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Temperature-Entropy Diagram for Parahydrogen Triple-Point Region

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U.S. DEPARTMENT OF COMMERCE
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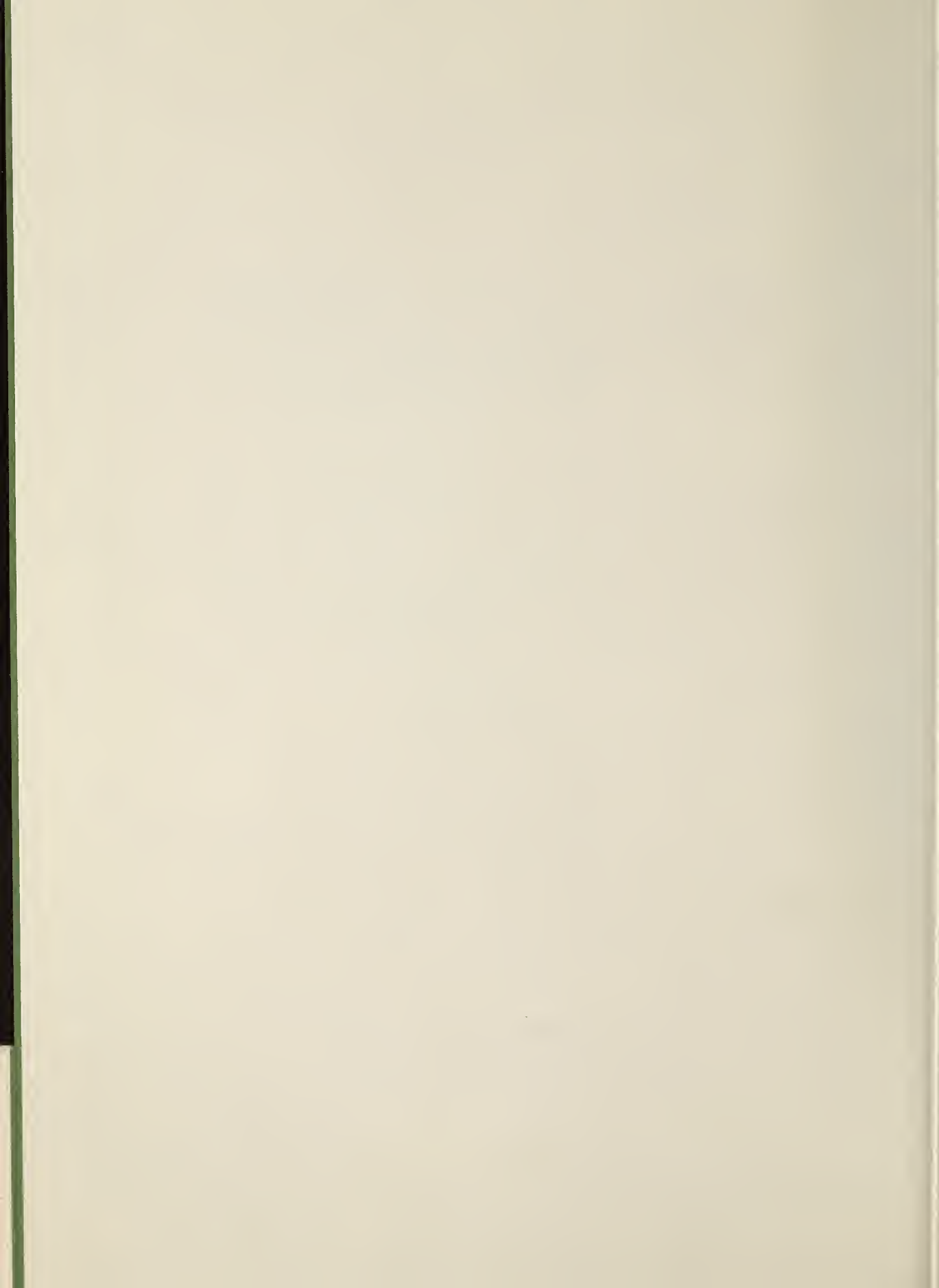
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TEMPERATURE-ENTROPY DIAGRAM FOR PARAHYDROGEN TRIPLE-POINT REGION

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by

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Abstract

The three-phase region at and near the triple point of parahydrogen is presented on the graphical coordinates of temperature and entropy. Isobars from 10 mm Hg to 340 atmospheres, temperatures from 11° to 23°K and specific volumes covering the range of from 10.5 cc/gm to 15,000 cc/gm are included. The energy base of enthalpy and entropy are consistent with previous data published by this laboratory.

