculated from Eq. (5) [ $\Delta p = (p_{\text{exp}} - p_{\text{calc}})$  kg/cm<sup>2</sup>]: a) data of [5] (1—20.34°, 2—22.96°, 3—25.81°, 4—30.11° K); b) data of [6] (5—16.66°, 6—17.909°, 7—20.42° K).

corresponding densities. It is unlikely that such an extrapolation will lead to large errors. Moreover, a considerable part of the error will be systematic, which will have little effect on the enthalpy and entropy increments.

To determine the enthalpy and entropy of normal hydrogen we used the following thermodynamic relationships

$$i(v, T) = i_0(T) + AT \int_{v_0}^v \left( \frac{\partial p}{\partial T} \right)_v dv + A \int_{v_0}^v \left( \frac{\partial p}{\partial v} \right)_T v dv,$$

$$s(v, T) = s_0(T) + A \int_{v_0}^v \left( \frac{\partial p}{\partial T} \right)_v dv. \quad (7)$$

We took the temperature dependence of the enthalpy  $i_0$  and the entropy  $s_0$  in the ideal-gas state from [13, 14]. These data are the most reliable at present. Equations (7) in each of the three regions of state variables were integrated in accordance with the corresponding analytical relationship for the thermal properties.

In the region of subcritical densities the derivatives  $(\partial p/\partial T)_v$  and  $(\partial p/\partial v)_T$  and the integrals from them were determined by differentiation and integration of the equation obtained in [12]. On the basis of these calculations we found the enthalpy and entropy in the range up to the critical density at  $T \geq T_c$  and up to the corresponding volumes of dry saturated vapor  $v''$  at  $T \leq T_c$ . We also found the specific volumes on the right boundary curve of  $v''$  from the equation from [12] by using known values of the saturated vapor pressure.

The enthalpy  $i'$  and the entropy  $s'$  on the left boundary curve were found from the corresponding values of  $i''$  and  $s''$  and the heat of vaporization  $r$ . Experimental values of the heat of vaporization for normal hydrogen are available only for pressures below atmospheric

[15]. For this reason we used values for the heat of vaporization calculated from the Clapeyron-Clausius equation [9].

In the calculation of the enthalpy and entropy in the single-phase region at  $v < v_c$  the analytical expressions obtained for  $(\partial p/\partial T)_v$  and  $(\partial p/\partial v)_T$  and the integrals from them were very complicated and unsuitable for calculations. In addition, the interpolation relationships for  $p$  $v$  $T$  are alternating series and, hence, the calculated values of the derivatives  $(\partial p/\partial T)_v$  and  $(\partial p/\partial v)_T$  might show some undulation on the isochors and isotherms. To avoid this and to simplify the calculations we found the derivatives by the numerical method. For the whole required density range we used the interpolation formulas to compile a comprehensive table of reference values for the thermal quantities. The tabulated data were differentiated numerically by means of a Lagrange interpolation polynomial. Each value of the derivatives  $(\partial p/\partial T)_v$  and  $(\partial p/\partial v)_T$  on the isochor or isotherm was calculated by using four adjacent points (two on each side). The numerical values of the derivatives found in this way were graphically smoothed on the isotherms and isochors and their net was then constructed.

Equations (7) were integrated numerically from the smoothed values of the derivatives within the range of specific volumes from the corresponding specific volume on the left boundary curve at  $T < T_c$  or on the critical isochor at  $T \geq T_c$  to the required specific volume. We thus constructed  $i$  $p$ ,  $i$  $v$ ,  $s$  $p$ ,  $s$  $v$ , and  $T$  $s$  diagrams.

In all these diagrams the enthalpy and entropy were smoothed. This was fairly easy within the limits of accuracy of the experimental data and construction of the diagrams. The Mollier diagram was drawn from the smoothed values. On it we plotted the isochors, isobars, and isotherms, and in the two-phase region,

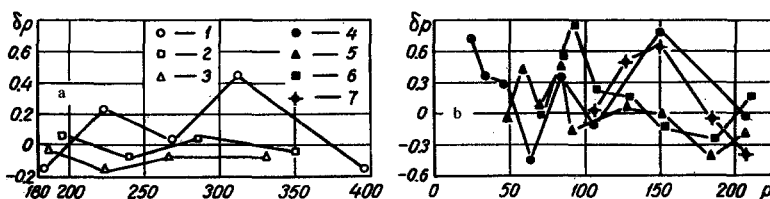


Fig. 3. Comparison of experimental  $p$  $v$  $T$  data with those calculated from Eq. (6) ( $\delta p = [(p_{\text{exp}} - p_{\text{calc}})/p_{\text{calc}}] \cdot 100\%$ ): a) Data of [17, 18] (1—at 113.6°, 2—103.16°, 3—98.16° K); b) data of [7] (4—40°, 5—50°, 6—60°, 7—75° K).

