

Data of Geochemistry

Sixth Edition

Chapter KK. Compilation of Stable Isotope Fractionation
Factors of Geochemical Interest

GEOLOGICAL SURVEY PROFESSIONAL PAPER 440-KK



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MICHAEL FLEISCHER, *Technical Editor*

Chapter KK. Compilation of Stable Isotope Fractionation Factors of Geochemical Interest

By IRVING FRIEDMAN and JAMES R. O'NEIL

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Isotope separation factors for the stable isotopes of hydrogen, carbon, oxygen, and sulfur are plotted as a function of temperature, in degrees Celsius



UNITED STATES DEPARTMENT OF THE INTERIOR

THOMAS S. KLEPPE, *Secretary*

GEOLOGICAL SURVEY

V. E. McKelvey, *Director*

Library of Congress Cataloging in Publication Data

Friedman, Irving, 1920-

Chapter KK. Compilation of stable isotope fractionation factors of geochemical interest.

(Data of geochemistry, Sixth Edition, Michael Fleisher, Technical Editor)

(Geological Survey Professional Paper 440-KK)

Bibliography: p.

1. Geochemistry.

I. O'Neil, James R., 1934- , joint author. II. Data of geochemistry, Sixth Edition. III. Title. IV. Series. V. United States Geological Survey Professional Paper 440-KK.

QE75.P9 No. 440-KK [QE515] 557.3'08s [551.9] 72-604861

For sale by the Superintendent of Documents, U.S. Government Printing Office

Washington, D.C. 20402

Stock Number 024-001-02942-1

DATA OF GEOCHEMISTRY, SIXTH EDITION

Michael Fleischer, *Technical Editor*

The first edition of the Data of Geochemistry, by F. W. Clarke, was published in 1908 as U.S. Geological Survey Bulletin 330. Later editions, also by Clarke, were published in 1911, 1916, 1920, and 1924 as Bulletins 491, 616, 695, and 770. This, the sixth edition, has been written by several scientists in the Geological Survey and in other institutions in the United States and abroad, each preparing a chapter on his special field. The current edition is being published in individual chapters, titles of which are listed below. Chapters already published are indicated by boldface.

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- A. The chemical elements
 - B. Cosmochemistry
 - C. Internal structure and composition of the earth
 - D. **Composition of the earth's crust**, by R. L. Parker
 - E. Chemistry of the atmosphere
 - F. **Chemical composition of subsurface waters**, by Donald E. White, John D. Hem, and G. A. Waring
 - G. **Chemical composition of rivers and lakes**, by Daniel A. Livingstone
 - H. Chemistry of the oceans
 - I. Geochemistry of the biosphere
 - J. Chemistry of rock-forming minerals
 - K. **Volcanic emanations**, by Donald E. White and G. A. Waring
 - L. **Phase equilibrium relations of the common rock-forming oxides except water**, by G. W. Morey
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 - N. **Chemistry of igneous rocks, Part I, The chemistry of the peralkaline oversaturated obsidians**, by Ray Macdonald and D. K. Bailey
 - O. Chemistry of rock weathering and soils
 - P. Chemistry of bauxites and laterites
 - Q. Chemistry of nickel silicate deposits
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 - S. **Chemical composition of sandstones—excluding carbonate and volcanic sands**, by F. J. Pettijohn
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 - U. Chemical composition of shales and related rocks
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 - AA. Chemistry of coal
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 - DD. Abundance and distribution of the chemical elements and their isotopes
 - EE. Geochemistry of ore deposits
 - FF. Physical chemistry of sulfide systems
 - GG. The natural radioactive elements
 - HH. Geochronology
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**COMPILATION OF STABLE ISOTOPE FRACTIONATION FACTORS OF
GEOCHEMICAL INTEREST**

By IRVING FRIEDMAN and JAMES R. O'NEIL

ABSTRACT

Selected fractionation factors for D, O¹⁸, C¹³, and S³⁴ have been compiled from the literature and plotted on a convenient linear temperature coordinate system. Elementary discussions of terminology and the problems of isotope standards are presented, together with equations relating the various standards used for reporting O¹⁸ values. Where data are available at only a few temperatures, the fractionations are given in tabular form. For each fractionation factor, a reference to the original work is given.

INTRODUCTION

Beginning with the classic paper of Urey (1947), in which he calculated stable isotope fractionation factors between species of geochemical interest, there has been an increasing use of stable isotope variations in natural materials for studies in the Earth and cosmic sciences. Equilibrium fractionation factors that measure the distribution of a rare stable isotope between two species have been determined directly by laboratory experiments and also by calculations using the methods of statistical thermodynamics. They have also been inferred from regularities in the stable isotope ratios of natural materials. These fractionation factors have been used in geochemistry, meteorology, oceanography, water and aqueous-solution chemistry, cosmochemistry, paleontology, and in other scientific fields for a variety of purposes.

We believe that a compilation of selected fractionation factors for D, O¹⁸, C¹³, and S³⁴, plotted on a convenient coordinate system, will be very useful to workers in the field and will also focus attention on the state of the art of this aspect of stable isotope geochemistry. In addition, for the benefit of students and new workers in the field, elementary discussions of conventional terminology and the problem of isotope standards are presented.

We thank H. G. Thode, Y. Bottinga, and R. H. Becker for their helpful comments.

TERMINOLOGY

1. THE δ VALUE

For most geochemical purposes, knowledge of only the *difference* in absolute isotope ratios between two substances is sufficient. In addition, differences can be mea-

sured far more precisely than can absolute ratios. Consequently, this difference, or δ value, is used almost exclusively in the Earth sciences for reporting stable isotope abundances and variations. If the absolute ratios of the standards employed are known, then the absolute ratio of any sample is readily calculated from its δ value.

The δ value is defined as follows:

$$\delta_x = \left(\frac{R_x - R_{STD}}{R_{STD}} \right) 10^3,$$

where $R_x = (D/H)_x, (C^{13}/C^{12})_x, (O^{18}/O^{16})_x, (S^{34}/S^{32})_x$, and so forth, and R_{STD} is the corresponding ratio in a standard. Note that R is always written as the ratio of the heavy (rare) isotope to the light (common) isotope. The δ value, then, is the difference in isotope ratio between a sample and a standard, expressed in parts per thousand, or per mil ($^{\circ}/_{\infty}$). A sample with a δO^{18} value of +10.0 is enriched in O¹⁸ (or is greater in O¹⁸/O¹⁶ ratio) by 10 per mil, or 1 percent, relative to the standard. Negative δ values indicate that the sample is depleted by that amount relative to the standard. The δ value is the quantity actually measured on isotope ratio mass spectrometers.

Over the years, stable isotope geochemists have tacitly developed a certain uniformity in the presentation of their data. However, there are still a few noteworthy differences. Some workers write $\delta(O^{18}/O^{16})$, $\delta(D/H)$, and so forth, whereas others write δO^{18} and δD , and so forth, the latter being more common. In the earlier literature δD values were given in percent, but, because so many laboratories now report both δD and δO^{18} values for the same substances (particularly water), it has become standard practice to report both values in per mil to avoid confusion. The δC^{13} values reported from most laboratories in the Soviet Union are given in percent.

2. THE FRACTIONATION FACTOR, α

The isotope fractionation factor between two substances, A and B , is defined as:

$$\alpha_{A-B} = \frac{R_A}{R_B},$$

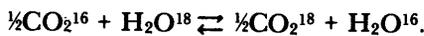
In terms of the quantities actually measured in the laboratory (δ values), this expression becomes:

$$\alpha_{A-B} = \frac{1 + \frac{\delta_A}{1,000}}{1 + \frac{\delta_B}{1,000}} = \frac{1,000 + \delta_A}{1,000 + \delta_B}$$

If the isotopes are randomly distributed over all possible sites or positions in the species *A* and *B*, the fractionation factor (α) is related to the equilibrium constant, *K*, for isotope exchange reactions in the following way:

$$\alpha = K^{1/n}$$

where *n* is the number of atoms exchanged.¹ For simplicity, isotope exchange reactions are usually written such that only one atom is exchanged. For example, the oxygen isotope exchange reaction between CO₂ and water vapor can be written:



The equilibrium constant for this reaction is

$$K = \frac{(\text{CO}_2^{18})^{1/2} (\text{H}_2\text{O}^{16})}{(\text{CO}_2^{16})^{1/2} (\text{H}_2\text{O}^{18})}$$

This formalism is normally used in the calculation of fractionation factors from spectroscopic and thermodynamic data. CO₂¹⁸ means that both oxygen atoms in the molecule are O¹⁸. The equilibrium constants for these reactions as written are equal to the fractionation factor:

$$K = \alpha = \frac{(\text{O}^{18}/\text{O}^{16})_{\text{CO}_2}}{(\text{O}^{18}/\text{O}^{16})_{\text{H}_2\text{O}}}$$

Values of α are normally very close to unity, typically 1.00X. Commonly, isotopic fractionations are discussed in terms of the value of *X*, in per mil ("per mil fractionations"). For example, the sulfur isotope fractionation factor between ZnS and PbS at 200°C is 1.0036. It is accepted parlance to state that at 200°C (1) the sphalerite-galena "fractionation" is 3.6 (or 3.6 per mil), or (2) sphalerite is enriched in S³⁴ by 3.6 per mil relative to galena.

3. 10³ln α AND THE Δ VALUE

It is a useful mathematical fact that 10³ln(1.00X) \cong X. For the S³⁴ example mentioned above where $\alpha = 1.0036$, 10³ln $\alpha = 3.6$. That is, 10³ln α is the "per mil fractionation." This logarithm function has added theoretical and experimental significance. For perfect gases, ln α varies as 1/T² and 1/T in the high- and low-temperature limits, respectively (Bigeleisen and Mayer, 1947). In addition, smooth and often linear curves have been found to obtain when 10³ln α is plotted against 1/T² for experi-

mentally determined fractionation factors between mineral pairs or mineral-water pairs.