Key words: Enthalpy, entropy, parahydrogen, pressure-volume, properties, temperatures, triple-point region, T-S diagram.



Temperature-Entropy Diagram for Parahydrogen Triple-Point Region*

An extension of the temperature-entropy state diagram to cover temperatures and pressures near the triple point is required as a useful tool in analysis of processes originating or terminating in this region. Recent interest in this low temperature area has been supplied by the relatively poor storage characteristics of liquid hydrogen under high heat fluxes at the normal boiling point. The studies of liquid subcooling with controlled mixing and, more recently, the characterization of liquid-solid (slush) mixtures are only two of the many processes requiring coherent thermophysical property data at temperatures below the normal boiling point.

It is the purpose of this note to correlate the principle analytical and experimental data already in the published literature in respect to common energy bases and dimensional units. The result is a temperature-entropy diagram of a rather restricted scope for properties near the triple point, but compatible with existing diagrams which extend to conditions at or above ambient.

Figure 1 shows the relative location of the phase boundaries for parahydrogen near the triple point. Region I has been defined by the extensive experimental and analytical work of Roder and Goodwin [1961], and Roder et al. [1965]. Regions II and III have been described by Mullins et al. [1961]. Recent experimental work of Dwyer et al. [1965a] along with the more dated solid-liquid phase data of Bartholomé [1936] define region IV.

Figure 2 shows the temperature-entropy surface generated using the above data.

*Sponsored by NASA Marshall Space Flight Center, Huntsville, Alabama.

