# An Equation for the Liquid and Vapor States of Nitrogen

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**An equation of state which describes vapor and liquid states of nitrogen in the temperature and density range to three times the critical and the two-phase boundary is presented. The root mean square error is less than 0.7% in describing the available data for nitrogen. The equation contains thirteen coefficients, only three or four of which are independent, and can be written in virial form.**

A great variety of equations of state for gases and liquids has been proposed over the past 75 yrs. Within the past 20 yrs. equations of excellent accuracy over fairly extensive ranges of temperature and density have been proposed for the vapor phase, and in some cases application to vapor-phase mixtures has been demonstrated. To date no single equation of state has been shown to be applicable to both compressed vapor and liquid states. This paper reports the development of an equation which describes the vapor and liquid states of nitrogen in the temperature range to three times the critical temperature and the density range to three times the critical density, including the two-phase boundary. The root mean square error in density prediction over the range specified is 0.7%, and maximum errors in density prediction are less than 1.5%, except in the vicinity of the critical point. The critical region itself is adequately described, if errors in pressure prediction are used as a criterion.

Of the more recent equations of state proposed the work of Benedict, Webb, and Rubin (*2*, *3*), Martin and Hou (*14*, *15*), Hirschfelder, et al. (*11*), and Sage and Pings (*19*) require consideration. The equation of Benedict, Webb and Rubin (hereafter referred to as the *Benedict equation*) was developed originally for the paraffin hydrocarbons and has since been applied to various unsaturated hydrocarbons, to carbon dioxide, carbon monoxide, and nitrogen. The density range covered is to 1.4 to 1.8 times the critical density at some temperatures. The compressed liquid region is not described; prediction of vapor pressure requires modification of the constants determined from vapor-phase data. The equation should be regarded as basically applicable to the not-too-dense vapor phase.

Noteworthy success has been obtained with the Benedict equation in the prediction of vapor-liquid equilibria for hydrocarbon systems. It is this singular achievement with the Benedict equation which led to the present work, which was undertaken with a view to overcoming the limitations inherent in the Benedict equation. The advent of high speed digital computers makes possible the application of mathematical techniques which remove the former limitations on functional form; that is the equation need not be amenable to easy hand calculation.

The equation of Martin and Hou applies in the region to 1.4 times the critical density, which excludes all the liquid region below reduced temperatures of 0.99, that is virtually the entire liquid field. The equation is a modified virial expansion whose coefficients have been correlated with various physical properties. Hirschfelder, et al. propose the use of three equations to cover the liquid and vapor regions. The parameters in these equations have also been related to physical properties of the fluids, so that a minimum of data is necessary to describe the properties of single-component fluids. Since the equations do not provide for continuity across the two-phase region, the system of equations is not applicable to prediction of vapor-liquid equilibrium in multicomponent systems. The work of Martin and Hou and of Hirschfelder, et al. are best regarded as an alternate to the graphic or tabular presentation of the data for pure components, based on the theorem of corresponding states and exemplified by the work of Lyderson, et al. (*13*). The present work was not intended as competition for these methods where they are applicable.

Sage and Pings demonstrated the use of orthogonal polynomials for fitting experimental data for propane. Two alternate polynomial fits were obtained, requiring twenty-seven and twenty-nine coefficients. The advantage in the use of orthogonal polynomials is that the coefficients are evaluated independently. The independence of coefficients ensures that they are only related to the particular data used in the fitting process, so they will not fit within the framework of the theorem of corresponding states. It will not be possible to develop coefficients for mixtures based on the data for pure components; that is equations based on orthogonal polynomials are not suitable for predicting vapor-liquid equilibria.

