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TECHNICAL NOTE 3270

EFFECT OF DISSOCIATION ON THERMODYNAMIC PROPERTIES

OF PURE DIATOMIC GASES

By Harold W. Woolley

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EFFECT OF DISSOCIATION ON THERMODYNAMIC PROPERTIES
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SUMMARY

A graphical method for obtaining charts for the thermodynamic properties enthalpy and entropy for the equilibrium mixture of atoms and diatomic molecules for pure gaseous elements is described. The procedure is equivalent in principle to numerical calculation based on the same fundamental data, but gives directly the location of points of intersection of curves for constant pressure and curves for constant values of the compressibility factor PV/RT . In combination, the resulting graphs for enthalpy and entropy are equivalent to Mollier diagrams for the gaseous fluid in the dissociation region. Results are given for hydrogen H_2 , oxygen O_2 , and nitrogen N_2 .

A table of equilibrium constants is included for the reactions $H_2 \rightarrow 2H$, $O_2 \rightarrow 2O$, and $N_2 \rightarrow 2N$. The effect of dissociation on the heat capacity is also discussed briefly.

INTRODUCTION

This report is the first of a series of reports on the thermodynamic properties of gases of aeronautical interest which have been prepared at the National Bureau of Standards under the sponsorship and with the financial assistance of the National Advisory Committee for Aeronautics.

The thermodynamic properties for gases are usually given without the effect of dissociation. At high temperatures, a considerable proportion of the gas is not in the form of pure molecular species of lower temperatures, but instead is broken up into atoms and, in the case of polyatomic molecules, into molecules of intermediate size. This process of dissociation when the temperature is raised involves a large energy if the original molecules are relatively stable, so that large thermal effects occur over a considerable range of elevated temperature. The magnitude of the effect at a given temperature depends very markedly on the total pressure of the gas. Since the effect becomes much larger than the ordinary effects of equation of state involving interactions between

stable molecules, it will be appropriate in the following discussions to treat each constituent as an ideal gas.

The importance of these effects is well understood, but detailed calculations are often laborious. In this report a graphical method is described by which the enthalpy $(H - E_0^0)/RT_0$, the entropy S/R , and the compressibility factor PV/RT of the mixture may be obtained and shown for any dissociating diatomic gaseous element for which the necessary data exist, with the method applied to hydrogen H_2 , oxygen O_2 , and nitrogen N_2 . The procedure is equivalent in principle to numerical calculation based on the same fundamental data but gives directly the location of points of intersection of curves for constant pressure and curves for constant values of PV/RT .

While the effect of dissociation on the thermodynamic properties is indicated explicitly for diatomic elements in the present report, similar effects have, in general, not been included in the other reports of this series on the thermodynamic properties of gases (air excepted). The reason for this is very simple. For the calculation of the properties of a reacting gas mixture at equilibrium it is far more convenient to have separate tables for the pure atomic species and for the pure molecular species for all of the components present in the gas mixture. This is in accord with the standard methods of computation. The general problem with several components is treated very completely by Huff, Gordon, and Morrell in reference 1. A summary of extensive analyses of the many component problems has been given by Damköhler (ref. 2).

SYMBOLS

| | |
|--------------|--|
| A | representing chemical symbol for an element as an atomic gas |
| A_2 | representing chemical symbol for an element as a diatomic gas |
| C_p | heat capacity at constant pressure of equilibrium mixture per mole of original gas |
| C_v | heat capacity at constant volume of equilibrium mixture per mole of original gas |
| E_0^0 | internal energy of 1 mole of ideal gas at absolute zero; $E_0^0 = H_0^0$ |
| F^0 | free energy for 1 mole of ideal gas at atmospheric pressure |
| ΔF^0 | increment in free energy for a reaction as written |

| | |
|----------------|---|
| H | enthalpy for a quantity of gas; in figures 4, 6, 8, and 10, H is used for the enthalpy above that of 1 mole of the molecular gas at absolute zero |
| H_0° | enthalpy of 1 mole of ideal gas at absolute zero |
| K | equilibrium constant for a reaction |
| P | total pressure of gas |
| P_A, P_{A_2} | partial pressures of constituents A and A_2 |
| R | gas constant |
| S | entropy for a quantity of gas |
| S° | entropy for 1 mole of ideal gas at 1 atmosphere |
| T | absolute temperature, $^{\circ}\text{K}$ |
| T_0 | absolute temperature of ice point, 273.16°K |
| V | specific volume for a quantity of gas |
| Z | compressibility factor (In this report Z is ratio of the number of moles to original number of moles of diatomic gas. Other contributions to the compressibility are being ignored in the present treatment.) |
| ρ | density of gas in any units; for example, in Amagat units $\rho = V_0/V$, where V_0 is specific volume at standard conditions |

THERMODYNAMIC FORMULAS FOR DISSOCIATION

Let A_2 represent a diatomic molecule of a gas. For constituents that are ideal gases, the reaction $A_2 \rightarrow 2A$ has an equilibrium constant $K = P_A^2/P_{A_2} = \exp(-\Delta F^{\circ}/RT)$, where $\Delta F^{\circ} = 2F_A^{\circ} - F_{A_2}^{\circ}$. The total pressure is the sum of the partial pressures, $P = P_A + P_{A_2} = K^{1/2}P_{A_2}^{1/2} + P_{A_2}$. If $K/4$ is added, the square root leads to $\sqrt{K + 4P} = K^{1/2} + 2P_{A_2}^{1/2}$. The compressibility factor $PV/RT = Z$ is given by

$$Z = \frac{P_A + P_{A_2}}{(P_A + 2P_{A_2})^{1/2}} = 1 + \frac{(K^{1/2}P_{A_2}^{1/2})^{1/2}}{P_{A_2} + (K^{1/2}P_{A_2}^{1/2})^{1/2}} = 1 + \sqrt{K/(K + 4P)}$$

If there is originally 1 mole of the substance A_2 and if the dissociation reaction has occurred to the extent of a fraction x of a mole, the amount of A_2 remaining is $1 - x$ moles, and the amount of the atomic gas A produced is $2x$ moles, so that the total amount of gas becomes $1 + x$ moles, giving $Z = 1 + x$. Thus, the extent of the reaction is $x = \sqrt{K/(K + 4P)}$.

