Vapor Pressure and Boiling Point of Pure Nitric Acid

J. A. DUISMAN
Linde Division, Research Laboratory, Union Carbide Corp., Tonawanda, N.Y.

S. A. STERN
Department of Chemical Engineering and Metallurgy,
Syracuse University, Syracuse, N. Y.

The vapor pressure of pure nitric acid was calculated from the latest thermodynamic data and found in disagreement with the most reliable measurements reported in the literature. This discrepancy is attributed to an error in the standard enthalpy of vaporization, $\Delta H^\circ_{298.15}$, used as reference in the calculations. Other possible sources of error are also discussed. New vapor pressure measurements reported by Holéci were subjected to a third-law consistency test and found satisfactory. A new value of $\Delta H^\circ_{298.15}$ obtained from these data was used to recalculate the vapor pressure between 263° and 373° K. These computations yielded a normal boiling point of 357.05° K. (83.90° C.) for pure nitric acid.

MANY of the physicochemical properties of pure nitric acid are difficult to determine because of the well-known thermal instability of this compound at temperatures above its melting point, 231.56° K. (−41.59° C.). Thus, liquid nitric acid decomposes according to the stoichiometric relation

$$2HNO_3 \rightleftarrows 2NO_2 + H_2O + 1/2\ O_2 \qquad (1)$$

where NO_2 stands for an equilibrium mixture of nitrogen dioxide and dinitrogen tetroxide. The pure liquid acid is colorless, but in a few hours at room temperature will acquire the yellowish tinge characteristic of nitrogen dioxide. The rate of thermal decomposition increases rapidly with increasing temperature. In 1960, Stern *et al.* (*13*) critically reviewed the literature on the physicochemical properties of nitric acid and concluded that, due to the instability of the compound, vapor pressures calculated from thermodynamic data were more reliable than the experimental vapor pressures available at that time. Accordingly, they calculated the vapor pressure of nitric acid between 273° and 373° K., based on the calorimetric measurements of Forsythe and Giauque for the liquid (*2, 3, 4*) and the thermodynamic functions for the vapor derived by Palm and Kilpatrick from spectroscopic measurements (*12*). It was assumed that the vapor pressure is equal to the fugacity; this assumption is satisfactory at the lower pressures, while near 1 atm. the fugacity would be expected to be a few per cent lower than the vapor pressure. The calculations yielded a normal boiling point of 357.25° K. (84.10° C.) for pure nitric acid.

Recently, the vapor pressure of nitric acid was remeasured by Holéci (*6*) in the pressure range from 58 to 743 torr, using an improved flow ebulliometer. He expressed his results by the equation

$$\log p(\text{torr}) = 7.61628 - \frac{1486.238}{t\,(^\circ\text{C.}) + 230} \qquad (2)$$

A boiling point of 357.00° K. (83.85° C.) is calculated at 760 torr from this relation.

Since nitric acid is a compound of considerable scientific and industrial importance, it was useful to recalculate the vapor pressure and normal boiling point of the pure acid, using the latest thermodynamic data. The present note reports the results of these calculations, which are compared with Holéci's measurements. A consistency test of Holeci's data based on the third law of thermodynamics is also presented.

VAPOR PRESSURE CALCULATIONS

It was assumed again that the vapor pressure is equal to the fugacity, which was calculated by conventional procedures from the standard free energy of vaporization of nitric acid.

The heat capacity of liquid nitric acid was obtained from the measurements of Forsythe and Giauque (*2, 3, 4*) after correction for several factors: the temperature scale, from the ice point value of 273.10° K. used by these investigators to that of 273.15° K.; the size of the degree of temperature, based on the new ice point; the difference between the international calorie and the defined calorie; and the difference between the molecular weight scale based on carbon^{12} and the chemical scale.

All these corrections were very small. Thus, the last three corrections decreased the reported heat capacity values by less than 0.02%. The data of Forsythe and Giauque actually represent C_{sat}, the heat capacity under the saturated vapor pressure, rather than C_p, the constant-pressure heat capacity (*5*). However, the difference between C_{sat} and C_p was estimated to be less than 0.005% by means of the exact thermodynamic relation

$$C_p - C_{\text{sat}} = T\left(\frac{\partial V}{\partial T}\right)_p \left(\frac{\partial P}{\partial T}\right)_{\text{sat}} \qquad (3)$$

and available values for the thermal expansion and the vapor pressure (*13*). The difference between C_p and C_p°, the constant-pressure heat capacity for the standard state at 1 atm., is also negligible. A linear least-squares fit of the corrected (unsmoothed) heat capacity data for liquid nitric acid yielded the expression

$$C_p^\circ\,(l) = 28.415 - (7.153 \times 10^{-3})T \qquad (4)$$

where T is the absolute temperature. The equation represents the data to within ±0.3%, from the melting point to the highest experimental temperature of about 303° K. A quadratic least-squares fit did not result in a significant improvement.