The per mil fractionation, 10³ln α , is then of prime importance in stable isotope geochemistry. This quantity is very well approximated by the Δ value:

$$\Delta_{A-B} = \delta_A - \delta_B \cong 10^3 \ln \alpha_{A-B}$$

That is, merely subtracting δ values will be an excellent approximation to the per mil fractionation and identical to it within the limits of analytical error for values of both Δ 's and δ 's, which are less than about 10. In table 1 a comparison between Δ and 10³ln α is presented to illustrate the magnitudes of the approximations. The use of Δ was common in the earlier literature. The definition $\Delta = 10^3 \ln \alpha$ has appeared in some recent papers. This difference in the use of the symbol Δ is normally of minor consequence, and there can be no confusion if the authors clearly state how Δ is calculated. However, as the figures in table 1 indicate, it is important to calculate the exact 10³ln α when the per mil fractionations or the δ values are greater than 10.

A few authors have used another fractionation factor, ϵ , defined as $\epsilon = (\alpha - 1)10^3$. Again, for small values of ϵ , $\epsilon \cong 10^3 \ln \alpha$ as mentioned previously.

TABLE 1.—Comparison between values of Δ , α , and 10³ln α

δ_A	δ_B	Δ_{A-B}	10 ³ ln α_{A-B}	α
1.00	0	1.00	1.00	1.00000
5.00	0	5.00	4.99	1.00500
10.00	0	10.00	9.95	1.01000
12.00	0	12.00	11.93	1.01200
15.00	0	15.00	14.89	1.01500
20.00	0	20.00	19.80	1.02000
10.00	5.00	5.00	4.96	1.00496
20.00	15.00	5.00	4.91	1.00493
30.00	25.00	5.00	4.87	1.00488
30.00	20.00	10.00	9.76	1.00980
30.00	15.00	15.00	14.67	1.01478
30.00	10.00	20.00	19.61	1.01980

STANDARDS

Certain irregularities concerning standards, particularly oxygen isotope standards, have developed over the years and have been responsible for considerable confusion on the part of workers in the field. Some laboratories are "tied" to each other by acceptance of the δ values of certain interlaboratory comparison samples. Other laboratories use independent means of arriving at δ values. In some cases interlaboratory agreement is good, while in others it is poor, even though the laboratories may be "tied" to one another. The reasons for these discrepancies are often obscure and usually ignored. With the recent rapid growth in the number of laboratories engaged in stable isotope research, informal arrangements for interlaboratory standardization are impractical. In the future these problems may be resolved by the use of international reference standards being made available by the U.S. National Bureau of Standards (Gaithersburg, Md.)

¹Some authors have used the symbol α' to refer to a measured fractionation factor, even though it may not be an equilibrium fractionation.

and the International Atomic Energy Agency (Vienna, Austria).

OXYGEN

There are two internationally accepted reference standards used to report variations in oxygen isotope ratios: PDB (Peedee belemnite) and SMOW (Standard Mean Ocean Water). The PDB standard is normally used only in ocean paleotemperature studies wherein CaCO₃ from fossil shells is analyzed. The PDB standard is a sample of belemnite guard from the Peedee Formation in North Carolina and was the laboratory working standard used at the University of Chicago during the time that the oxygen isotope paleotemperature scale was developed. Inasmuch as there is confusion in the literature, note also that the PDB standard is the *solid carbonate*, not the acid-liberated CO₂. The original supply of this standard has long been exhausted; however, numerous secondary standards have been developed and exchanged among workers in the field. The oxygen isotopic composition of carbonates is determined by the analysis of CO₂ generated from the carbonates by reaction with 100 percent phosphoric acid (McCrea, 1950).

There are variations in the carbonate analytical procedures used in different laboratories which bear on the question of standards and interlaboratory comparisons. Apparent differences in δO¹⁸ of a carbonate sample can arise, depending, for example, on (1) temperature of the acid reaction, (2) procedure used to remove organic material (Emiliani, 1966), (3) carbonate to acid ratio (Fontes and others, 1965), and, (4) grain size of the carbonate (Fritz and Fontes, 1966). Inasmuch as only two-thirds of the oxygen is liberated from the carbonate during acid decomposition, these observed variations are not unexpected. In the oxygen isotope analysis of carbonates, identical physical and chemical conditions must be operative during preparation of standard and sample so that systematic errors will cancel.

The SMOW standard was originally a hypothetical water sample with isotope ratios of oxygen and hydrogen similar to those of an average sample of ocean water. It was defined by Craig (1961) in terms of a National Bureau of Standards reference water, NBS-1, as follows:

$$(O^{18}/O^{16})_{SMOW} = 1.008 (O^{18}/O^{16})_{NBS-1}$$

Subsequent to this definition, two additional SMOW standards have appeared, causing some confusion. In most of their papers, Taylor and Epstein of the California Institute of Technology have used a standard called SMOW against which a sample of Potsdam Sandstone (the Caltech internal standard) is +15.50‰. Finally, a large quantity of water called SMOW was prepared by R. Weiss and H. Craig for the International Atomic Energy Agency (Vienna) as one of four standard reference waters available to stable isotope geochemists. This latter

SMOW has been analyzed in many laboratories, and the oxygen isotope composition has been found by many investigators to be identical to the originally defined SMOW within the limits of analytical uncertainty (±0.05‰). There is some indication that random and significant variations in δO¹⁸ exist between different samplings of the main storage vessels of the NBS water standards.

SMOW is a water standard. In order to relate the oxygen isotope composition of nonaqueous substances to it, SMOW (or related waters) must be analyzed directly by fluorination or carbon reduction techniques. If water is analyzed by the CO₂-equilibration method, the fractionation factor between CO₂ and H₂O must be known at the temperature of equilibration. In most laboratories, water is normally analyzed by the CO₂-equilibration technique. For many years the value of 1.0407 measured by Compston and Epstein (1958) and O'Neil and Epstein (1966a) has generally been accepted and used to relate oxygen isotope compositions of nonaqueous materials to SMOW. However, several recent determinations of this factor indicate that the factor is probably larger than 1.0407 (table 2). Although it is possible to determine this factor with a precision of ±0.0001, it is impossible, owing to the present limitations of mass spectrometry, to determine a factor as large as this with an accuracy of more than ±0.0004 (approximately 1 percent of the difference in δ between the CO₂ and H₂O). Therefore, to avoid further confusion, we suggest that a new value of this factor, based on an average of 10 determinations, be accepted by everyone working in this field. We propose the value of 1.0412, which is the average of 10 of the 11 values known to us.

Recently, a reference standard of "African Glass Sand" (quartz) has been made available through the U.S. National Bureau of Standards as NBS-28. The δ value of

TABLE 2.—Experimental determinations of the CO₂-water fractionation factor at 25°C

Reference	α	10 ³ lnα
Compston and Epstein (1958)	1.0407	39.89
Staschewski (1964).....	1.0424	41.53
Majzoub (1966).....	1.0417	40.85
O'Neil and Epstein (1966a)	¹ 1.0412	40.37
Bottinga and Craig (1969).....	1.0409	40.09
Matsuhisa, Matsubaya, and Sakai (1971)	1.0412	40.37
Blattner (1973).....	1.0417	40.85
Horibe, Shigehara, and Takakuwa (1973)	1.0414	40.57
I. Friedman and J.D. Gleason (unpub. data, 1974).....	1.0414	40.57
O'Neil, Adami, and Epstein (1975).....	1.0412	40.37
R.N. Clayton (unpub. data, 1975).....	1.0406	39.80

¹Corrected from the published value of 1.0407 using revised mass spectrometer correction factors.

NOTE.—The average of all the published analyses, excepting the value of 1.0424 (Staschewski, 1964), is 1.0412. Bottinga (1968a) has calculated values of 1.0409. Bottinga and Craig (1969) have calculated a value of 1.0411.

+10.0 reported by Friedman and Gleason (1973) was based on their fluorination of two NBS-1 water samples. The δO^{18} value of NBS-28 reported to the authors from several laboratories indicate a range between 9.5 and 9.9.

The relationships between the oxygen isotope standards and the CO_2 gases normally prepared from them are shown in figure 1. For studies involving only carbonates or carbonates and water, some authors choose to use the PDB scale exclusively. In his paper establishing the SMOW scale, Craig (1961) stated that "The δO^{18} value of Chicago PDB-1 carbonate standard (CO_2 from reaction with 100 percent H_3PO_4 at $25^\circ C$) is +0.22 per mil on the SMOW scale." The correct statement should have been that the δO^{18} value of the CO_2 produced by reaction of 100 percent H_3PO_4 with PDB calcite at $25^\circ C$ is +0.22 per mil relative to CO_2 equilibrated at $25^\circ C$ with SMOW water. In order to relate the two standards, the fractionation factor for the CO_2-H_2O equilibration and for the acid reaction that produces the CO_2 must be known. The uncertainty in these fractionation factors will result in an

uncertainty in the relation between PDB and SMOW. The relationship between these two standards has been further confused by the fact that some authors have used the CO_2 liberated from the calcite as the PDB standard rather than the solid calcite. To relate δO^{18} values of calcite on the PDB and SMOW scales, the following expressions are used:

$$\delta_{SMOW} = 1.03086 \delta_{PDB} + 30.86, \text{ and}$$

$$\delta_{PDB} = 0.97006 \delta_{SMOW} - 29.94.$$

These relationships are based on the following fractionation factors at $25^\circ C$:

1.0412 for CO_2-H_2O ,

1.01025 for H_3PO_4 -liberated CO_2 from calcite and,

1.00022 for H_3PO_4 -liberated CO_2 from PDB- CO_2 in equilibrium with SMOW.

HYDROGEN

The SMOW standard is also used for reporting hydrogen isotope compositions and was defined by Craig (1961), again in terms of NBS-1:

$$(D/H)_{SMOW} = 1.050 (D/H)_{NBS-1}.$$

Therefore, by definition δD of NBS-1 is -47.6 on the SMOW scale. When the results of deuterium analyses of the four I.A.E.A. standard waters were compared several years ago, significant discrepancies in δD were apparent. The differences were attributed to the use of incorrect mass spectrometer correction factors by some investigators. The H_3^+ contribution to the mass 3 beam cannot be determined precisely. Consequently, when this contribution is large (> 10 percent), the correction may result in incorrect δ values. Some laboratories have circumvented this problem, calibrating their machines by accepting Craig's δD values of -47.6 and -183.3 for NBS-1 and NBS-1A, respectively. Recent measurements by Coplen and Clayton (1973) on a high-resolution mass spectrometer (H_3^+ contribution only 0.3 percent) have verified Craig's results. Coplen and Clayton's δD for NBS-1A is -183.0 ± 0.5 .

