TEMPERATURE ENTROPY CHART OF THERMODYNAMIC PROPERTIES OF NITROGEN

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1/ Mechanical engineer.

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INTRODUCTION AND SUMMARY

The temperature entropy (T,S) chart of thermodynamic properties of nitrogen herewith presented is a complete revision and a considerable extension of similar charts prepared by the author for use of the helium section of the Bureau of Mines about 25 years previously on the basis of inadequate data then obtaining.

During the interval since that early effort, much experimentally determined information on nitrogen properties and behavior has been published, which now permits a more nearly accurate layout and more extensive charting of these relations.

Still lacking, however, is an exact equation of state for nitrogen 2 applicable to both liquid and gas phases, through which rigid thermodynamic relations might be smoothly combined by calculation with a minimum of observational data, which always involve some uncertainties. Graphical methods of plotting and cross plotting, differentiation and integration, occasionally assisted by empirical formulations, have to be employed to consummate the final portrayal. Because of these limitations, and the physical difficulties of plotting data and drawing curves with the precision desired and the character indicated, some inconsistencies are bound to remain in the final chart, which is regrettable. It is hoped and believed that values read from this chart on the scale presented concord with supporting data and thermodynamic requirements to about the precision of its readability.

A preliminary large-scaled isobaric temperature enthalpy (T,H) chart covering the ranges 65° to 660° K. and zero to 200 atmospheres was first laid out to facilitate utilization of the extensive experimental Joule-Thomson throttling data reported by Roebuck and Osterberg (1) in 1935. When higher-pressure isobars are added to such a chart, their locations overlie those at lower pressures, resulting in so confusing a portrayal that it is impractical to use; hence, it is not reproduced for publication.

DATA AND METHOD OF PREPARATION

The following brief notes record source material with numerous references, methods of data treatment and assembly, and checks thereon used in the preparation of this T,S chart.

2/ Numbers in parentheses, unless otherwise obviously significant, refer to references listed at the end of this paper.
Nitrogen "constants" at present accepted.

Atmospheric boiling point................................. 77.35° K. (-195.8° C.)
Critical-point temperature................................ 126° K. (-147.15° C.)
Critical-point pressure.................................... 33.49 atmospheres
Critical-point volume...................................... 90.1 ltr./kg. mol. (3.216 ml./gm.)
Triple-point temperature.................................. 63.15° K. (-210.0° C.)
Triple-point pressure...................................... 0.1237 atm. (940 mm.Hg.)

The above "constants", plus vapor-phase and liquid-phase densities, vapor pressures, heats of vaporization (estimated), and some low-temperature moderate-pressure P, V, T determinations and other data are to be found in "Communications" of the Leiden Laboratory from 1914 through 1937 (2).

Vapor pressure-temperature formula, by Dodge and Davis (1927) (3).

\[
\log_{10} P_{\text{atm.}} = 4.47582 - 316.824/T - 0.00717 T + 0.294 (T/100)^2
\]

(Equation yields \( P_c = 33.47 \) atm. at \( T_c = 126° K. \))

The Dodge and Davis formula yields values in excellent agreement with best data then available, including "High Vapor Pressure of Nitrogen" by Porter and Perry (4) (Bureau of Mines, 1926).

Total heats of vaporization; empirical equation by Burnett (1924).

\[
L = 331 (T_c - T)^{3/8} - 0.404 (T_c - T)^{11/8}, \quad (\text{kg. cal./kg. mol.})
\]

This equation, used and reported by Wiebe and Brevoort (5) (Bureau of Mines, 1930), was based (1924) on meager experimental data from Landolt-Bornstein Tabellen (1923) and on values derived from the Clapeyron-Clausius relation,

\[
L = T/J (V_V - V_L) \frac{dP}{dT}_{\text{sat}}
\]

in which \( V_V \) and \( V_L \), respectively the vapor and liquid-phase specific volumes, are not well-defined throughout the whole range. Burnett's equation for \( L \) was also used by Miller and Sullivan (6), Bureau of Mines Technical Paper No. 424 (1928). A 1949 recheck confirms its suitability. (Note also Giauque and Clayton (7), 1933).