For the amount of gas considered, the high-temperature properties will be in accord with the equations

$$\begin{aligned} (H - E_0^0)/RT = (1 - x) \left[(H^0 - E_0^0)/RT \right]_{A_2} + 2x \left[(H^0 - E_0^0)/RT \right]_A + \\ 2x(E_0^0/RT)_A - x(E_0^0/RT)_{A_2} \end{aligned}$$

and

$$\begin{aligned} S/R = (1 - x)(S^0/R)_{A_2} + 2x(S^0/R)_A + (1 + x) \log_e (1 + x) - \\ (1 - x) \log_e (1 - x) - 2x \log_e 2x - (1 + x) \log_e P \end{aligned}$$

The heat capacity at constant pressure for an equilibrium mixture of the atomic and molecular forms of a diatomic element is given by

$$C_p/R = 2x(C_p^0/R)_A + (1 - x)(C_p^0/R)_{A_2} + \frac{1}{2}(1 - x^2)x(\Delta H^0/RT)^2$$

where

$$\begin{aligned} \Delta H^0/RT = 2(H^0/RT)_A - (H^0/RT)_{A_2} \\ = 2 \left[(H^0 - E_0^0)/RT \right]_A - \left[(H^0 - E_0^0)/RT \right]_{A_2} + 2(E_0^0/RT)_A - (E_0^0/RT)_{A_2} \end{aligned}$$

The heat capacity at constant volume for an equilibrium mixture of atomic and molecular forms of a diatomic element C_v/R may be computed from C_p/R and $(C_p - C_v)/R$ which is given by

$$-T \left(\frac{\partial V}{\partial T} \right)_P \bigg/ \left(\frac{\partial V}{\partial P} \right)_T = \left[Z + T \left(\frac{\partial Z}{\partial T} \right)_P \right]^2 \bigg/ \left[Z - P \left(\frac{\partial Z}{\partial P} \right)_T \right]$$

This may be evaluated as

$$(C_p - C_v)/R = \left\{ 1 + x + 2x^3 K^{-1} P \left[2 \left(H^0/RT \right)_A - \left(H^0/RT \right)_{A_2} \right] \right\}^2 \bigg/ (1 + x + 2x^3 K^{-1} P)$$

Alternatively, the heat capacity at constant volume for an equilibrium mixture of atomic and diatomic molecular forms of an element has also been given by Wildt (ref. 3) as

$$C_v/R = 2x (C_v^0/R)_A + (1 - x) (C_v^0/R)_{A_2} + \frac{x(1-x)}{2-x} (\Delta E^0/RT)^2$$

where

$$\begin{aligned} \Delta E^0/RT &= 2(E^0/RT)_A - (E^0/RT)_{A_2} \\ &= 2 \left[(E^0 - E_0^0)/RT \right]_A - \left[(E^0 - E_0^0)/RT \right]_{A_2} + 2(E_0^0/RT)_A - (E_0^0/RT)_{A_2} \end{aligned}$$

He also shows the exponents for isentropic expansion as

$$\left(\frac{d \log_e P}{d \log_e T} \right)_S = \frac{C_p/R}{1 + x + \frac{x}{2}(1 - x^2) (\Delta E^0/RT)} = 1/\eta$$

$$\left(\frac{d \log_e \rho}{d \log_e T} \right)_S = \frac{C_v/R}{1 + x + \frac{x(1-x)}{2-x} (\Delta E^0/RT)} = 1/\zeta$$

$$\left(\frac{d \log_e P}{d \log_e \rho} \right)_S = \zeta/\eta = \xi$$

and includes a table of these quantities for hydrogen at elevated temperature. Möglich, Riewe, and Rompe (ref. 4) have also considered the effects of dissociation and ionization on gaseous specific heat and show diagrams with both effects for hydrogen.

GRAPHICAL METHOD

In order to obtain a graphical representation of the entropy and enthalpy, the following procedure was adopted:

(1) Values of $\log_{10} K$ for the dissociation reaction were obtained and plotted for the entire temperature range of interest.

(2) Next, a set of values of x was chosen. These were taken as 0.01, 0.05, 0.1, 0.2, 0.4, 0.6, 0.8, 0.9, 0.95, and, for part of the calculation, 0.99. Noting that the relation $x = \sqrt{K/(K + 4P)}$ is equivalent to $\log_{10} K = \log_{10} \left[\frac{4x^2}{(1 - x^2)} \right] + \log_{10} P$, values of $\log_{10} K$ corresponding to the chosen values of x were found for various values of $\log_{10} P$. The pressures 10^{-8} , 10^{-6} , 10^{-4} , 10^{-2} , 1, 10, and 100 atmospheres were selected, giving uniform increments in $\log_{10} P$, apart from the 10 atmospheres which was inserted for better coverage. These values of $\log_{10} K$ gave corresponding values of T according to the curve plotted for $\log_{10} K$ versus T . This is illustrated in figure 1, showing how, with $\log_{10} \left[\frac{4x^2}{(1 - x^2)} \right]$ plotted permanently on a movable vertical scale, the zero could be aligned with the horizontal line for the logarithm of the pressure to give directly the temperatures at which these combinations of x and P occur.

(3) Values of $(H^{\circ} - E_0^{\circ})_{\text{molec}}/RT_0$ and $[2H_{\text{atomic}}^{\circ} - (E_0^{\circ})_{\text{molec}}]/RT_0$ were plotted on one graph and $(S^{\circ}/R)_{\text{molec}}$ and $2(S^{\circ}/R)_{\text{atomic}}$ for 1-atmosphere pressure on another graph. To get $(H - E_0^{\circ})/RT_0$ or H/RT_0 for the mixture, points on the final graph for each value of T determined were found quite simply at a fraction x of the distance upward from the molecular graph to the atomic graph. This was done by plotting on another sheet a line of slope equal to 1 and other lines having slopes equal to the chosen values of x , all coming out of a common origin. The triangle of graph paper between the lines of slope zero and unity was cut out and slid, without being rotated, over the enthalpy curves until its upper edge was on the atomic curve and its lower edge was on the molecular curve for a temperature determined from the curve of $\log_{10} K$

versus T for a chosen x and P . Then a pin point was located at this value of T on that line on the triangle having the chosen x as its slope. This is illustrated in figure 2. Curves were thus obtained for various values of P ; and, intersecting with them, other curves were obtained for various values of x .

For S/R a more complicated process was followed, since an additional contribution due to entropy of mixing of atoms and molecules was required. A triangle of graph paper was formed, as before, between the line of zero slope and a line of unit slope, with intermediate lines between having slopes equal to the chosen values of x . These intermediate sloping lines were not made to pass through the intersection of the lines for $x = 0$ and $x = 1$, but were instead displaced upward a distance which in the S/R plots would be equivalent to the increase due to mixing. In terms of x , this increase in S/R , including the effect of increase in number of moles of gas due to dissociation, is equal to $(1 + x) \log_e (1 + x) - (1 - x) \log_e (1 - x) - 2x \log_e 2x$. The triangle was slid over the S^0/R curves for the constituents, without being rotated, until, for a chosen temperature corresponding through $\log_{10} K$ to an x and P , it matched both atomic and molecular curves at its top and base, respectively. A point was then located on the line of slope x at the temperature in question as shown in figure 3. Next, it was displaced vertically by a distance corresponding to $-(1 + x) \log_e P$. For the upward displacement, two points were located, one upward by $-\log_e P$ and the other at $-2 \log_e P$, with a prepared scale for the pressures used, which was usable without change at all temperatures. The location of a point at a fraction x of the distance from the first to the second was made with the technique and sloping lines used in the case of enthalpy and illustrated for it in figure 2. The actual displacement is upward for P less than 1 atmosphere and downward for P greater than 1 atmosphere. Curves were then drawn to follow the points to represent entropy for constant values of P as a function of temperature, while other curves show constant values of x and thus of PV/RT .