The I.A.E.A. sample of water called SMOW has been analyzed in several laboratories and is not identical in D/H ratio to the defined SMOW. Coplen and Clayton (1973), for example, report a δD value of -1.2. Friedman has recently measured the hydrogen isotope compositions of 4 separate samples of NBS-1 that he received over the past 20 years and found differences in δD as high as 8‰. Therefore some of the interlaboratory differences observed may depend on the batch of NBS-1 standard utilized. An Antarctic water sample is now being distributed by the I.A.E.A. This light water has been called SNOW and SLAP (Standard Light Antarctic Precipitation). Because the acronyms SNOW and SMOW resemble each other too closely, SLAP is to be preferred as a designation for this sample.

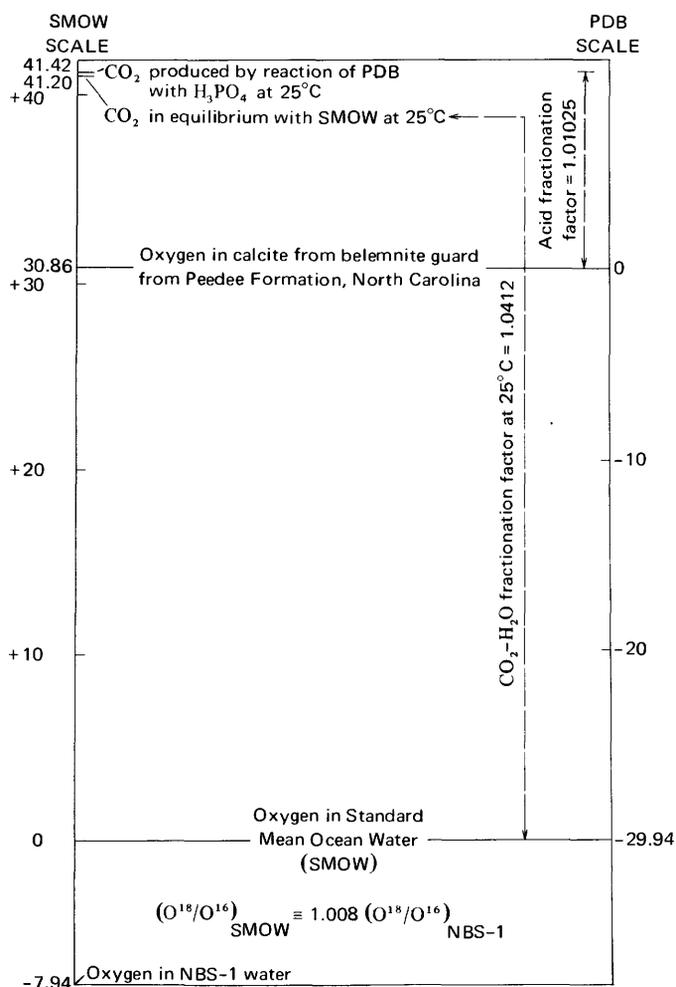


FIGURE 1.—Relationship between PDB, SMOW, and other oxygen standards.

TABLE 3.—Absolute deuterium-hydrogen isotope ratios, and δ values for reference samples
[Leaders (...) indicate no data]

Sample	Horibe and Kobayakawa (1960)	Craig (1961)	Hagemann, Nief, and Roth (1970)	Brown, Robertson and Thurston (1971)	Coplen and Clayton (1973)
(D/H) _{SMOW}	157±1×10 ⁻⁶	158±2×10 ⁻⁶	155.76×10 ⁻⁶	157.6±0.3×10 ⁻⁶
(D/H) _{NBS-1}	149±1×10 ⁻⁶	150±2×10 ⁻⁶	148.34×10 ⁻⁶	150.1±0.3×10 ⁻⁶
(D/H) _{NBS-1A}	128±1×10 ⁻⁶	129±2×10 ⁻⁶
(D/H) _{SLAP}	89.02±0.05×10 ⁻⁶
$\delta D_{NBS-1A/SMOW}^1$	2-47.6
$\delta D_{NBS-1A/SMOW}^1$...	-182.2	-183.3	-183.0±0.5
$\delta D_{SLAP/SMOW}^1$	-428.50±1	³ -426.4±1
$\delta D_{NBS-1A/NBS}^1$	-141.3±2.3	⁴ -425.8±1
					-142.13

¹ $\delta D_{X/Y}$ is the δD value of X relative to Y.

²Defined values.

³Compared to SMOW from NBS-1.

⁴Compared to SMOW, Vienna.

In some of the early United States literature on the deuterium abundance in natural materials, a sample of Lake Michigan water was used as a standard. The Lake Michigan standard is -42.4 on the SMOW scale.

Table 3 lists absolute values of various standards used for δD as well as ratios of relative deuterium values between common standards.

CARBON

There are a few problems associated with carbon isotope standards. The universally accepted standard for reporting carbon isotope compositions is PDB, which is no longer available. Two reference standards distributed by the U.S. National Bureau of Standards are NBS-20 (Solenhofen Limestone) and NBS-21 (spectrographic graphite). The δ values given by Craig (1957) for these standards are -1.06 and -27.79, respectively. Recent determinations indicate that the latter value is closer to -28.10 (Mook, 1971; Létolle, 1971; F. C. Tan, unpub. data, 1973; J. D. Gleason and I. Friedman, unpub. data, 1973). The Solenhofen Limestone standard is actually too fine grained to be a good and lasting standard. Care must be taken to store it, well-stoppered, in a desiccator to prevent exchange between the sample and CO₂ in moist air. A new carbonate reference standard is being prepared by us for distribution by the U.S. National Bureau of Standards.

SULFUR

Troilite from the Canyon Diablo meteorite is the internationally accepted standard used to report δS^{34} variations. An NBS-120 sulfur reference sample exists, but few workers have made use of it. Instead, sulfur isotope geochemists have made interlaboratory exchanges of working standards. The mass spectrometric corrections for sulfur dioxide are large, and we suggest that two international reference standards differing in δS^{34} by a large amount be used as interlaboratory comparison samples. Sulfur hexafluoride, SF₆, for mass spectrometric analysis of sulfur has been used by Thode, Cragg, Hulston, and

Rees (1971) for S³⁶/S³², as well as for S³⁴/S³² ratio measurement. The preparation of SF₆ has been described by Puchelt and Kullerud (1970). Sulfur hexafluoride has some advantages over sulfur dioxide for sulfur isotopic analysis.

STABLE ISOTOPE FRACTIONATION CURVES

We have made this compendium in order to provide a single reference work in which stable isotope fractionation factors of geologic interest are presented in a readily usable format.

Some features of the curves are:

1. Fractionations ($10^3 \ln \alpha$) can normally be read to ±0.2 per mil.
2. Temperatures can be read to ±0.5°C on some curves and to ±5°C on others.
3. The temperature axes are linear in degrees Celsius.
4. The scale of the graph paper is metric for easy comparison and transposition.
5. Where appropriate, the curves have been drawn using values of $10^3 \ln \alpha$ recalculated using the CO₂-H₂O fractionation factor of 1.0412. (See p. KK3.) The corresponding corrected expressions in the figure captions are indicated with an asterisk.

Titles on the figures designate the systems presented thereon and are written such that the first-named phase concentrates the heavy isotope if the value of $1,000 \ln \alpha$ is positive. The curves have been extrapolated beyond the temperature ranges investigated and even beyond the range of stability of some minerals. This was done to provide rough estimates when no other information is available.

Not all pertinent equilibrium fractionation factors that have been measured or calculated are presented here. Those determinations which have been clearly superseded by later, more refined determinations (often by the same investigators) are not included in the compilation. Except for the carbonate-acid fractionation factors, non-

equilibrium isotope effects are not presented. However, some of the discrepancies among the experimental curves are undoubtedly the result of nonequilibrium or kinetic isotope effects, which can often be difficult to recognize.

The uncertainty in the CO₂-H₂O fractionation factor at 25°C has serious implications both in relating oxygen isotope standards and in comparing experimentally determined oxygen isotope fractionation factors. Except for the feldspars and micas (O'Neil and Taylor, 1967, 1969), rutile (Addy and Garlick, 1974), and magnetite (Bertenth and Friedrichsen, 1975) the factor 1.0407 was used in the determination of the isotopic compositions of the waters used in all the experiments. The waters in these studies were either analyzed directly or a value of 1.04120 was used in the original publication. In the compilation

published herein, *all the curves with the exception of those of Bottinga and Javoy (1973) have been recalculated to the newly proposed value of α (1.0412).*

The analytical expressions for the temperature dependence of the isotope fractionation factors are given in the figure captions, usually in the form given by the original authors but recast for consistency. Isolated fractionation factors that were determined at only a few temperatures are normally plotted on the figure most appropriate to the system in question. In these compilations an asterisk indicates that the values have been recalculated using the CO₂-H₂O fractionation proposed on page KK3. Those factors for which there is no appropriate figure are listed in table 4. In the figure captions T = temperature in kelvins; t = temperature in degrees Celsius.