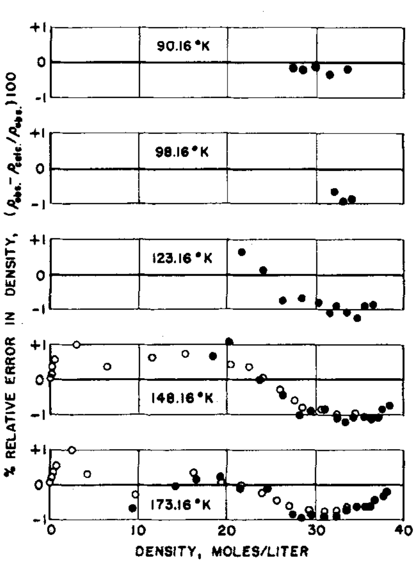

**Fig. 1. Relative error in density prediction, 90.16 to 173.16 K. Data source ○ Michels (*16*), ● Benedict. (*1*).**

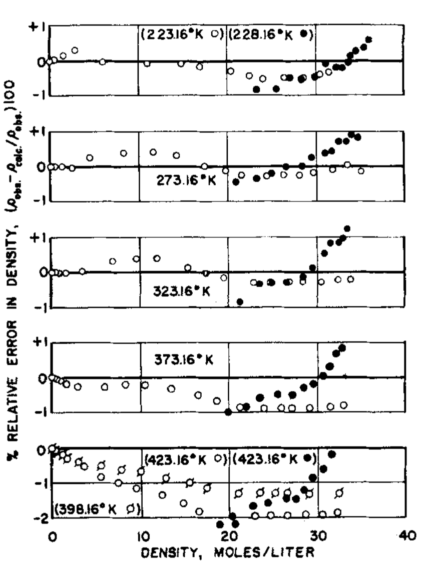

**Fig. 2. Relative error in density prediction, 223.16° to 423.16°K. Data source ○⌀ Michels (*16*), ● Benedict (*1*).**

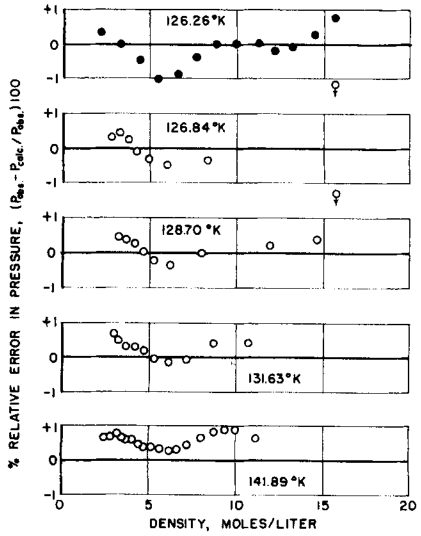

**Fig. 3. Relative error in pressure prediction vicinity of the critical. Data source ● Bloomer (*4*), ○ Onnes and Urk (*18*).**

The present work is the first step in a program aimed toward prediction of vapor-liquid equilibrium, that is development of an equation of state which describes both liquid and vapor regions. To that end the following requirements are imposed:

1. $\lim_{\rho \to 0} \left(\frac{\partial P}{\partial \rho}\right)_T = RT$
(ideal gas limit)

2. $\lim_{\rho \to 0} \frac{1}{2} \left(\frac{\partial^2 P}{\partial \rho^2}\right)_T = k$
(second virial coefficient limit)

3. At the two-phase boundary $P(\rho_{SV}, T) = P(\rho_{SL}, T)$; $G(\rho_{SV}, T) = G(\rho_{SL}, T)$ (equality of pressures and free energies of the phases in equilibrium). In addition

4. Prediction of density in the vapor and liquid regions should approach the experimental accuracy of the available data.

5. In the vicinity of the critical point, prediction of pressure should approach the experimental accuracy of the available data.

These requirements are rather well satisfied by the following equation in thirteen arbitrary coefficients:

$$P = \frac{-A\rho^2}{T}\left[1 - e^{B(\rho - \lambda_1)}\right] + \lambda_2 \rho^2 e^{-\lambda_3 \rho} + RT\rho e^{-I\rho/T} + J\rho^2 e^{\lambda_4} \quad (1)$$

$$\lambda_1 = 1/(C + DT^2)$$
$$\lambda_2 = ET^{0.5} + F/T$$
$$\lambda_3 = 1/(GT^4 + H)$$
$$\lambda_4 = -K(\rho - L)^2 - MT$$

With pressure in atmospheres, temperature in degrees Kelvin, and density in moles per liter the coefficients have the following values for nitrogen:

| Coefficient | Value |
|---|---|
| $A$ | 211.5 |
| $B$ | 0.08625 |
| $C$ | 0.02732 |
| $D$ | $6.073 \times 10^{-7}$ |
| $E$ | 0.1007 |
| $F$ | 135.1 |
| $G$ | $2.746 \times 10^{-9}$ |
| $H$ | 22.13 |
| $I$ | 22.71 |
| $J$ | 30.56 |
| $K$ | 0.0497 |
| $L$ | 13.1 |
| $M$ | 0.0505 |