The results are shown in the curves of figures 4 to 9. The curves give an over-all picture of the effect of dissociation on the enthalpy and entropy for the diatomic gases considered. The values of x , the degree of dissociation, may be found from these graphs for H_2 , O_2 , and N_2 , since the values of $PV/RT = 1 + x$ are given explicitly on a basis of negligible ordinary equation-of-state effects. The fundamental data upon which these calculations are based appear quite reliable except for O_2 for which the dissociation energy is 0.63 percent greater than the value used (ref. 5). The graphs for N_2 in figures 8 and 9 are based on the value of 9.756 electron volts as the listing of Herzberg (ref. 6) for dissociation energy as proposed by Gaydon (ref. 7). The older value of 7.373 electron volts of Herzberg (ref. 6) gave estimates differing considerably in the high-temperature region. A number of lines of evidence now

support Gaydon's value (refs. 8 to 11). Values of K , the equilibrium constant for dissociation, are given in table 1.

For each substance the two graphs together, for enthalpy and entropy, give data equivalent to a Mollier diagram for the high-temperature region. Some simple qualitative conclusions may be drawn readily from the graphs. For example, it will be seen that a compression at constant entropy tends to increase the degree of dissociation of the gas, and an expansion under such conditions decreases the dissociation. On the other hand, an expansion at constant enthalpy tends toward greater dissociation.

National Bureau of Standards,
Washington, D. C., October 15, 1954.

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TABLE 1.- VALUES OF K FOR DISSOCIATION

| T, °K | $K_{(H_2 \rightarrow 2H)}$ (a) | $K_{(O_2 \rightarrow 2O)}$ (a) | $K_{(N_2 \rightarrow 2N)}$ (Gaydon) |
|-------|-----------------------------------|-----------------------------------|--|
| 1,000 | 5.17×10^{-18} | 3.63×10^{-20} | |
| 1,200 | 3.90×10^{-14} | 8.63×10^{-16} | |
| 1,400 | 2.36×10^{-11} | 1.173×10^{-12} | |
| 1,600 | 2.952×10^{-9} | 2.659×10^{-10} | |
| 1,800 | 1.280×10^{-7} | 1.819×10^{-8} | |
| 2,000 | 2.639×10^{-6} | 5.378×10^{-7} | 7.898×10^{-19} |
| 2,200 | 3.161×10^{-5} | 8.628×10^{-6} | 1.510×10^{-16} |
| 2,400 | 2.520×10^{-4} | 8.741×10^{-5} | 1.207×10^{-14} |
| 2,600 | 1.467×10^{-3} | 6.218×10^{-4} | 4.945×10^{-13} |
| 2,800 | 6.657×10^{-3} | 3.346×10^{-3} | 1.195×10^{-11} |
| 3,000 | 2.482×10^{-2} | 1.441×10^{-2} | 1.893×10^{-10} |
| 3,200 | 7.856×10^{-2} | 5.176×10^{-2} | 2.130×10^{-9} |
| 3,400 | .2174 | .1600 | 1.808×10^{-8} |
| 3,600 | .5443 | .4366 | 1.211×10^{-7} |
| 3,800 | 1.214 | 1.0726 | 6.651×10^{-7} |
| 4,000 | 2.524 | 2.409 | 3.085×10^{-6} |
| 4,200 | 4.90 | 5.013 | 1.239×10^{-5} |
| 4,400 | 8.96 | 9.758 | 4.396×10^{-5} |
| 4,600 | 15.5 | 17.93 | 1.400×10^{-4} |
| 4,800 | 25.8 | 31.33 | 4.050×10^{-4} |
| 5,000 | 41.1 | 52.36 | 1.079×10^{-3} |

^aRef. 12.