TABLE 4.—Miscellaneous fractionations
[Leaders (...) indicate not measured or not calculated]

No.	Fractionation	t(°C)	10 ³ ln α		Reference	Remarks
			Measured	Calculated		
Oxygen						
1	H ₃ PO ₄ liberated CO ₂ -carbonates(s); CaCO ₃ (calcite)	25	10.20	Sharma and Clayton (1965; corrected by R. N. Clayton (oral commun., 1972).	
	CaCO ₃ (aragonite)	25	10.29do.	
	SrCO ₃	25	10.43do.	
	BaCO ₃	25	10.91do.	
	CaMg(CO ₃) ₂ (dolomite)	25	11.03do.	
	ZnCO ₃	25	11.24do.	
	CdCO ₃	25	11.39do.	
	MnCO ₃	25	10.07do.	
	PbCO ₃	25	10.08do.	
	MgCO ₃	50	11.53	Perry and Tan (1972).	
2	Hydromagnesite-H ₂ O(l).....	0	137.58	O'Neil and Barnes (1971).	
		25	131.69do.	
3	Magnesian calcite-H ₂ O(l).....	25	2.78(10 ⁶ T ⁻²)-2.89 +0.06 M MgCO ₃	Tarutani, Clayton, and Mayeda (1969).	Where M MgCO ₃ =mole percent MgCO ₃ in solid solution in carbonate mineral.
4	Illite-H ₂ O(l)	22	23.4	James and Baker (1976)	Gross average of six determinations.
5	H ₂ O(s)-H ₂ O(l).....	0	3.1	O'Neil (1968).	
6	H ₂ O(s)-2.5 M NaCl.....	-10	2.2	Stewart (1974).	
7	H ₂ O(s)-H ₂ O(g).....	0	11.8	Matsuo and Matsubaya (1969).	
		-5	12.2do.	
		-10	12.6do.	
		-15	13.0do.	
		-20	13.4do.	
8	H ₂ O ⁺¹ -H ₂ O(l).....	25	22.8	Thornton (1962).	
9	OH ⁻¹ -H ₂ O(l).....	25	37.8do.	
		15	39.2	Green and Taube (1963).	
10	CO ₂ (g)-D ₂ O(l)	25	23.2	Staschewski (1964).	
11	CO ₂ (g)-CO ₂ (l).....	-53	-1.03	-1.22	Grootes, Mook, and Vogel (1969).	O ¹⁸ is concentrated in the liquid phase
		-50	-0.98	-1.17do.....	Do.
		-43	-0.86	-1.05do.....	Do.
		-30	-0.69	-0.88do.....	Do.
		-25	-0.64	-0.83do.....	Do.
		-20	-0.58	-0.77do.....	Do.
		-10	-0.51	-0.68do.....	Do.

TABLE 4.—Miscellaneous fractionations—Continued

No.	Fractionation	t(°C)	10 ³ ln α		Reference	Remarks
			Measured	Calculated		
Oxygen—Continued						
11	CO ₂ (g)-CO ₂ (l)—Continued	0	-0.42	-0.58	Grootes, Mook, and Vogel (1969).	O ¹⁸ is concentrated in the liquid phase.
		10	-.32	-.45do.....	Do.
		20	-.21	-.32do.....	Do.
		30	-.06	-.09do.....	Do.
12	CO ₂ (g)-CO ₂ (aq)	0	-1.17	-.95	Vogel, Grootes, and Mook (1970)	O ¹⁸ is concentrated in the liquid phase.
		10	-1.13	-.93do.....	Do.
		20	-1.09	-.90do.....	Do.
		30	-1.05	-.87do.....	Do.
		40	-1.01do.....	Do.
		50	-.97do.....	Do.
		60	-.92do.....	Do.
13	O ₂ (g)-O ₂ (aq).....	1-23	0.85-0.01(t)	Kroopnick and Craig (1972)	This expression holds for O ₂ dissolved in either pure water or seawater. Where t is in °C.
14	Mirabilite (Na ₂ SO ₄ · 10H ₂ O)- H ₂ O(l)	0	2.0	Stewart (1974).....	The fractionation measured was between the hydrate water and the solution.
		25	1.4do.....	Do.
15	Gypsum-(hydrate water)-H ₂ O(l) ...	17-57	3.49	Gonfiantini and Fontes (1963).	
16	Grossularite-H ₂ O(l).....	600	-1.60	Taylor (1976).	
17	Andradite-H ₂ O(l).....	600	-3.28do.....	
18	Biotite (annite)-H ₂ O(v).....	400	-2.1	Bertenrath and Friedrichsen (1975).	The fractionation is independent of the iron ratio in the mica. The authors have reservations regarding the experimental value of 400°.
		600	-2.1do.....	
		800	-1.7do.....	
Carbon						
19	CO ₂ (g)-CO ₂ (l).....	-53	0.44	Grootes, Mook, and Vogel (1969).	C ¹³ is concentrated in the gaseous phase (measured).
		-50	.48do.....	Do.
		-43	.57do.....	Do.
		-30	.47do.....	Do.
		-25	.42do.....	Do.
		-20	.41do.....	Do.
		-10	.35do.....	Do.
		0	.34do.....	Do.
		10	.34do.....	Do.
		20	.24do.....	Do.
		30	.14do.....	Do.
20	Calcite-HCO ₃ ⁻¹	20	0.035+0.013	Emrich, Ehhalt, and Vogel (1970).	
		25	0.9+0.2	Rubinson and Clayton (1969).	
21	Aragonite-HCO ₃ ⁻¹	25	2.7+0.2do.....	
22	Argonite-calcite	25	1.8+0.2do.....	
		25	0.9do.....	
23	Gaylussite (Na ₂ CO ₃ · CaCO ₃ · 5H ₂ O)-CO ₃ ⁻²	8	3.09	Matsuo, Friedman, and Smith (1972).	
		18	2.50do.....	
		25	2.00do.....	
		30.5	1.90do.....	
		35	2.00do.....	
24	Trona (Na ₂ CO ₃ · NaHCO ₃ · 2H ₂ O)-CO ₃ ⁻²	18	1.1do.....	
		25	.8do.....	
		30.5	.7do.....	

TABLE 4.—Miscellaneous fractionations—Continued

No.	Fractionation	t(°C)	10 ³ ln α		Reference	Remarks
			Measured	Calculated		
Hydrogen						
25	H ₂ O(v)–H ₂ S(g)	25	791	Galley, Miller, Atherley, and Mohn (1972).	
		100	634do.	
		170	536do.	
		200	502do.	
26	H ₂ O(l)–H ₂ S(g)	25	861do.	
		100	660do.	
		170	534do.	
		200	492do.	
27	H ₂ O(s)–H ₂ O(l)	0	19.0	Weston (1955).	
		0	20.9	Posey and Smith (1957).	
		0	18.4	17.0	Kuhn and Thürkauf (1958).	
		0	23.2	Merlivat and Nief (1966).	
		0	19.3	O'Neil (1968).	
		0	20.6	Arnason (1969).	
28	H ₂ O(s)–2.5 M NaCl	–10	23.7	Stewart (1974).	
29	H ₃ O ⁺ –H ₂ O(l)	13.5	40.0	Heinzinger and Weston (1964a).	
30	OH [–] –H ₂ O(l)	13.5	–1,400	Heinzinger and Weston (1964b).	
31	Mirabilite (Na ₂ SO ₄ · 10H ₂ O–H ₂ O(l)	0	18.8	Stewart (1974).	
		25	16.9do.	
32	Borax (Na ₂ B ₄ O ₇ · 10H ₂ O–H ₂ O(l)	8–35	0	Matsuo, Friedman, and Smith (1972).	
33	Gaylussite (Na ₂ CO ₃ · CaCO ₃ · 5H ₂ O–H ₂ O(l)	18	–13.1do.	
		25	–13.1do.	
		30.5	–14.1do.	
		35	–15.1do.	
34	CuSO ₄ · 5H ₂ O–H ₂ O(l)	Heinzinger (1969)	The four waters coordinated to Cu ⁺² are 57 per mil depleted in deuterium relative to the hydrogen-bonded water molecule.
35	Crystal hydrate–H ₂ O(l): CuSO ₄	25	–21.8	Barrer and Denny (1964)	Deuterium is concentrated in the solution relative to the hydrate waters of all these salts.
	SrCl ₂	25	–23.7do.	Do.
	Al ₂ (SO ₄) ₃	25	–34.4do.	Do.
	KAl(SO ₄) ₂	25	–35.4do.	Do.
	CuCl ₂	25	–46.9do.	Do.
	BeSO ₄	25	–53.5do.	Do.
36	Gypsum–H ₂ O(l)	17–57	–15	Fontes and Gonfiantini (1967).	
37	Kaolinite–H ₂ O(l)	200	–34.5	O'Neil and Kharaka (1976)	Based on experiment with 29 percent exchange.
38	Illite–H ₂ O(l)	200	–39.8do.	Based on experiment with 28 percent exchange.
39	Montmorillonite–H ₂ O(l)	200	–43.9do.	Based on experiment with 82 percent exchange.
Sulfur						
40	PbS–S	300	2.3	Puchelt and Kullerud (1970).	
		500	.8do.	
41	H ₂ S(g)–H ₂ S (solution)	20	1.6	Sharan, Galas, Lees, and Zhook (1974).	

¹Value has been recalculated, using the CO₂–H₂O fractionation of 1.0412.

Because of some unresolved discrepancies in the oxygen isotope fractionations between minerals and water, it would be unwieldy and confusing to present all possible combinations of oxygen isotope fractionation between mineral pairs. The curves proposed by Bottinga and Javoy (1973, 1974) are presented, inasmuch as they are self-consistent and take into account much of the experimental work and theoretical considerations. Because of the involved manner in which these expressions were derived, we made no attempt to correct them for the new $\text{CO}_2\text{-H}_2\text{O}$ fractionation. The quartz-magnetite pair is potentially the most useful, and certainly the most sensitive, pair for oxygen isotope thermometry, and the curve proposed by Becker (1971) is presented along with that of Bottinga and Javoy in figure 20. It is encouraging that the two curves are so similar and that the slope for this important system is fairly certain.

The stable isotope fractionations presented have not been critically evaluated. It is clear from reading the details given in the original references that some systems have been examined more thoroughly than others. Presenting all these data together uncritically calls attention to the problem areas that require resolution. The calculated fractionation factors for gaseous systems are among the most reliable factors presented here. Of the minerals investigated, calcite has shown the most consistent oxygen isotope results among several investigations, including equilibrations with water and with carbon dioxide. The stable isotope relations are somewhat obscured by experimental difficulties and nonequilibrium effects, but even at our present state of knowledge, geologically reasonable temperatures are usually inferred. As geothermometers, stable isotope fractionation factors continue to show considerable promise for a variety of geologic environments. There is enough consistency in the natural data to warrant future investigations aimed at reconciling some of the discrepancies in the experimental data.