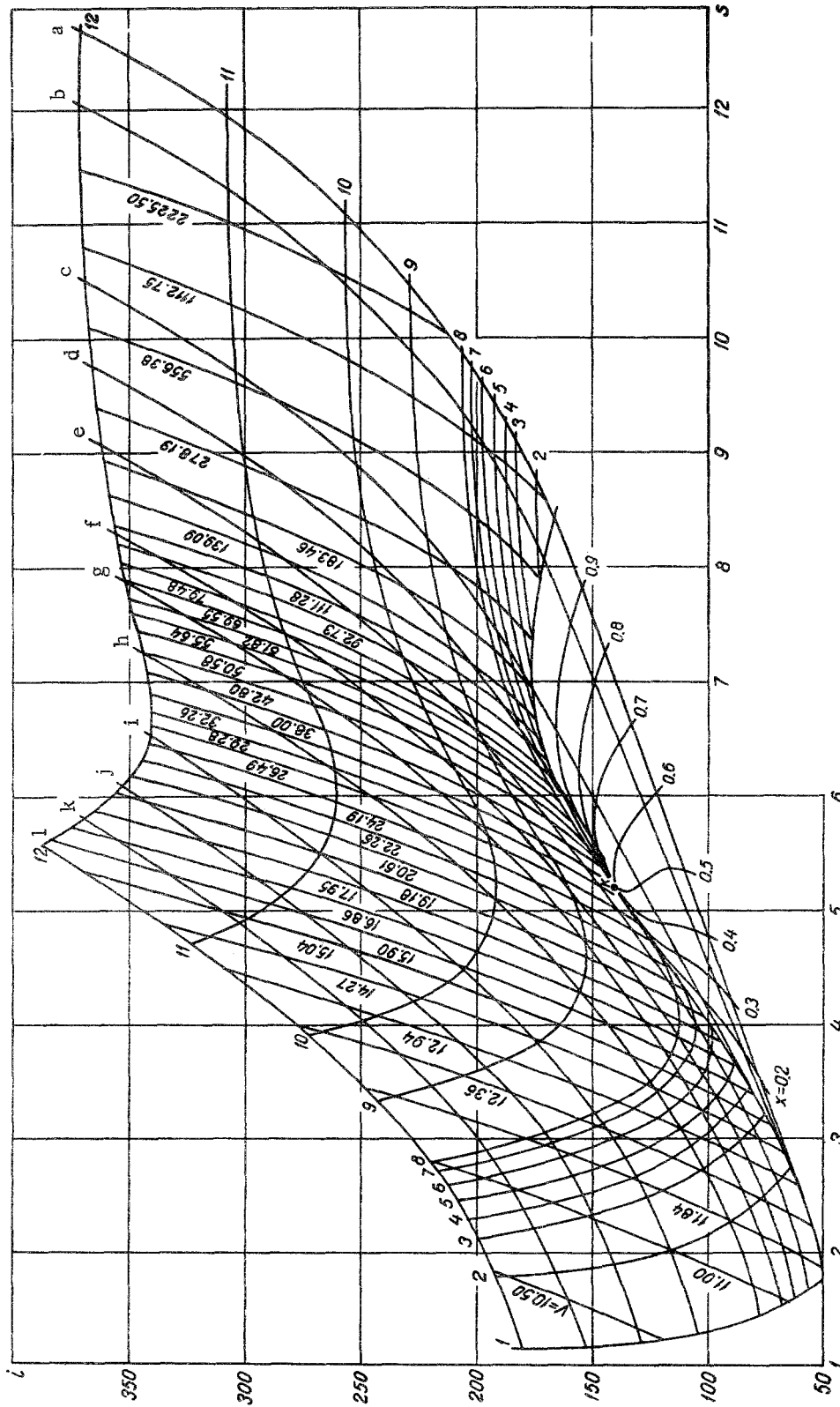


Fig. 4. Mollier diagram of normal hydrogen from 16 to 98° K and from 5 to 500 kg/cm<sup>2</sup>: 1) T = 16°; 2) 20°; 3) 24°; 4) 26°; 5) 28°; 6) 30°; 7) 32°; 8) 33.26°; 9) 43°; 10) 53°; 11) 73°; 12) 98°K: a) p = 0.5; b) 1; c) 5; d) 10; e) 20; f) 40; g) 60; h) 100; i) 200; j) 300; k) 400; l) 500 kg/cm<sup>2</sup>.

the lines of constant dryness at steps of 0.1. The inversion curve obtained in this diagram agrees well with the inversion curve in [6].

The accuracy of the presented Mollier diagram (Fig. 4) depends mainly on the accuracy and amount of initial experimental data. Unfortunately, at low temperatures, and especially in the region of high pressures, the experimental data are extremely meager and are not very accurate. According to our estimates, the error of the diagram is 2.25 kcal/kg for enthalpy at  $v \geq 14 \text{ cm}^3/\text{g}$ . At smaller specific volumes the error is greater and attains values of about 5 kcal/g at the greatest pressures and densities. In the case of entropy the average error is about 0.05 kcal/kg · deg.

#### NOTATION

$T$  is the temperature, °K;  $p$  is the pressure, kg/cm<sup>2</sup>;  $\rho$  is the density, g/cm<sup>3</sup>;  $v$  is the specific volume, cm<sup>3</sup>/g;  $i$  is the enthalpy, kcal/kg;  $s$  is the entropy, kcal/kg · deg;  $i_0$ ,  $s_0$  are the enthalpy and entropy in ideal-gas state;  $r$  is the specific heat of vaporization. Subscripts:  $c$  is the critical state;  $s$  is the saturation state; the single prime denotes the saturated liquid-saturated vapor line; the double prime denotes the gas-saturated vapor line.

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11 August 1966

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