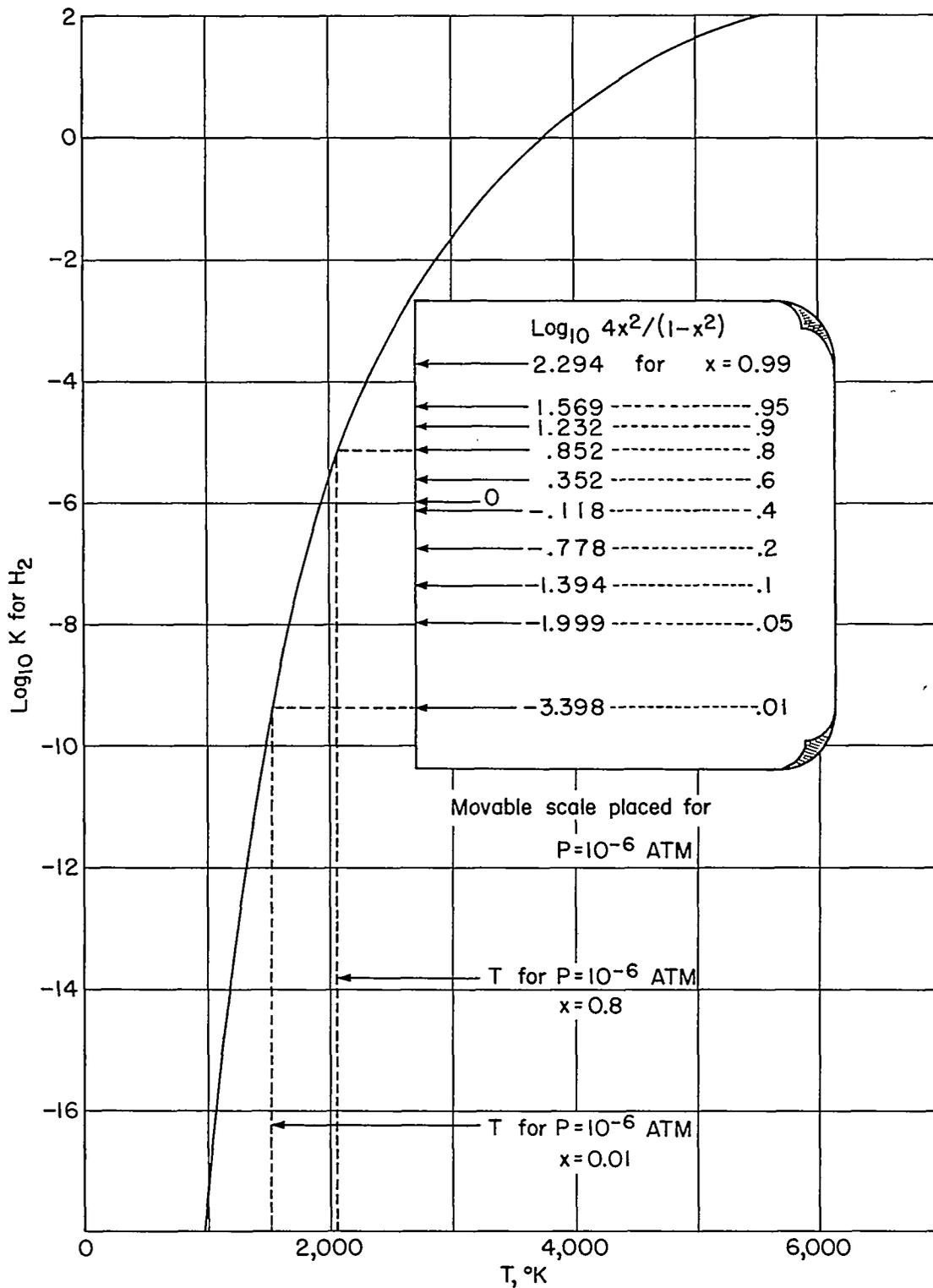


Figure 1.- Method of obtaining corresponding temperatures and pressures for various degrees of dissociation, using a curve for equilibrium constant for dissociation versus temperature.

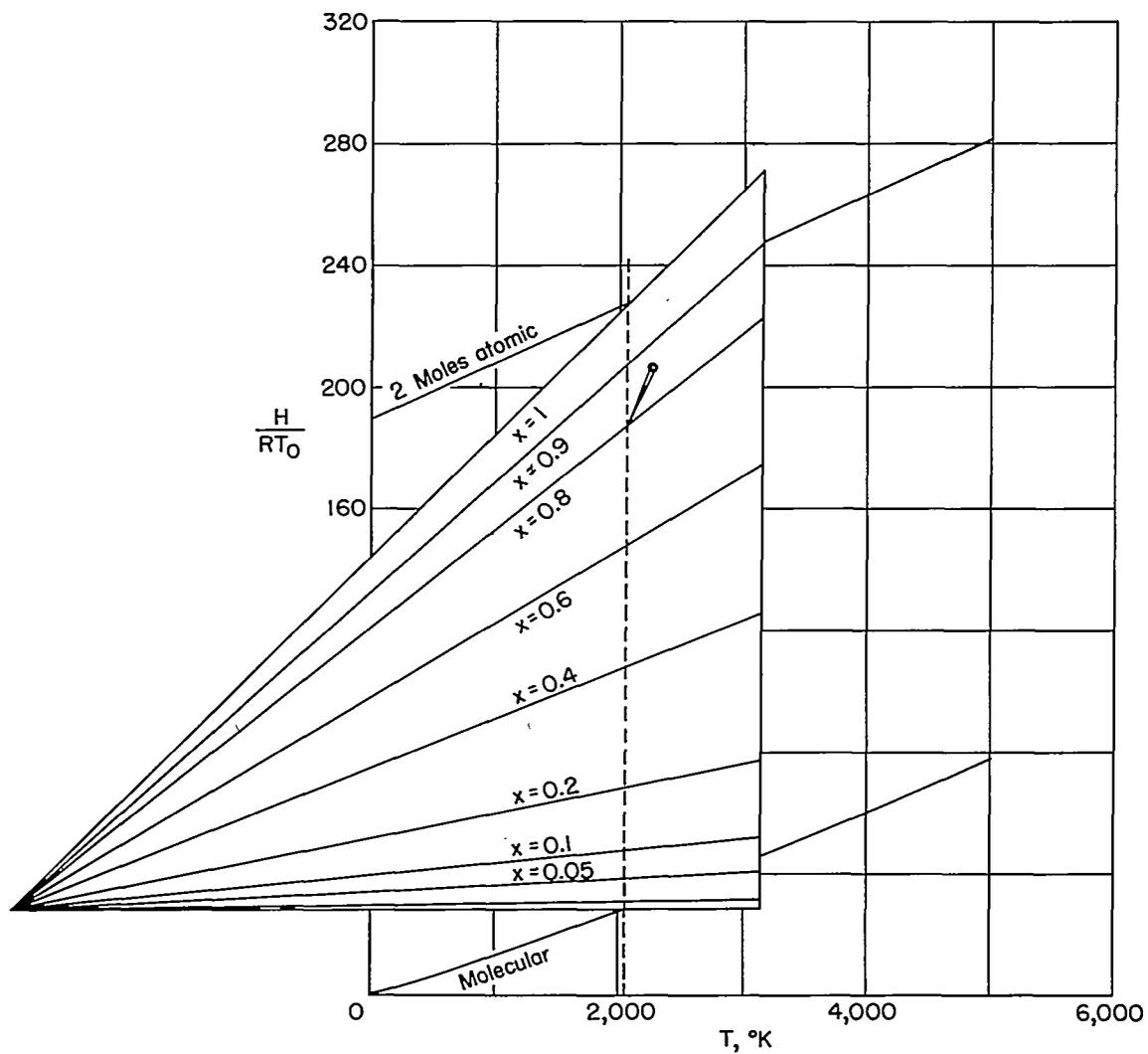


Figure 2.- Graphical method for determining enthalpy of a partially dissociated diatomic gas at temperature required to obtain a particular degree of dissociation at a chosen pressure.