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FIGURES 2-49

FIGURE 2

A, Epstein, Buchsbaum, Lowenstam, and Urey (1953):

$$t(^{\circ}\text{C}) = 16.5 - 4.3(\delta_c - \delta_w) + 0.14(\delta_c - \delta_w)^2.$$

B, Craig (1965):

$$t(^{\circ}\text{C}) = 16.9 - 4.2(\delta_c - \delta_w) + 0.13(\delta_c - \delta_w)^2,$$

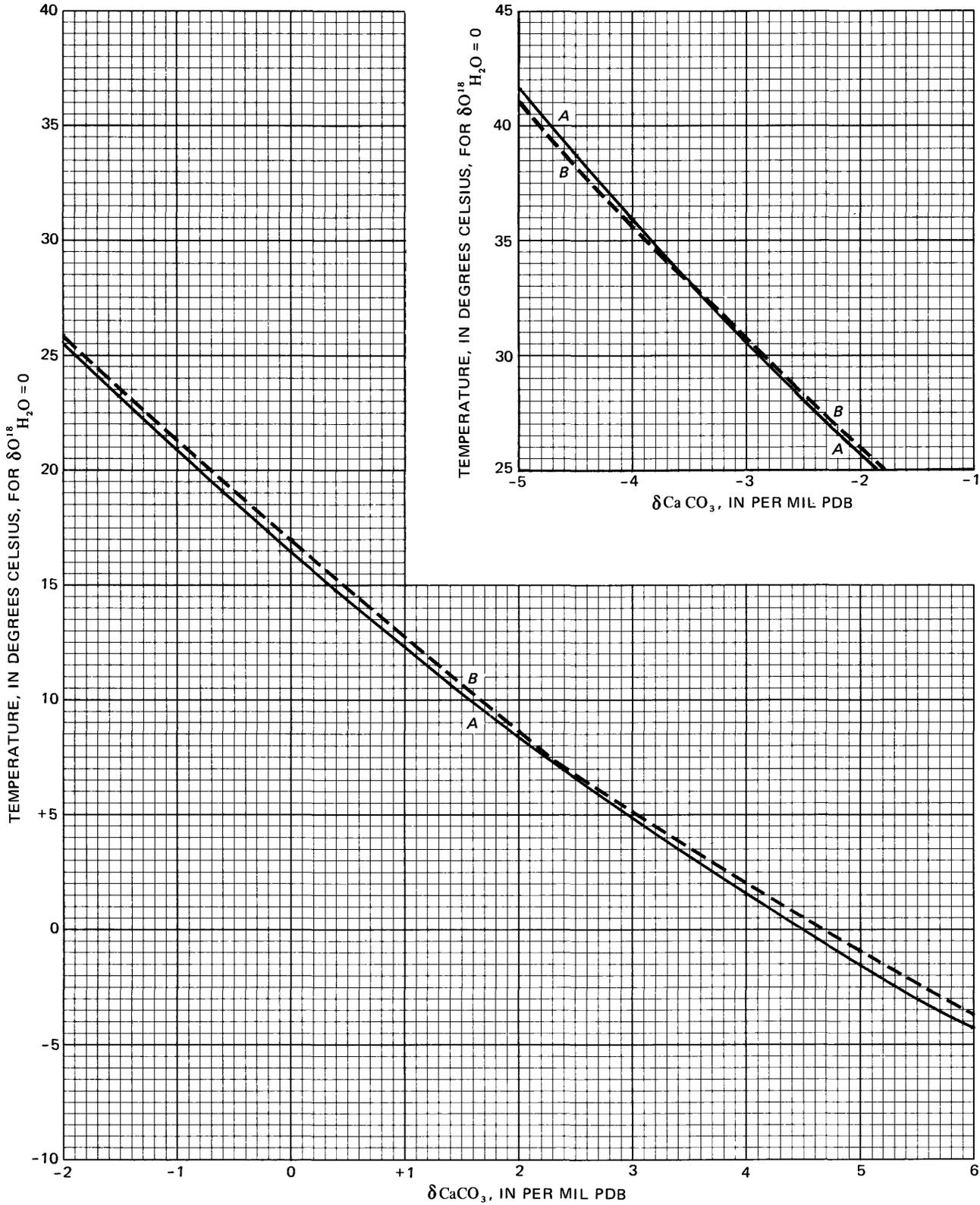
where

$\delta = \delta \text{O}^{18}$ of CO_2 from calcium carbonate by reaction with H_3PO_4 at 25°C , and

$\delta = \delta \text{O}^{18}$ of CO_2 in equilibrium with the water at 25°C .

The expressions are independent of the standard used.

NOTE.—S. Epstein (oral commun., 1975) states that the Craig paleotemperature scale is incorrect and that the latest scale (Epstein, 1976) corresponds to the 1953 scale within experimental error.



O
X
Y
G
E
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CARBONATE-WATER PALEOTEMPERATURE SCALE

FIGURE 3

Longinelli and Nutti (1973):

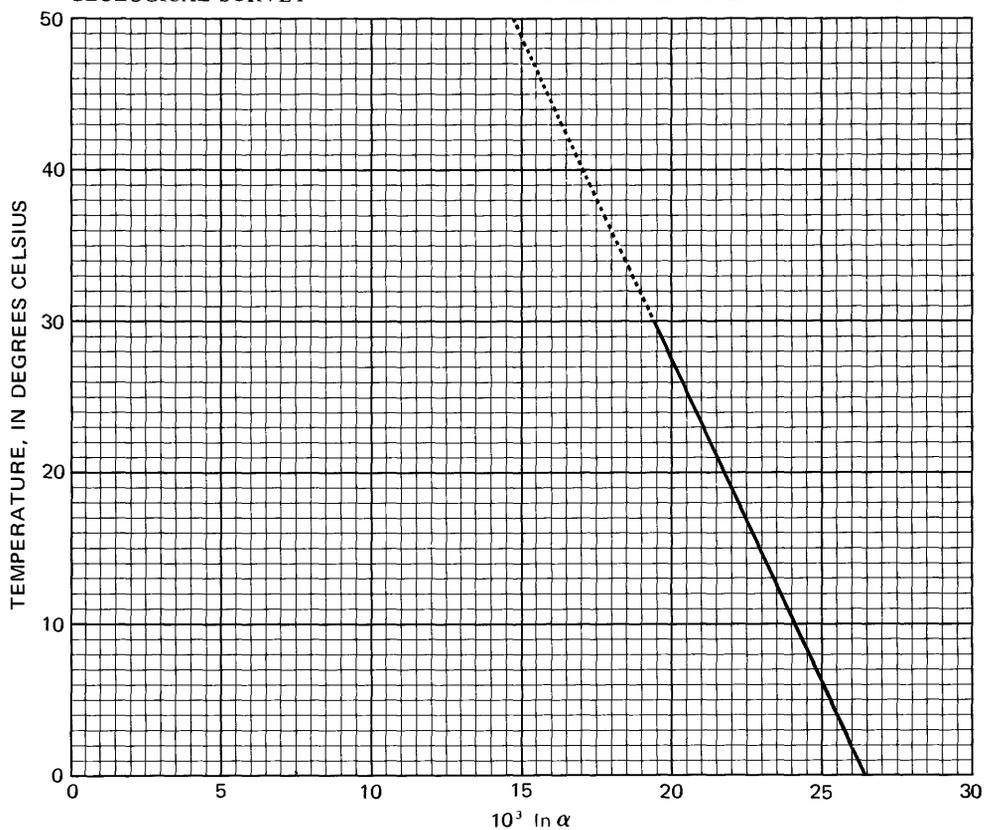
$$t(^{\circ}\text{C}) = 111.4 - 4.3(\delta_p - \delta_w + 0.5)^*$$

where

δ_p = δO^{18} of the phosphate on the SMOW scale, and

δ_w = δO^{18} of the water on the SMOW scale.

NOTE.— δ_w is incorrectly defined in the original paper.



PHOSPHATE-WATER PALEOTEMPERATURE SCALE

O
X
Y
G
E
N

FIGURE 4

A, Labeyrie (1974):