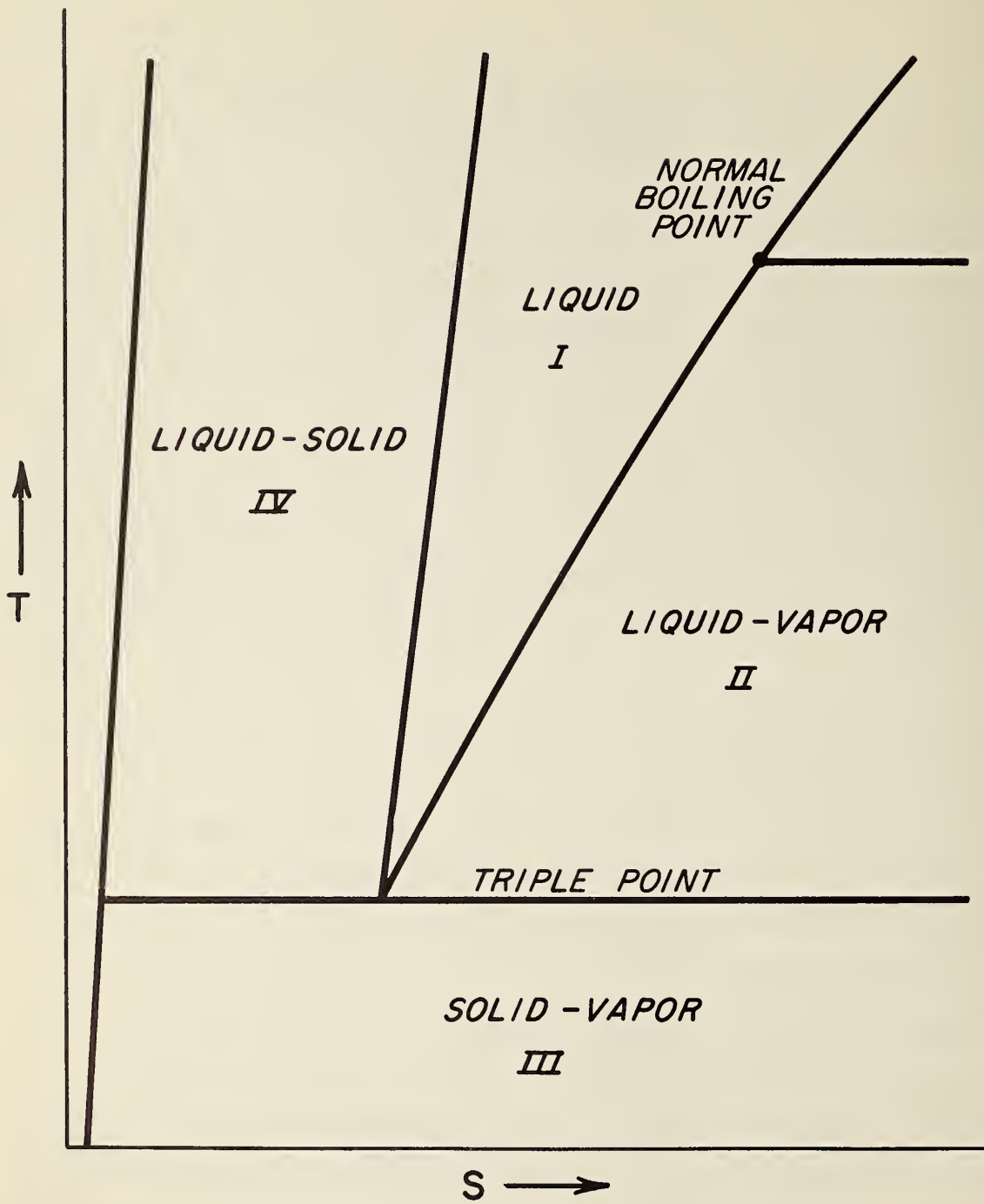


Figure 1. Hydrogen T-S Diagram Phase Boundaries

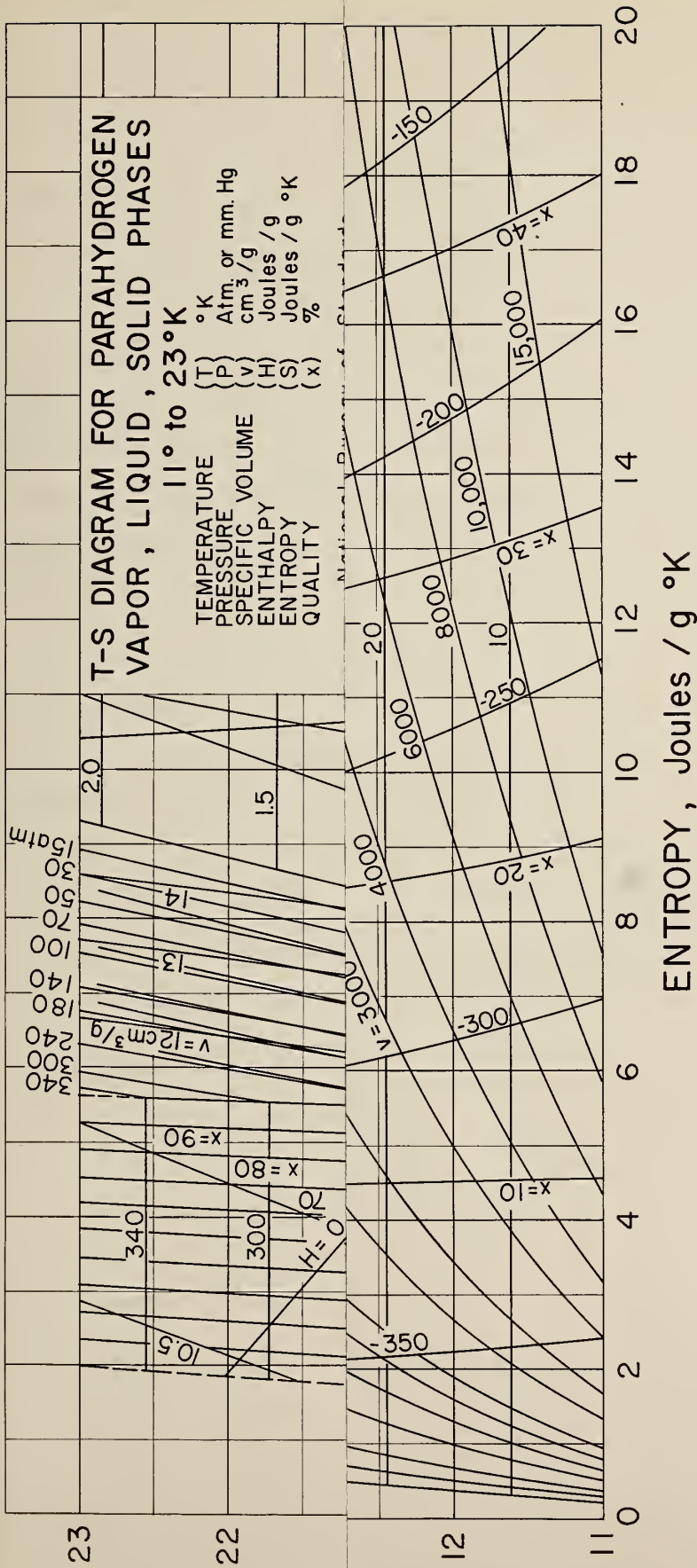