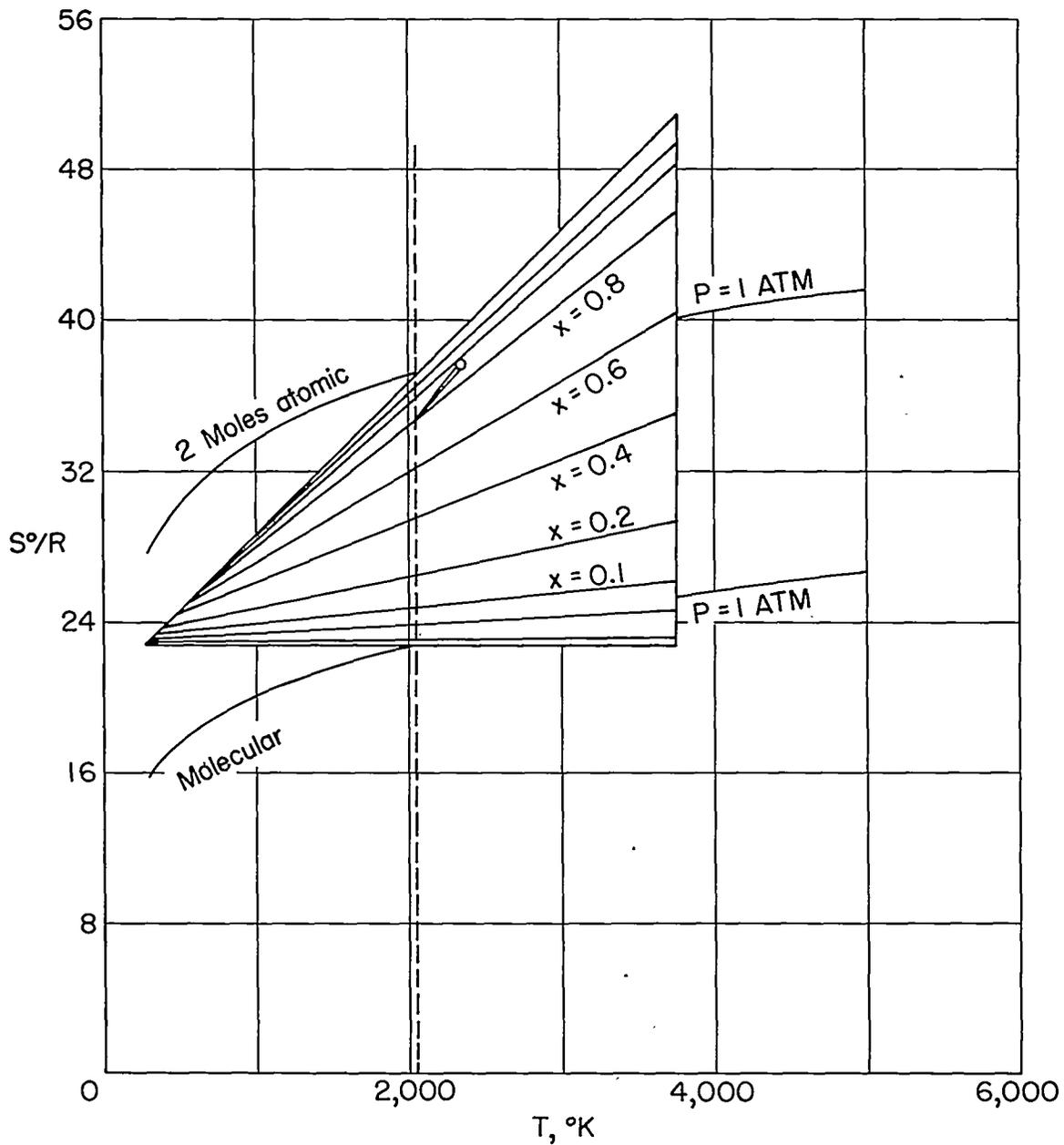


Figure 3.- Graphical method for determining entropy of a partially dissociated diatomic gas at temperature required to obtain a particular degree of dissociation at a chosen pressure. Entropy of mixing at atmospheric pressure is added automatically in the graphical interpolation process. See text for subsequent vertical shift of point to take account of $-(1+x)\log_e P$.

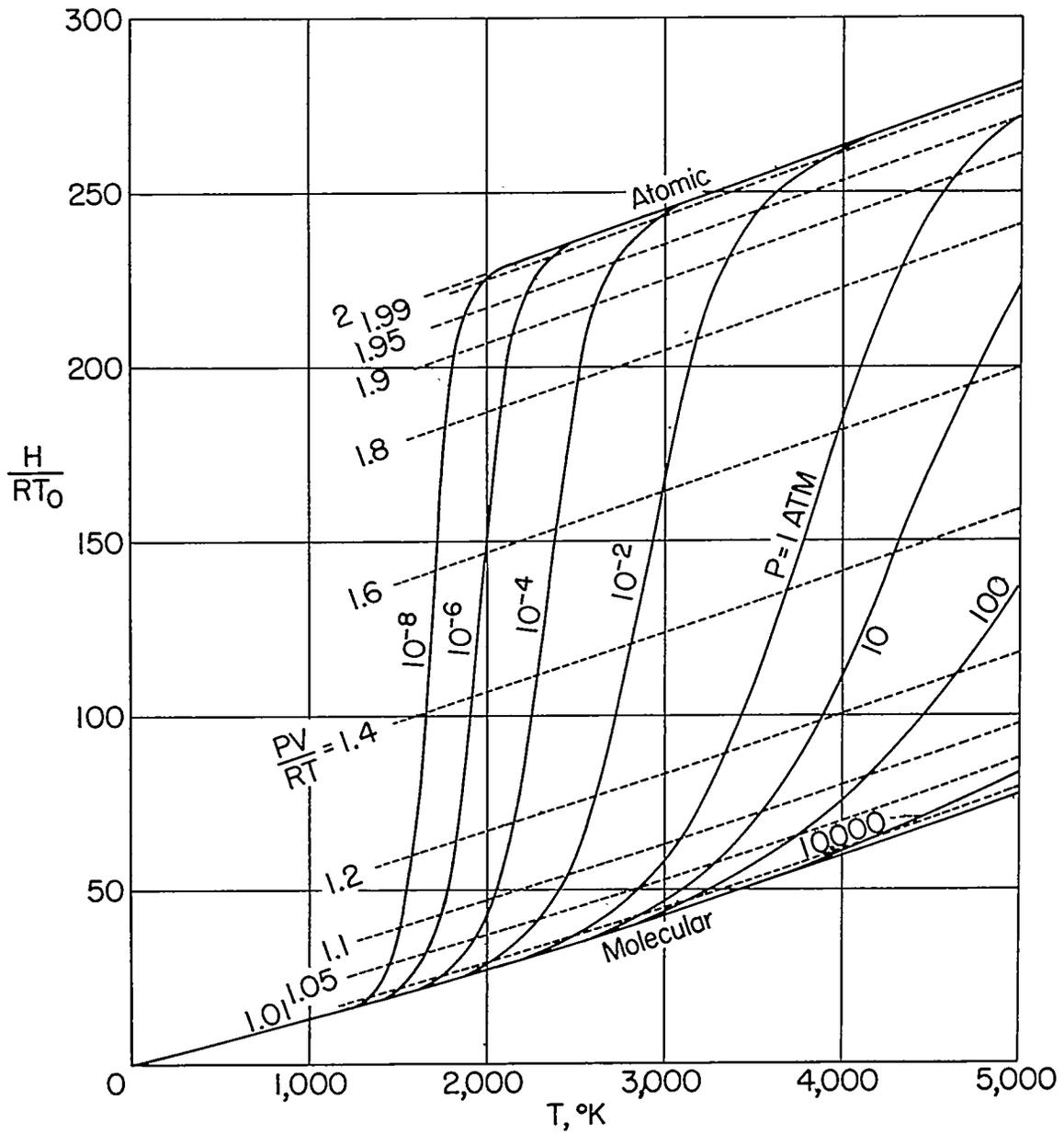


Figure 4.- Effect of dissociation on enthalpy of hydrogen.