Enthalpy and entropy changes along the two-phase boundary.

Liquid phase, boiling point to 120° K; (experimental) by Wiebe and Brevoort (5) (Bureau of Mines).

Wiebe and Brevoort determined \( C_dL \), the specific heat of liquid nitrogen under saturation conditions, from 77.4° to 117° K. and computed \( \Delta H \) along this boundary from the B.P. up to 120° K; as the integral of \( C_dLdT + V_dLdP \), probably by graphical integration.
Adding thereto \( \Delta H = L \), the heats of vaporization calculated from Burnett's equation, they obtained the vapor-phase T,S boundary values from B.P. to 120° K.

By integration of \((C_{\text{mL}}/T)\Delta T\) they determined the entropy changes \( \Delta S_{\text{mL}} \) along the liquid-phase boundary; adding thereto values of \( L/T \), the entropy change of vaporization, they located the vapor phase T,S boundary over the above-mentioned temperature range.

From 120° to \( T_c = 126° \) K, Wiebe and Brevoort closed these boundaries through their common critical point value by "fairing" the 50% quality line of the T,S diagram, coupled with L values taken from Keesom and Houthoff (8) (Leiden Laboratory Communications Supplement No. 65-c, 1927), which refers to a formula by Mathias, Crommelin, and Onnes (9) given in Leiden Communication No. 162-a (1923).

These Leiden formulas for L, and for vapor pressures, are inconsistent with their basic experimental data on approach to the critical point and with the Clapeyron-Clausius relation which involves that data, yielding too low values in all respects. Miller and Sullivan (6) (Bureau of Mines) stated (1928), "The heats of vaporization for nitrogen** given by E. S. Burnett*** are entirely consistent with the volumes and vapor pressures. Consequently, the closure of the two-phase boundary through the critical point of the T,S chart above 120° K, was accomplished in the present effort by fairing the 50% quality line coupled with an "L" spread conforming to Burnett's 1924 empirical equation.

There appears to be no definite independent thermodynamic criterion for location of the critical-point value of this boundary nor of the 50% quality line. Until further experimental boundary determinations are made, its exact location above 120° remains uncertain. This uncertainty is reflected in the courses of the T,H and T,S isobars on approach from the superheat region to their intersections with or proximity to the two-phase field.

Two-phase T,H boundary location, boiling point to triple point.

After location of the zero pressure T,H isobar, as described below, these boundaries were extended toward lower temperatures graphically, making the vapor-phase extensions asymptotic to that isobar, with an "L" spread to the liquid-phase extension computed from Burnett's equation; both extensions were drawn to yield a consistently smooth extension of the 50% quality line.

Precise low-temperature low-pressure isenthalpic throttling data, if available, would establish these extensions.

Temperature-enthalpy zero pressure isobar: computed from heat-capacity values calculated by Johnston and Davis (10) from spectroscopic data.

Location of this isobar 3.5° is enthalpically below vapor-phase boundary at B.P. is in accord with Joule-Thomson effect data by Rosebuck and Osterberg (1).
Temperature-enthalpy isobars to 200 atm.; located in accordance with distribution dictated by isenthalpic throttling curves of Roebuck and Osterberg (1). Some fairing required near saturation dome. Distribution data lacking for pressures greater than vapor pressures at temperatures below 110° K. (-163°C).  

Above locations checked by isothermal distribution of enthalpy with pressure as calculated by graphical integration of relation $(\frac{dH}{T})_T = V \int(T/V) \frac{dV}{dT}P - 1 \int_T^PdP$. Values in $\int$ by Deming and Shupe (11).