Figure 2. Parahydrogen Temperature - Entropy diagram

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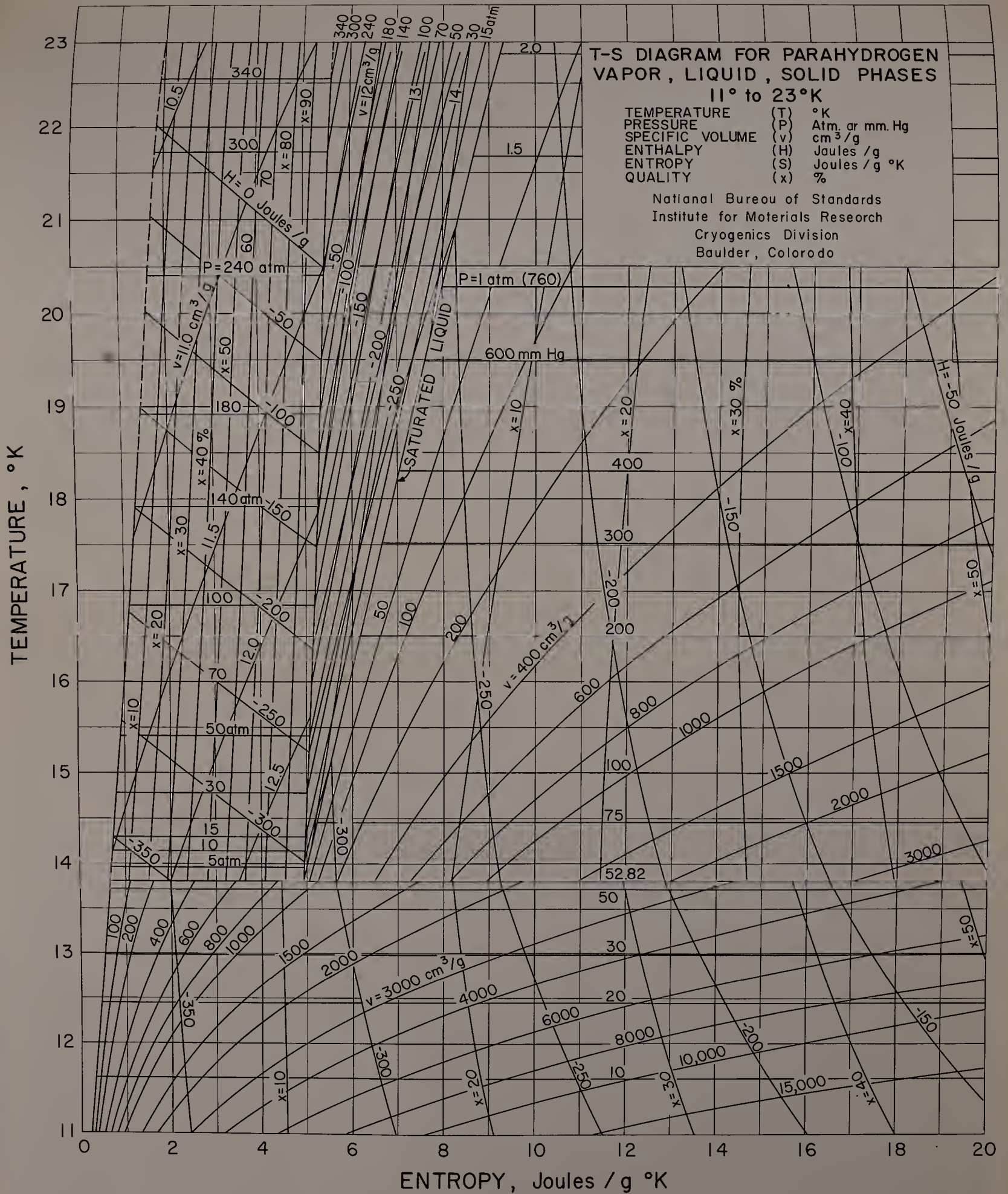