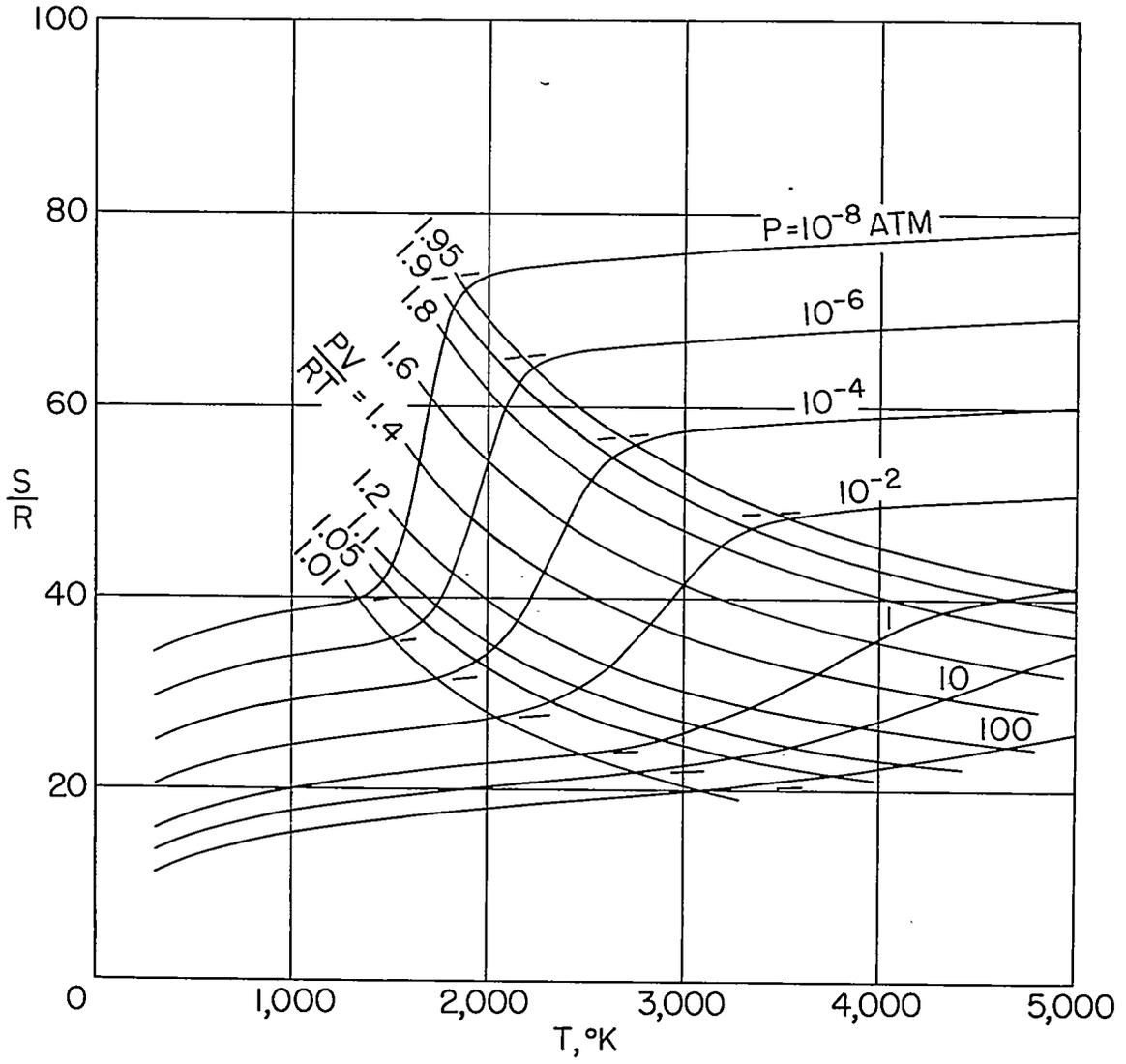


Figure 5.- Effect of dissociation on entropy of hydrogen.