The equation can be written in virial form by expanding the exponents and collecting terms. The process is straightforward except for the last term, which can be written as follows:

$$J\rho^2 e^{\lambda_4} = Je^{-KL^2 - MT} \left[\rho^2 + \rho^3 \frac{(2KL - K\rho)}{1!} + \ldots + \rho^m \frac{(2KL - K\rho)^{m-2}}{(m-2)!} + \ldots\right] \quad (2)$$

Expanding the general term by the binomial theorem one gets

$$(2KL - K\rho)^{m-2} = \sum_{r=0}^{m-2} \frac{(m-2)!}{(m-2-r)!\,r!} (-K\rho)^r (2KL)^{m-2-r} \quad (3)$$

The multiplier on $\rho^n$ includes all terms where $m + r = n$, or

$$J\rho^2 e^{\lambda_4} = \sum_{n=2}^{\infty} \sum_{r=0}^{n} \frac{(-K)^r (2KL)^{n-2r-2}}{(n-2r-2)!\,r!} \quad (4)$$

Thus Equation (1) can be written in virial form:

$$P = RT\rho + \sum_{n=2}^{\infty} b_n \rho^n \quad (5)$$

where

$$b_n = \frac{A}{T}\left[\frac{B^{n-2} e^{-B\lambda_1}}{(n-2)!} - \frac{1}{(2-n)!}\right] + \frac{\lambda_2(-\lambda_3)^{n-2}}{(n-2)!} + \frac{R(-I)^{n-1}}{(n-1)!\,T^{n-2}} + Je^{-MT^2 - KL^2} \sum_{r=0}^{n} \frac{(-K)^r (2KL)^{n-2r-2}}{(n-2r-2)!\,r!} \quad (6)$$

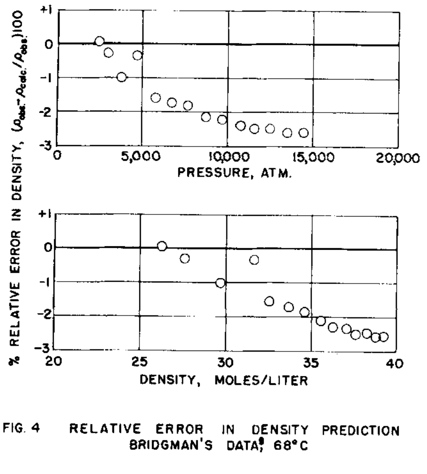

**Fig. 4. Relative error in density prediction, Bridgman's data (9), 68°C.**

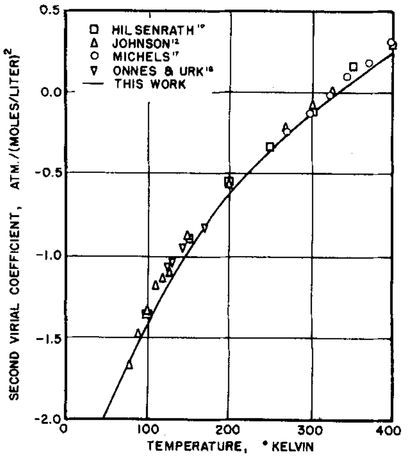

**Fig. 5. Various predictions of second virial coefficient.**

The resulting virial form is exact if all significant terms are evaluated.

The exponential form of the equation was arrived at by correlating the medium-to-high-density data first and then seeking terms which would modify the original correlation so that the low-density region might be described. It was found that isothermals in the medium-to-high-density vapor states could be described by

$$\frac{P}{\rho^2} = c_1 e^{c_2 \rho} + c_3 e^{-c_4 \rho} \quad (7)$$

The compressed liquid region was found to be fitted by

$$\frac{PT}{\rho^2} = -A(1 - e^{B(\rho - \rho^*)}) \quad (8)$$

where

$$\rho^* = \rho_{SV} + \rho_{SL}$$

Equation (8) was found to fit the data for thirty-four liquids studied by Bridgman (*6, 7, 8*) to pressures of 12,000 atm. in the temperature ranges from 0° to 95°C. Equations (7) and (8) are obviously compatible and equivalent if $c_1 = \frac{A}{T} e^{-B\rho^*}$, and if $A/T$ and $c_3 e^{-c_4 \rho}$ become sufficiently small in appropriate regions. With these conditions, both equations can be expressed:

$$\frac{P}{\rho^2} = \frac{-A}{T}(1 - e^{B(\rho - \rho^*)}) + c_3 e^{-c_4 \rho} \quad (9)$$