Figure 2. Parahydrogen Temperature-Entropy diagram

Construction of the diagram was complicated by differences in entropy and enthalpy bases and temperature scales. These differences were resolved in a number of ways.

Dimensional units and energy bases were those selected by Roder and Goodwin [1961]. The reasons are based on continuity of data for engineering calculations. The Roder data cover the temperature range of 20 - 300°K and pressures to 100 atmospheres. Higher pressure data below 100°K is also included. The Roder et al. [1965] data are of higher accuracy but of limited scope. Therefore, figure 2 of this report extends the data range of Roder and Goodwin [1961] in a continuous manner to 11°K.

Referring to figure 1, region I was plotted directly from Roder and Goodwin [1961] above 20°K and Roder et al. [1965] below 20°K. The latter data were converted to a gram basis using the molecular weight of 2.01572 grams/mole. There is a slight shift in entropy (0.5% at NBP), enthalpy (0.25%) values on matching data of Roder and Goodwin [1961] and Roder et al. [1965]. Improved calculation procedures are responsible for this small discontinuity and the change which is within the error claimed by Roder et al. [1965] is not significant when graphically plotted as in figure 2.

Regions II and III are plotted from the data of Mullins et al. [1961]. Again methods of calculating the energy states have been improved but in this case the base difference is of such magnitude that the data of Mullins were changed to match the data of Roder and Goodwin [1961]. Entropy values of Mullins were reduced by 0.33 joules/gm-K° which reflects the difference at the normal boiling point. This difference reflects the more critical evaluation of the specific heat of the solid by Ahlers [1964] and a similar reevaluation of the liquid specific heats by Younglove and Diller [1962]. The Roder enthalpy base was chosen to be consistent with the previous work of Woolley et al. [1948]. Therefore the values of enthalpy of Mullins were reduced by 378.7 joules/gm.