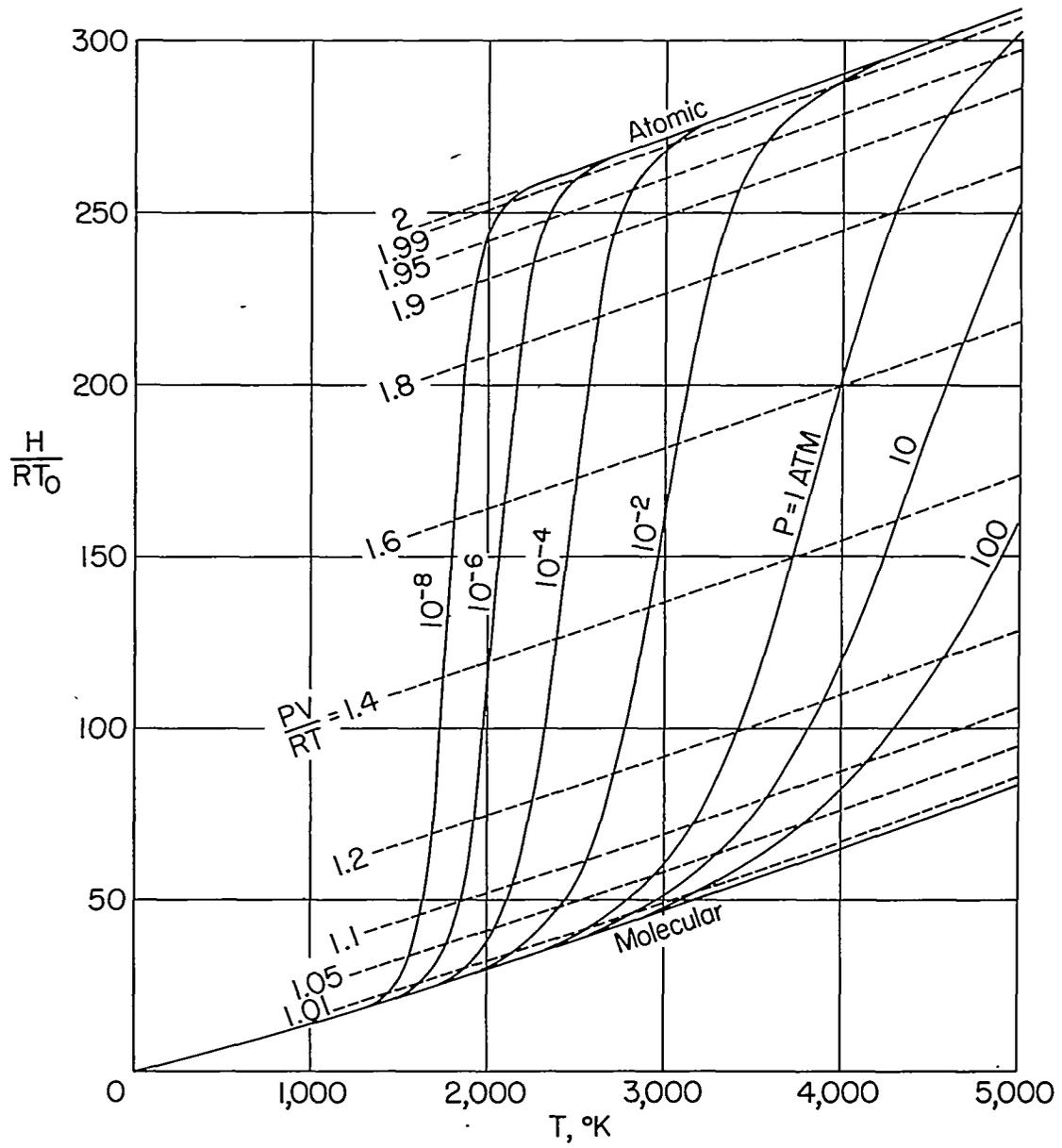


Figure 6.- Effect of dissociation on enthalpy of oxygen.

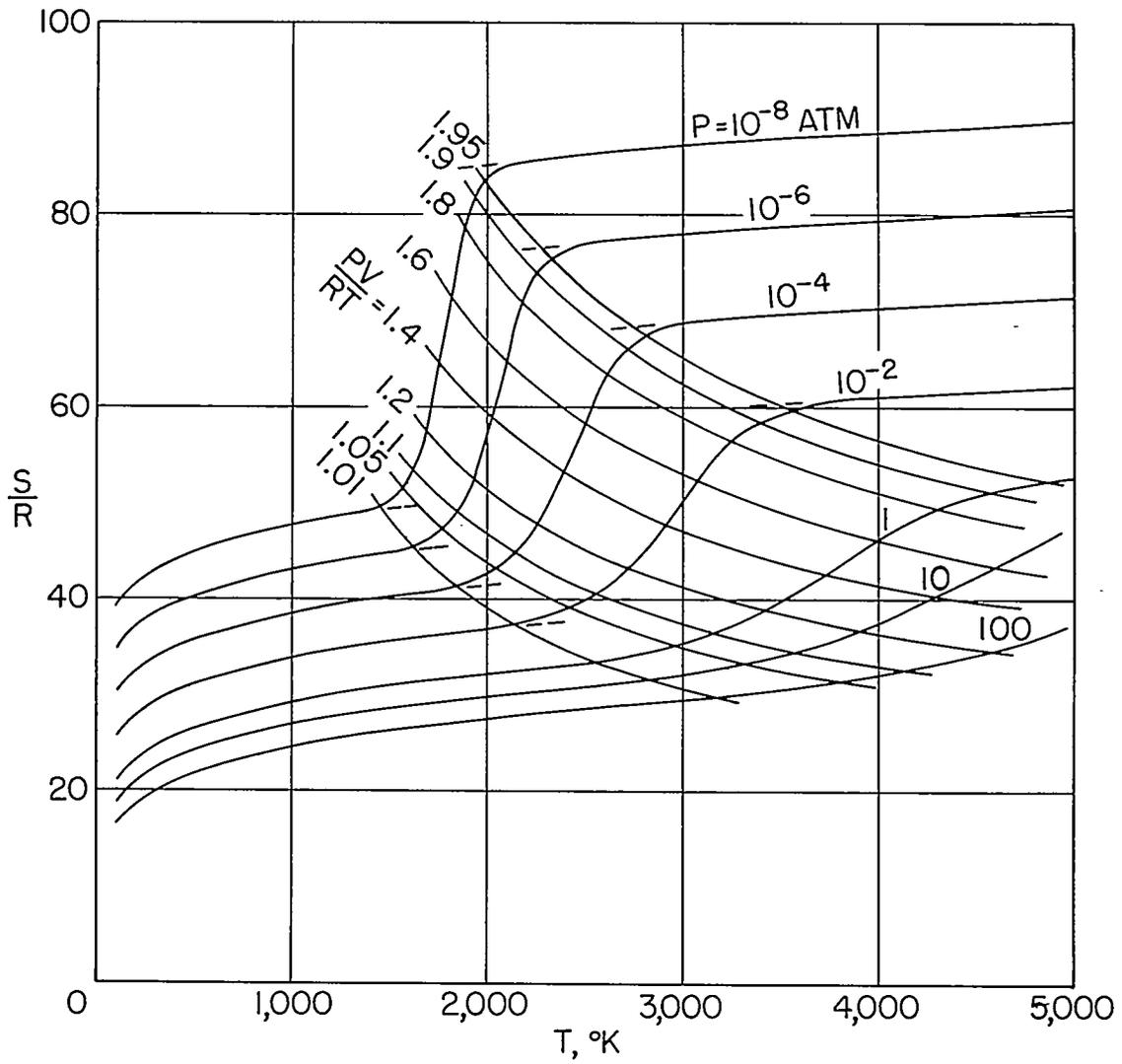


Figure 7.- Effect of dissociation on entropy of oxygen.