$$t (^{\circ}\text{C}) = 169 - 4.1(\delta_s - \delta_w + 0.5)^*$$

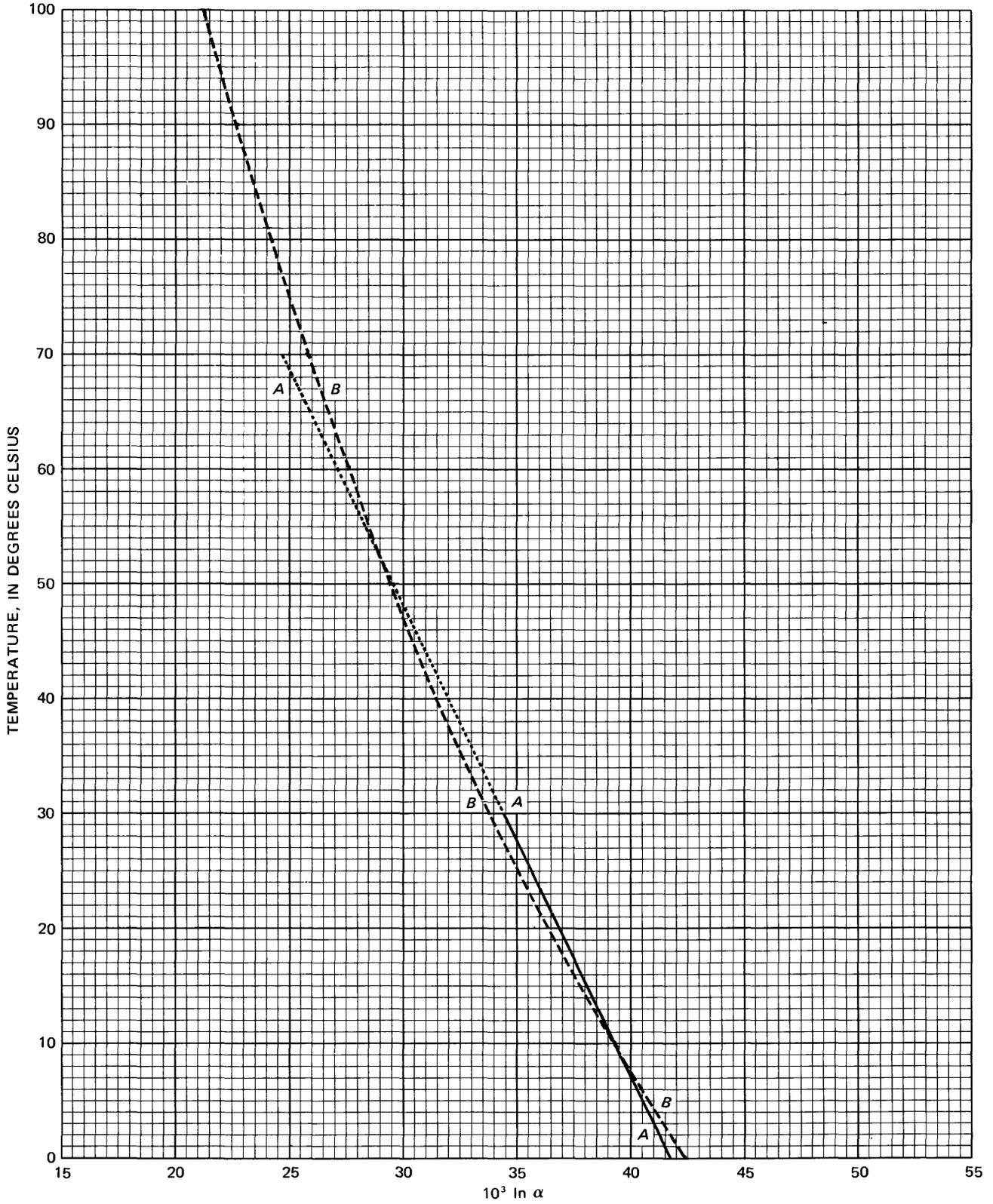
where

δ_s = δO^{18} of the silica on the SMOW scale, and

δ_w = δO^{18} of the water on the SMOW scale.

B, Clayton, O'Neil, and Mayeda (1972):

This is an extrapolation of their lower temperature data. (See fig. 16, this report.)



O
X
Y
G
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N

SILICA-WATER PALEOTEMPERATURE SCALE

FIGURE 5

A, Expression given in Bottinga (1968b) for his calculated factors were corrected in 1973 (Y. Bottinga, written commun., 1973).

$$10^3 \ln \alpha = -0.0206(10^6 T^{-2}) + 17.9942(10^3 T^{-1}) - 19.97.$$

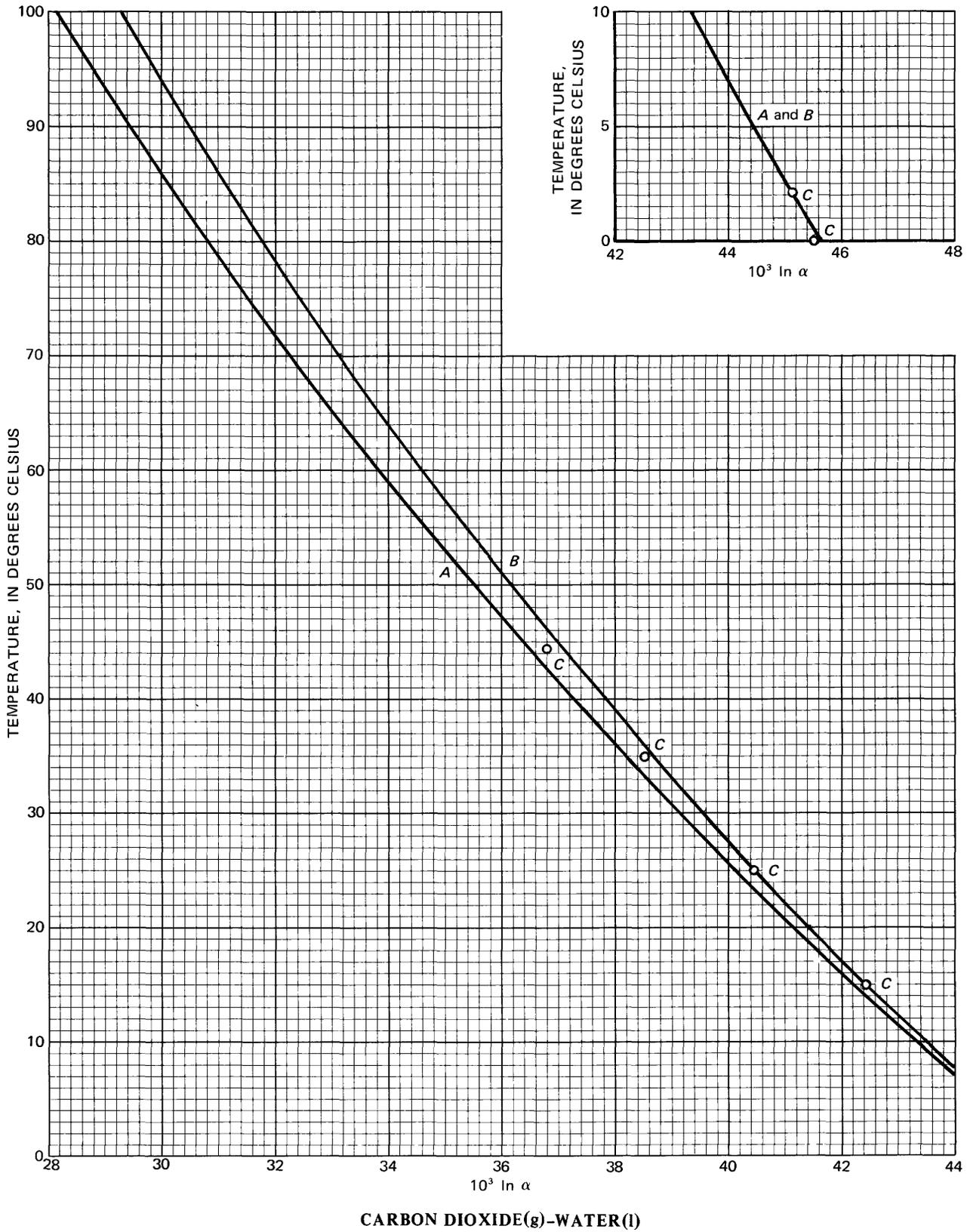
B, O'Neil and Adami (1969) experimental data:

$$10^3 \ln \alpha = 16.60(10^3 T^{-1}) - 15.19^*.$$

C, Individual data points from Bottinga and Craig (1969).

GEOLOGICAL SURVEY

PROFESSIONAL PAPER 440-KK FIGURE 5



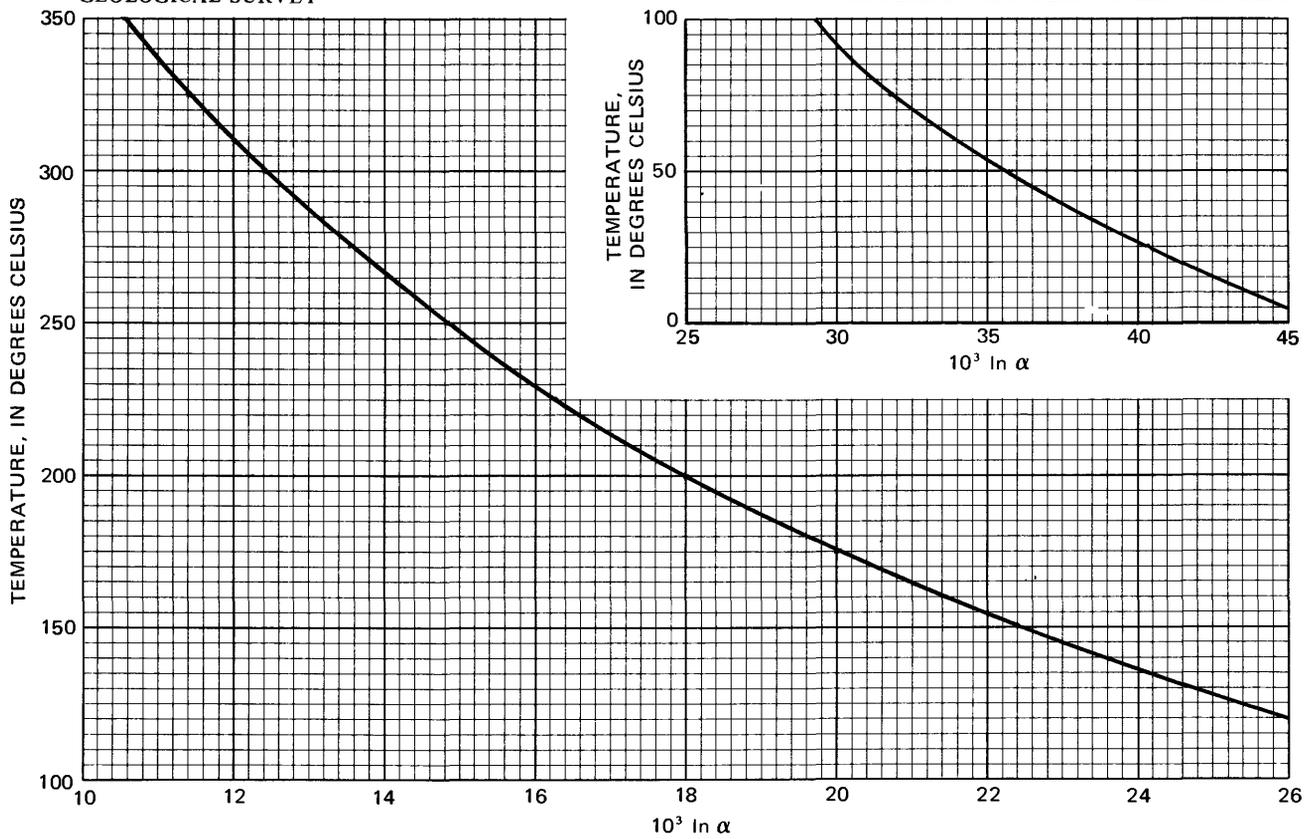
O
X
Y
G
E
N

FIGURE 6

Truesdell (1974) gives the temperature coefficient of the $\text{CO}_2\text{-H}_2\text{O}$ fractionation. The data have been plotted assuming that the fractionation at 25°C is 40.37.