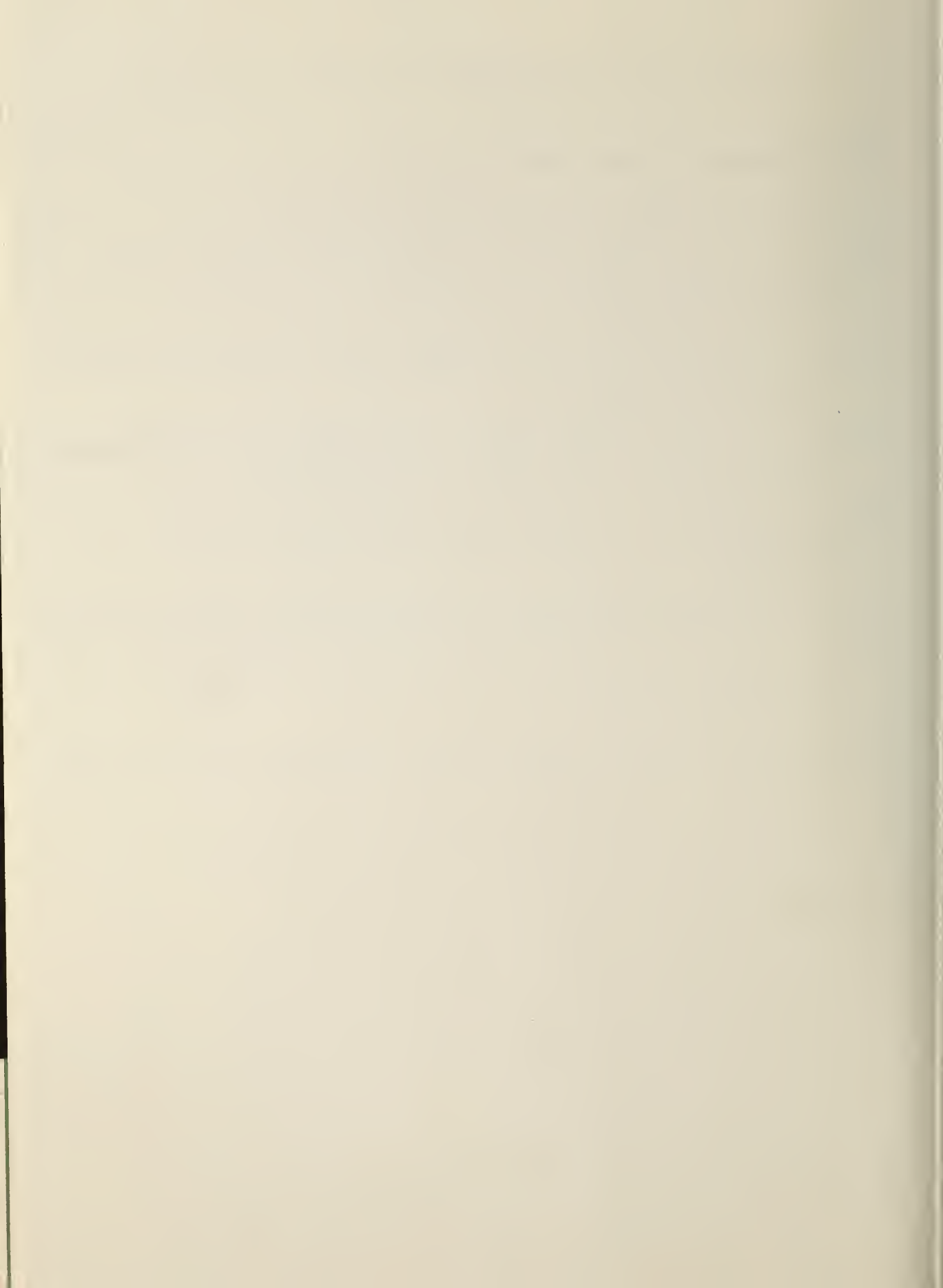
The difference in temperature scales, a matter of 0.01°K , was neglected.

Region IV was calculated using the volume change on freezing of Bartholome [1936] and Dwyer et al. [1965a]. A correlation of these data with the measured heats of fusion of Dwyer et al. [1965b] has yet to be completed. In consideration of the heats of fusion an uncertainty in entropy is possible along the saturated solid line of $0.25 \text{ joules/gm-K}^{\circ}$ at 300 atmospheres decreasing to $0.05 \text{ joules/gm-K}^{\circ}$ at 100 atmospheres.

The lines of constant specific volume in the liquid region were constructed from cross plots of entropy versus specific volume with lines of constant pressure and temperature. The specific volume along the saturated solid line was calculated using the Clapeyron equation, the equation for specific volume of saturated liquid for solidification from Roder, and the heats of fusion. Enthalpies, qualities and volume lines in the two phase regions were calculated directly from the data given by Mullins and Roder.

References

- Ahlers, G. (1964). J. Chem. Phy. 41, 89-94.
- Bartholomé, E. (1936). Z. Physik. Chem. (B) 33, 387.
- Dwyer, R. F., G. A. Cook, O. A. Berwaldt and H. E. Nevins (1965a).
J. Chem. Phys., 43, 801.
- Dwyer, R. F., G. A. Cook, B. M. Shields, and D. H. Stellrecht (1965b).
J. Chem. Phys., 42, 3809.
- Mullins, J. C., W. T. Ziegler and B. S. Kirk (1961). Technical Report 1,
Contract A-593, Eng. Exp. Station, Georgia Inst. Tech.
- Roder, H. M. and R. D. Goodwin (1961). NBS Technical Note 130,
PB 161631.
- Roder, H. M., L. A. Weber and R. D. Goodwin (1965). NBS Monograph 94.
- Woolley, H. W., R. B. Scott and F. G. Brickwedde (1948). NBS J. of
Research, 41, 379-475.
- Younglove, B. A. and D. E. Diller (1962). Cryogenics 2, No. 5, 283-287.





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