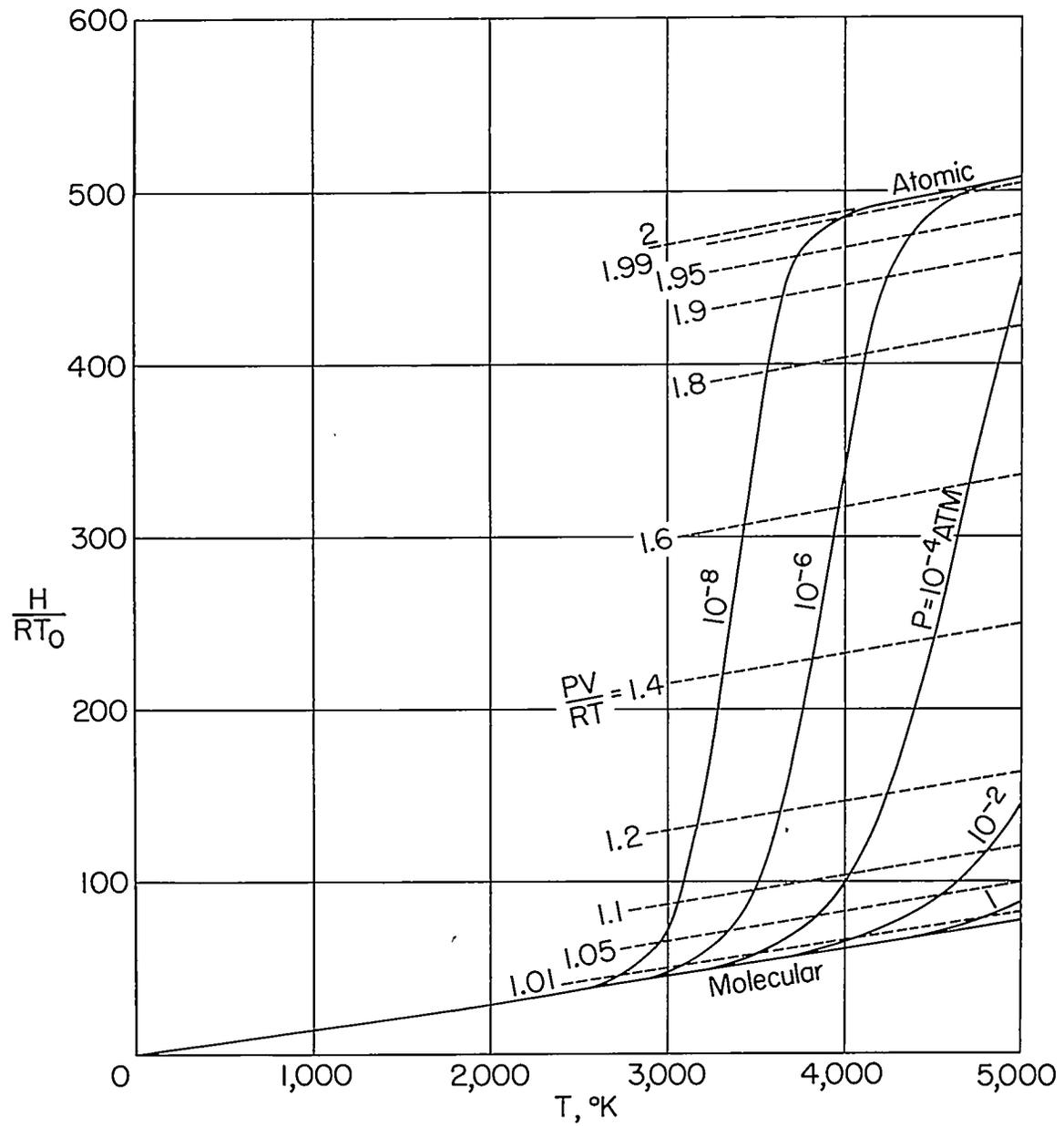


Figure 8.- Effect of dissociation on enthalpy of nitrogen.

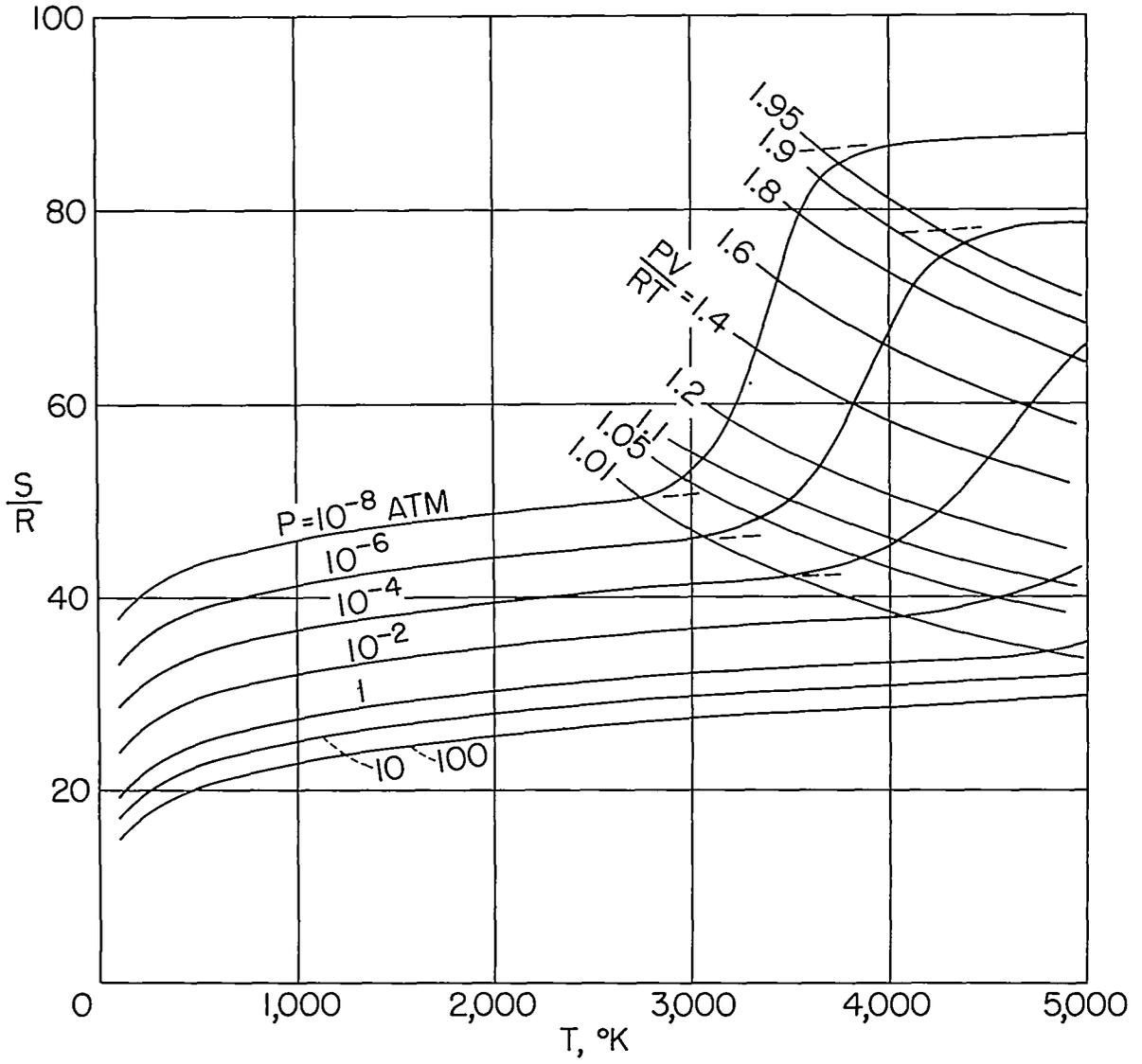


Figure 9.- Effect of dissociation on entropy of nitrogen.