GEOLOGICAL SURVEY

PROFESSIONAL PAPER 440-KK FIGURE 6



CARBON DIOXIDE(g)-WATER (l)

O
X
Y
G
E
N

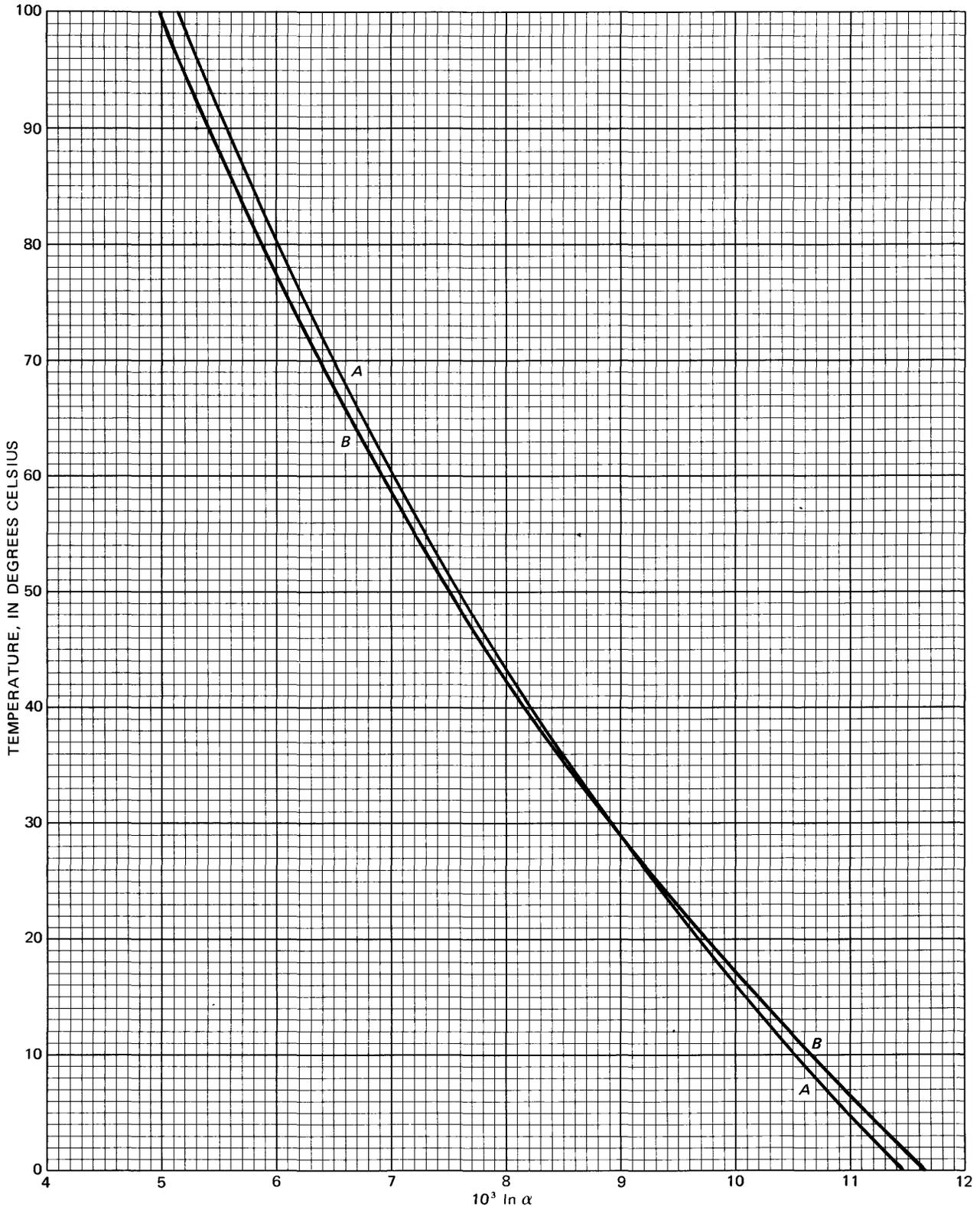
FIGURE 7

A, The experimental data of Baertschi and Thürkauf (1960) and of Craig, Gordon, and Horibe (1963) were combined in the expression given by Bottinga and Craig (1969):

$$10^3 \ln \alpha = 1.534(10^6 T^{-2}) - 3.206(10^3 T^{-1}) + 2.644.$$

B, Majzoub (1971): (0° to 100°C).

$$10^3 \ln \alpha = 1.137(10^6 T^{-2}) - 0.4156(10^3 T^{-1}) - 2.0667.$$



WATER(l)-WATER(v) BETWEEN 0° AND 100°C

O
X
Y
G
E
N

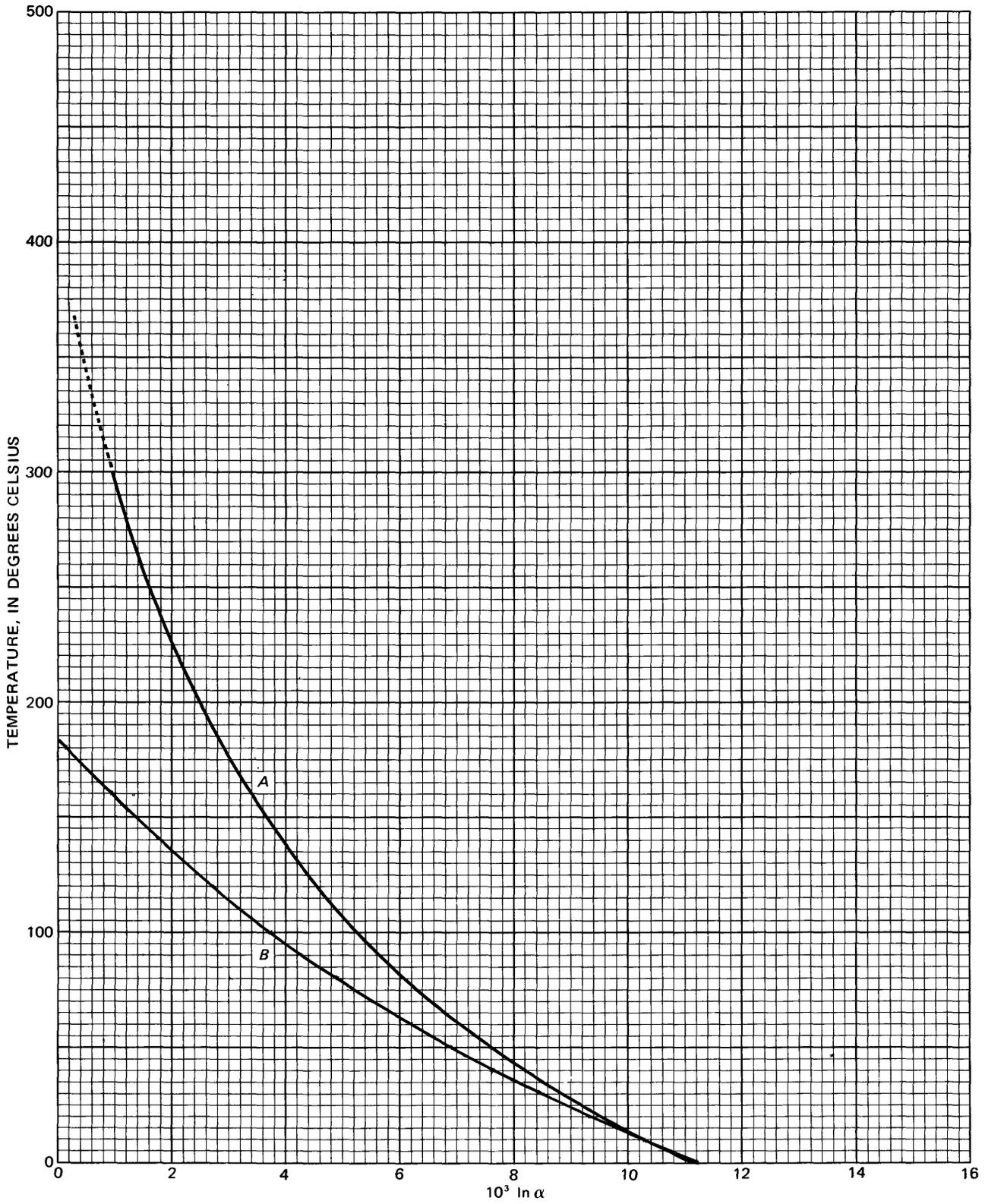
FIGURE 8

A, This expression is based on the experimental data from 134° to 300°C (Bottinga, 1968b; Bottinga and Craig, 1968) and the data presented in figure 5 (Y. Bottinga, written commun., 1973):

$$10^3 \ln \alpha = +0.7.664(10^8 T^{-2}) + 1.2051(10^5 T^{-1}) - 3.493.$$

B, Uvarov, Sokolov, and Zavoronkov (1962): (0° to 209°C).