The heat capacity of nitric acid vapor as an ideal gas at 1-atm. pressure was obtained from the tabulation of McGraw *et al.* (*9*), who have calculated the thermodynamic

Table I. Summary of Vapor Pressure Measurements and Calculations for Pure Nitric Acid

	Vapor Pressure, Torr									
									Third-Law Values Based on $\Delta H^\circ_{298.15}$ =	
Temp., °K.	Taylor (*15*)	Berl & Saenger (*1*)	Klemenc & Rupp (*7*)	Wilson & Miles (*17*)	Vandoni (*16*)	Lloyd & Wyatt (*8*)	Potier (*10, 11*)	Holéci[a] (*6*)	9358.3[b] (cal. mole^{-1})	9431.4 (cal. mole^{-1})
263.15	...	...	...	...	6.97	6.93[c]	...	7.25	7.93	6.90
273.15	11	14.0	14.9	14.7	14.02	14.0[c]	14.15	14.27	15.73	13.75
278.15	15	19.6	...	20.1	...	...	19.76	19.58	21.65	18.99
283.15	22	26.5	...	27.1	26.42	26.26	26.52	26.53	29.42	25.86
285.65	...	...	31.5	...	...	...	...	30.72	34.13	30.02
288.15	30	35.5	...	36.2	...	...	35.6	35.48	39.48	34.77
293.15	42	47.3	...	48.0	46.96	47.0[c]	47.5	46.92	52.33	46.19
298.15	57	61.0	62.1	62.9	...	...	...	61.36	68.57	60.66
303.15	77	77.4	...	...	...	...	...	79.43	88.90	78.80
313.15	133	...	...	...	...	...	...	129.3	145.00	129.03
323.15	215	...	...	...	...	...	...	203.4	227.98	203.60
333.15	320	...	...	...	...	...	...	310.0	346.80	310.76
343.15	460	...	...	...	...	...	...	459.4	512.04	460.30
353.15	625	...	...	...	...	...	...	663.7	735.86	663.51
363.15	820	...	...	...	...	...	...	937.1	1031.9	933.10
373.15	...	...	...	...	...	...	...	1295.8	1415.1	1283.1
Normal boiling point	360° K. (87° K.)	356° K. (83° C.)						357.00° K. (83.85° C.)	354.07° K. (80.92° C.)	357.05° K. (83.90° C.)

[a] Calculated from Equation 2. [b] Value used for computation and based on $\Delta H^\circ_{293.15} = 9426$ cal. mole^{-1} (*17*). [c] Interpolated.

functions of nitric acid vapor on the basis of recent spectroscopic work. A least-squares fit of their data between 250° and 400° K. yielded the expression

$$C^\circ_p(v) = 3.4959 + (3.738 \times 10^{-2})T - (19.3 \times 10^{-6})T^2 \quad (5)$$

which represents the data within ± 0.05% in the stated temperature range.

An analytical expression for the difference between the heat capacity of the vapor and liquid phases in their standard states, ΔC°_p, as a function of temperature was obtained from Equations 4 and 5. Alternate methods of calculating ΔC°_p were examined, but yielded results which were not significantly different from those obtained from the above equations.

Expressions for the standard enthalpy of vaporization, ΔH°_T, and the standard entropy of vaporization, ΔS°_T, as a function of temperature were calculated from the ΔC°_p relation mentioned above, in conjunction with the following reference values

$$\Delta H^\circ_{293.15} = 9426 \text{ cal. mole}^{-1}$$

obtained from the calorimetric measurements of Wilson and Miles (*17*), and

$$\Delta S^\circ_{298.15} = 26.61 \text{ Gibbs mole}^{-1}$$

from the tabulated entropy of nitric acid vapor (*9*) and the entropy of the liquid (*2*), corrected as mentioned above. Finally, the standard free energy of vaporization, ΔF°_T, and, hence, the vapor pressure or fugacity of nitric acid, were calculated from these thermodynamic functions.

The results of the calculations are summarized in Table I, in the column before the last. The vapor pressure values are significantly higher than those obtained from previous calculations and than all the experimental data. The normal boiling point, 354.07° K. (80.92° C.), is correspondingly lower than reported previously. The discrepancy between this and previous calculations is due largely to the use of different reference data. For example, Stern *et al.* (*13*) based their vapor pressure computations on the values of $\Delta H^\circ_{298.1} = 9355$ cal. mole^{-1} and $\Delta F^\circ_{298.15} = 1476$ cal. mole^{-1}; the former was obtained from Forsythe and Giauque, while the latter was calculated from an experimental vapor pressure of 62.9 torr at 298.15° K. reported by Wilson and Miles (*17*). When these are combined using the relation

$$\Delta S^\circ = \frac{\Delta H^\circ - \Delta F^\circ}{T}$$

a value of $\Delta S^\circ_{298.15} = 26.43$ Gibbs mole^{-1} is obtained, which is lower than the more reliable value, $\Delta S^\circ_{298.15} = 26.61$ Gibbs mole^{-1}, given above.