Were the experimental isenthalpic throttling curves on a $T,P$ chart for nitrogen, reported by Roebuck and Osterberg, which intersect the $T,P$ "saturation curve" sufficiently precise to locate those intersections (and their mutual intersections) with accurately smooth progression, then such locations would serve to fix the corresponding two-phase boundary on the $T,H$ and $T,S$ charts, assuming the "L" values are correct. An accurate extension of this particular group of throttling curves sufficiently to lower (subatmospheric) pressures would also help. Unfortunately, the experimental data obtained by Roebuck and Osterberg for the curves of this group lack the necessary individual and progressive smoothness and low-pressure extensions.

Entropy changes at 1 atmosphere, B.P. to 400° K; computed from empirical relation by Burnett expressing temperature variation of specific heat $C_p$ in accord with Joule-Thomson data by Roebuck and Osterberg (1). Results checked against entropy changes at 1 atm. (ideal state) calculated by Johnston and Davis (10) as corrected for actual state, B.P. to 873° K., by Deming and Deming (12). Thus extended to 900° K.

Isoberic entropy changes above vapor phase boundary values; for pressures to critical pressure obtained by stepwise summations:

$$\Delta S = \Delta(\frac{A,H}{T_m})$$ for small intervals $(T_2 - T_1)$ along the $T,H$ isobars. $T_m$ taken as $(T_2 + T_1)/2$ or as $\sqrt{T_2 \cdot T_1}$. Summations adjusted for increment magnitudes.

Isothermal entropy changes, 203° to 873° K.

By Deming and Deming (12), based on their graphical or empirical integration of the isothermal relation $dS = -(dV/dT)P$ in which $(dV/dT)P$ was derived graphically by Deming and Shupe (11) from their consideration of $P,V,T$ measurements reported by Bartlett and co-workers (13).

Results, 33.5 to 200 atm., checked by summation process mentioned above applied to these $T,H$ isobars as previously located by throttling data of Roebuck and Osterberg from 110° to 500° K.

Constant H curves of $T,S$ chart to 200 atm., 110° to 500° K.

Obtained by cross-reading $T,H$ isobars located as above.
Checked to 200 atm. and extended to 1,200 atm. (and to 900° K.) by graphical integration of the relation,

\[(dH)_T = -V \int (T/V \cdot (dV/dT)P) - 1 \int_T dP\]

in which the values on the right were tabulated by Doming and Shupe (11).

Constant (P V) curves on T, S chart.

Cross-read from appropriate large-scale plots of all available data which, with few exceptions, are concordant (13, 15, 16).

Constant P V curves (which might be called "Isocomes", from "equal compressibility") are substituted for the customary constant-volume lines (isochoros) because the latter cross the constant-pressure lines (isobars) at such acute angles and are so nearly parallel to them that differentiation is confusing. Except at pressures in excess of 600 atm., the "isocomes" cross other curves at fairly open angles nearly orthogonal at low pressures.

In many calculations involving properties of a fluid, pressure volume products are required quite as often as volume values; they can be read directly from the isocomes. Corresponding volumes are simply determined as PV/P.

No data are available for extending the high pressure isobars (above 200 atm.) to temperatures below 200° K., nor for the liquid-phase isobars at pressures of 200 atm. and under, below 110° K. As drawn, the latter group appears to converge toward the triple point. Their true shape and location awaits experimental data in that region to evaluate the most useful relations:

\[\int dS/dP = -(dV/dT)_P \int T\]

\[\int dH/dP = V - T(dV/dT)_P \int T\]

\[(dT/dP)_H = \lambda\]

The effort here reported was made to produce a chart as consistent and as agreeable with its supporting data as the methods of assembly and the precision of reading it will permit.

3/ After preparation of the manuscript, the author's attention was called to the work of M. Benedict, Jour. Am. Chem. Soc., Vol. 59, 1937, pp. 2224-33.
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Nitrogen P,V,T Data

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