Modification of Equation (9) by the addition of $\frac{RT}{\rho} e^{-I\rho/T}$ extended applicability to the low-density and ideal-gas regions. Addition of the term $Je^{-K(\rho - L)^2 - MT}$ further extended Equation (9) to include the critical region.

The equation was fitted to the experimental data by the method

Table 1. Prediction of Two-Phase Boundary

| | Observed boundary | | | Predicted boundary | | | % error | | |
|---|---|---|---|---|---|---|---|---|---|
| Temp., °K. | Vapor pressure | Liquid density | Vapor density | Vapor pressure | Liquid density | Vapor density | Vapor pressure | Liquid density | Vapor density |
| 77.36 | 1.000 | 28.81 | 0.1647 | 0.9989 | 28.754 | 0.1651 | 0.11 | 0.19 | −0.24 |
| 88.72 | 3.166 | 26.86 | 0.4813 | 3.0989 | 26.862 | 0.4734 | 2.13 | −0.01 | 1.64 |
| 99.83 | 7.571 | 24.69 | 1.126 | 7.4342 | 24.703 | 1.0951 | 1.81 | −0.05 | 1.47 |
| 110.95 | 15.252 | 21.97 | 2.386 | 15.1130 | 22.106 | 2.3492 | 0.91 | −0.14 | 1.50 |
| 116.49 | 20.684 | 20.28 | 3.461 | 20.5508 | 20.552 | 3.3816 | 0.64 | −1.18 | 2.35 |
| 122.07 | 27.410 | 17.67 | 5.298 | 27.3485 | 18.434 | 5.0471 | 0.23 | −4.32 | 4.73 |

of Newton and Raphson so as to achieve least squares in the residual function defined by $R = \frac{P_{obs} - P_{calc}}{\rho \left(\frac{\partial P}{\partial \rho}\right)}$. The approximate temperature dependence of the various terms was first established by plotting appropriate functions in regions where given terms predominate. Thus by plotting log $P/\rho^2$ vs. $\rho$ values of $A/T\ e^{-B\rho *}$, $B$, $c_3$, and $c_4$ were obtained at various temperatures so that correlations of $\rho^*$, $c_3$, and $c_4$ with temperature might be devised. These correlations were then subject to modification as the behavior of the best fit suggested, until the final form of the equation was found.

Nitrogen was chosen as the basis for development of the equation because it has been extensively investigated in both liquid and vapor regions. Figures 1 through 5 and Table 1 illustrate the accuracy of the equation in describing the experimental data. The root mean square error in fitting Benedict's *(1)* data is 0.7%; in fitting Michel's *(16)* data the root mean square error is 0.5%. In general, where the errors are largest, the disagreement among investigators is also large, and the equation can be fairly said to fit the available data to the same order of magnitude as the experimental error. Note that Bridgman believed his data accurate to a few percent in density. Figure 6 illustrates the range covered by the equation of the present work and enables comparison with the range covered by the Benedict equation with the constants of Stotler and Benedict *(20)*. Stotler and Benedict's constants predict saturated liquid densities 15% in error; the present work covers twice the density range of the Benedict equation and is of comparable accuracy in the range where the Benedict equation is accurate.

Analysis of the inverted least squares matrix obtained from the last iteration of the Newton-Raphson process reveals that the variance of the coefficients is fairly large. From the matrix of coefficients of linear correlation it appears that at most three or four of the coefficients are independent; thus the equation is consistent with correlations based on the theorem of corresponding states, and it should be possible to correlate the independent coefficients with suitable physical properties.

In summary an equation of state has been developed which describes the vapor and liquid regions of nitrogen with excellent accuracy in the range to three times the critical temperature and density. The equation can be reduced to the virial form. Of the thirteen coefficients required not all are independent, and it should be possible to reduce the number of coefficients to three or four. Extension of the work reported here is in progress, so that the application of the equation to fluids other than nitrogen can be demonstrated. Future work contemplated includes determination of a set of the independent coefficients, their correlation with physical properties, and application of the equation to prediction of vapor-liquid equilibria.