Since the more recent experimental data at the lower temperature are mutually consistent and relatively reliable (*6, 8, 10, 11, 16*), the thermal decomposition of nitric acid being slow at these temperatures, the newly calculated vapor pressures are considered unsatisfactory. The high values obtained in these calculations may be attributed to the unreliability of the standard enthalpy of vaporization used as reference—namely, $\Delta H^\circ_{293.15} = 9426$ cal. mole^{-1}. A more reliable reference value can be obtained, as shown below, from Holéci's measurements.

THIRD-LAW TEST OF NEW VAPOR PRESSURE MEASUREMENTS

A third-law consistency check of Holéci's measurements was first made by the following method. The standard free energy of vaporization was calculated at various temperatures from Holéci's experimental data, assuming that the vapor pressure and the fugacity are equal. The ΔF°_T's obtained in this manner were combined with the corresponding third-law ΔS°_T's, to obtain values for ΔH°_T. Finally, a value for $\Delta H^\circ_{298.15}$ was calculated from each ΔH°_T, using the above heat capacity equations. The results of these calculations are summarized in Table II.

The constancy of $\Delta H^\circ_{298.15}$ in Table II shows that Holéci's data withstand this test very well and, therefore, his values for the vapor pressure of nitric acid are self-consistent. The mean value of $\Delta H^\circ_{298.15}$ is 9431.4 cal. mole^{-1}, with mean and standard deviations of 2.6 and 3.5 cal. mole^{-1}, respectively. By comparison, a value of 9358 cal. mole^{-1} is obtained for $\Delta H^\circ_{298.15}$ from the calorimetric measurements

Table II. Third-Law Consistency Test of Holéci's (6) Vapor Pressure Measurements

Temp., ° K.	Standard Enthalpy of Vaporization, $\Delta H^\circ_{298.15}$ (Cal. Mole^{-1})
297.05	9423.2
308.05	9433.5
312.80	9423.7
316.55	9430.6
322.40	9430.5
322.3	9432.1
324.4	9430.2
327.0	9436.9
330.85	9436.7
332.60	9435.6
333.40	9433.1
335.45	9433.6
337.00	9431.9
338.85	9432.5
340.4	9434.0
341.9	9429.3
345.1	9431.2
347.8	9430.3
350.35	9430.3
352.02	9427.0
353.90	9433.8
356.40	9431.6

of Wilson and Miles (*17*)—based on $\Delta H^\circ_{293.15}$ (mean) = 9426 cal. mole^{-1}—in conjunction with Equations 3 and 4. The discrepancy between the calculated vapor pressure and Holéci's data can be traced largely to this difference in the standard enthalpy of vaporization.

CONCLUSIONS

Because of the thermodynamic consistency and the larger temperature range of Holéci's data, the new value of $\Delta H^\circ_{298.15}$ = 9431.4 cal. mole^{-1} appears reliable within the stated limits of accuracy. A recalculation of the vapor pressure of the acid based on the new $\Delta H^\circ_{298.15}$ is presented in Table I. The results are in satisfactory agreement with Holéci's measurements and are believed to be the best available.

In the above discussion, it was assumed that the discrepancy between the experimental and the previously calculated vapor pressures was due entirely to the inaccuracy of the enthalpy of vaporization used in these calculations. However, part of the discrepancy could arise also from minor uncertainties in the entropies of gaseous and liquid nitric acid. Thus, more recent calculations of ideal gas entropies (*14*) show that the value of $S^\circ_{298.15}$ is 0.04 Gibbs mole^{-1} lower than reported by McGraw *et al.* The use of this value would decrease the calculated vapor pressures. A new calorimetric determination of the enthalpy of vaporization of pure nitric would therefore prove informative.

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NOMENCLATURE

C_p = heat capacity at constant pressure, Gibbs mole^{-1}
C°_p = heat capacity at constant pressure for standard state, Gibbs mole^{-1}
C_{sat} = heat capacity under saturated vapor pressure, Gibbs mole^{-1}
p = vapor pressure, torr
t = temperature, ° C.
T = absolute temperature, ° K.
V = vapor volume, cc. mole^{-1}
ΔC°_p = difference between the standard heat capacities of the vapor and liquid phases, Gibbs mole^{-1}
ΔF°_T = standard free energy of vaporization, cal. mole^{-1}, at temperature T
ΔH°_T = standard enthalpy of vaporization, cal. mole^{-1}, at temperature T
ΔS°_T = standard entropy of vaporization, Gibbs mole^{-1}, at temperature T

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