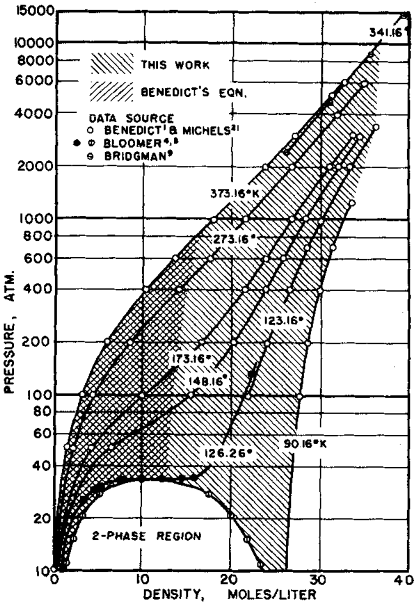

Fig. 6. Comparison of regions fitted.

## NOTATION

$A$ to $M$ = coefficients in an equation of state

$P$ = pressure, atm.

$R$ = gas law constant, 0.082054 liter-atm./g.-mole —°K.

$T$ = temperature, °K.

$\rho$ = density, g.-mole/liter

$c_1$-$c_4$ = temperature dependent coefficient in an equation of state

$\lambda_1$-$\lambda_4$ = temperature dependent coefficient in an equation of state

### Subscripts

calc = calculated from equation of state

obs = observed

$SL$ = saturated liquid

$SV$ = saturated vapor

## LITERATURE CITED

1. Benedict, Manson, *J. Am. Chem. Soc.*, **59**, 2224-42 (1937).
2. ———, G. B. Webb, and L. C. Rubin, *J. Chem. Phys.*, **8**, 334-45 (1940).
3. ————, *Chem. Eng. Progr.*, **47**, 419-22, 571-78, 609-20 (1951).
4. Bloomer, O. T., Ph.D. dissertation, Ill. Inst. Technol., Chicago, Ill. (1953).
5. ———, and K. N. Rao, *Res. Bull. 18*, Institute of Gas Technology (1952).
6. Bridgman, P. W., "American Institute of Physics Handbook," McGraw-Hill New York (1957).
7. ———,"International Critical Tables," Vol. 3, p. 40, McGraw-Hill, New York (1928).
8. ———, *Proc. Am. Acad. Arts Sci.*, **66**, 198-233 (1931).
9. *Ibid.*, **59**, 171-211 (1923).
10. Hilsenrath, J., *U.S. Natl. Bur. Standards*, Circ. 564 (1955).
11. Hirschfelder, J. O., R. J. Buehler, H. A. McGee, and J. R. Sutton, *Ind. Eng. Chem.*, **50**, 375-85 (1958).
12. Johnson, H. L., "American Institute of Physics Handbook," McGraw-Hill, New York (1957).
13. Lyderson, A. L., R. A. Greenkorn, and O. A. Hougen, *Univ. Wisc. Eng. Expt. Sta. Report No. 4* (1955).
14. Martin, J. J., and Y. C. Hou, *A.I.Ch.E. Journal*, **1**, 142-51 (1955).
15. Martin, J. J., K. M. Kapoor, and Noel de Nevers, *A.I.Ch.E. Journal*, **5**, 159 (1959).
16. Michels, A., R. J. Lunbeck, and G. J. Wolkers, *Appl. Sci. Res.*, **A3**, 197-210 (1952).
17. Michels, A., J. Otto, and H. Wouters, "Chemical Engineers Handbook," 3 ed., McGraw-Hill, New York (1950).
18. Onnes, K., and Urk, "International Critical Tables," Vol. 3., pp. 18-19, McGraw-Hill, New York (1928).
19. Pings, C. J., and B. H. Sage, *Ind. Eng. Chem.*, **49**, 1315-28 (1957).
20. Stotler, H. H., and Manson Benedict, *Chem. Eng. Progr. Symposium Ser. No. 6*, **49**, 25-36 (1953).

*Manuscript received October 28, 1960; revision received February 7, 1961; paper accepted February 9, 1961. Paper presented at A.I.Ch.E. Washington meeting.*