$$10^3 \ln \alpha = 7.599(10^5 T^{-1}) - 16.62.$$



O
X
Y
G
E
N

WATER(l)-WATER(v) BETWEEN 0° AND 300°C

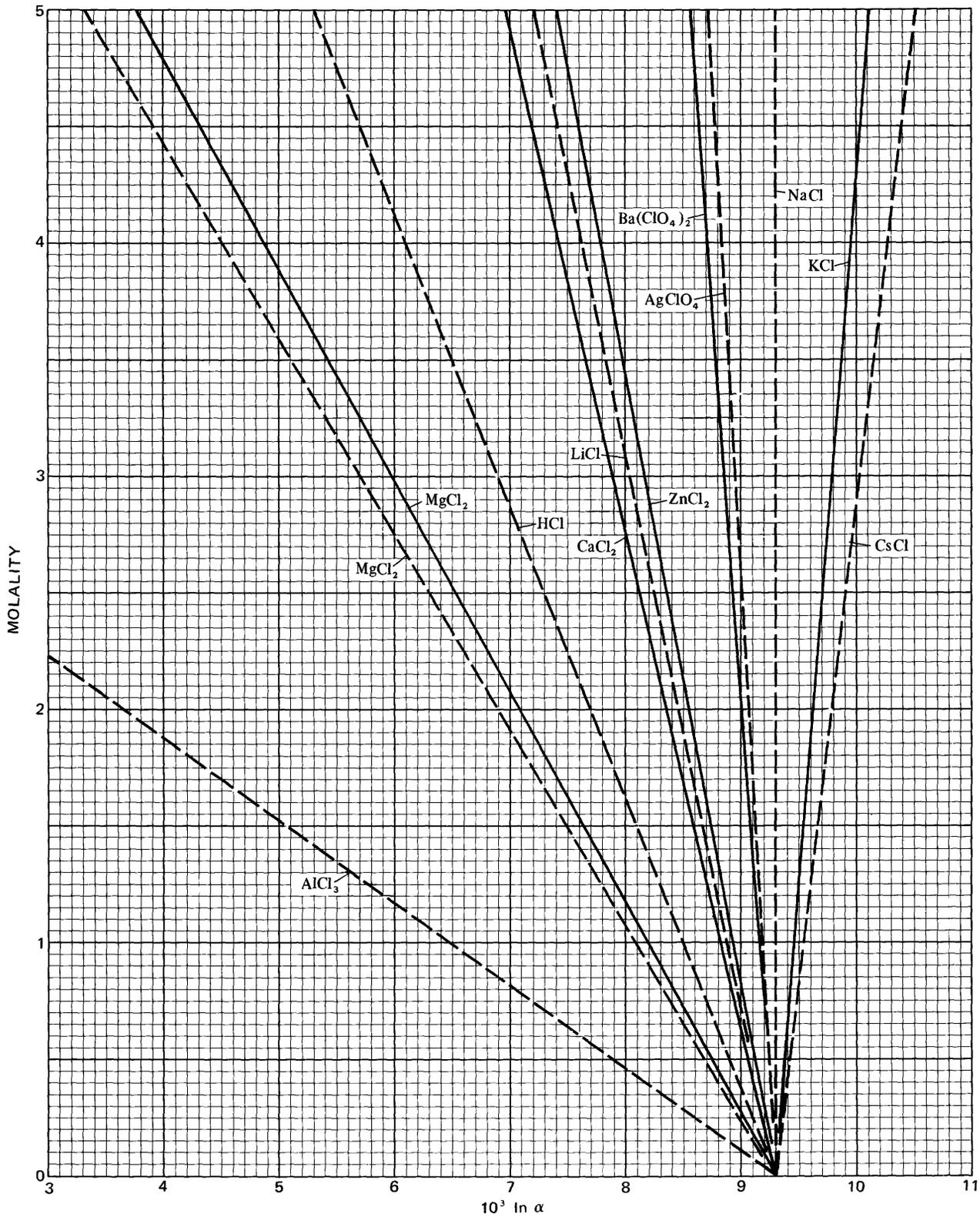
FIGURE 9

Solid curves from Sofer and Gat (1972).

Dashed curves from Taube (1954).

NOTE 1.—Additional data on these systems by O'Neil and Truesdell (written commun., 1976) are not shown but are in agreement with those of Sofer and Gat (1972) and of Taube (1954).

NOTE 2.—In these three studies the CO₂-equilibration method was used to obtain the data. Thus, the fractionations actually measured were between CO₂ in equilibrium with pure water and CO₂ in equilibrium with the solutions. A value of the fractionation factor between water(l) and water(v) was then taken from the literature (fig. 7, this report) to construct the curves.



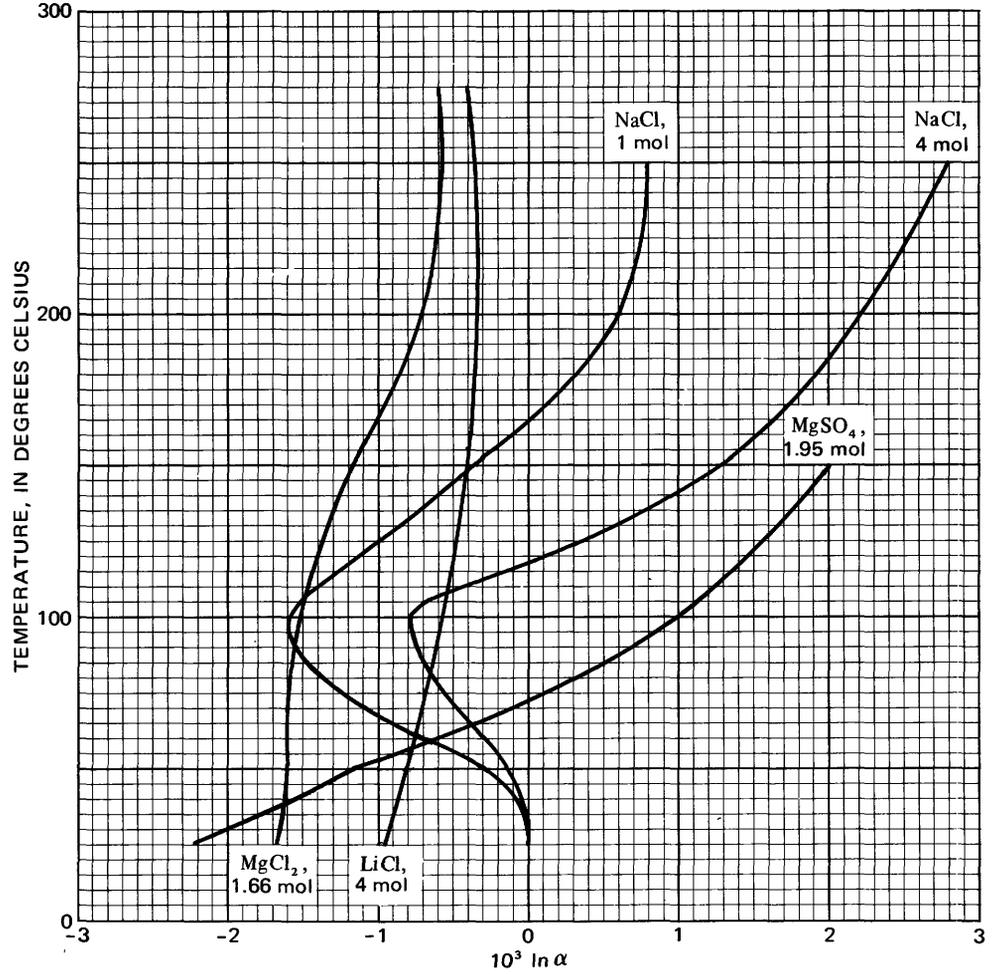
O
X
Y
G
E
N

WATER(l)-WATER(v), SOLUTE EFFECTS AT 25°C

FIGURE 10

Truesdell (1974).

As in figure 9 (note 2), the fractionations measured were between CO₂ equilibrated with pure water and CO₂ equilibrated with various solutions. From these figures can be obtained the oxygen isotope activity ratio of the solutions relative to pure water.



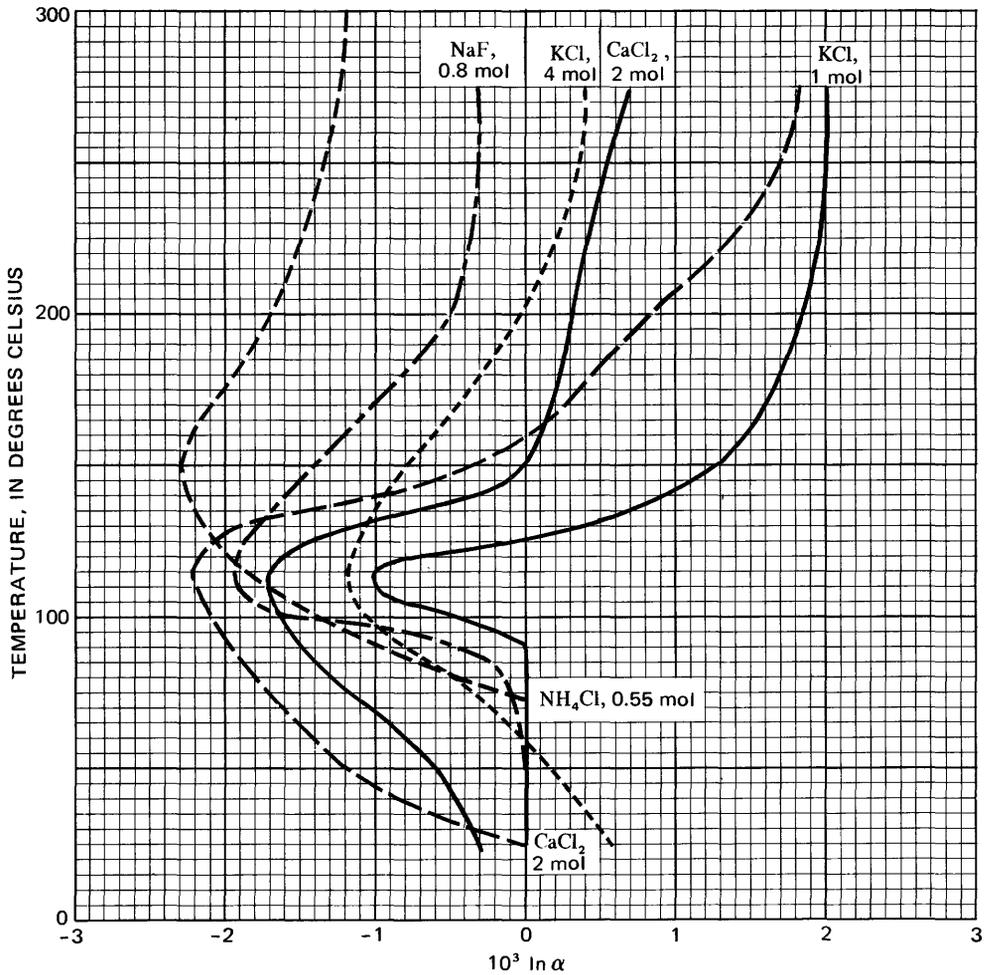
O
X
Y
G
E
N

MgCl₂, LiCl, NaCl, and MgSO₄ SOLUTIONS(l)-WATER(l)

FIGURE 11

Truesdell (1974).

As in figure 9 (note 2), the fractionations measured were between CO_2 equilibrated with pure water and CO_2 equilibrated with various solutions. From these figures can be obtained the oxygen isotope activity ratio of the solutions relative to pure water.



O
X
Y
G
E
N

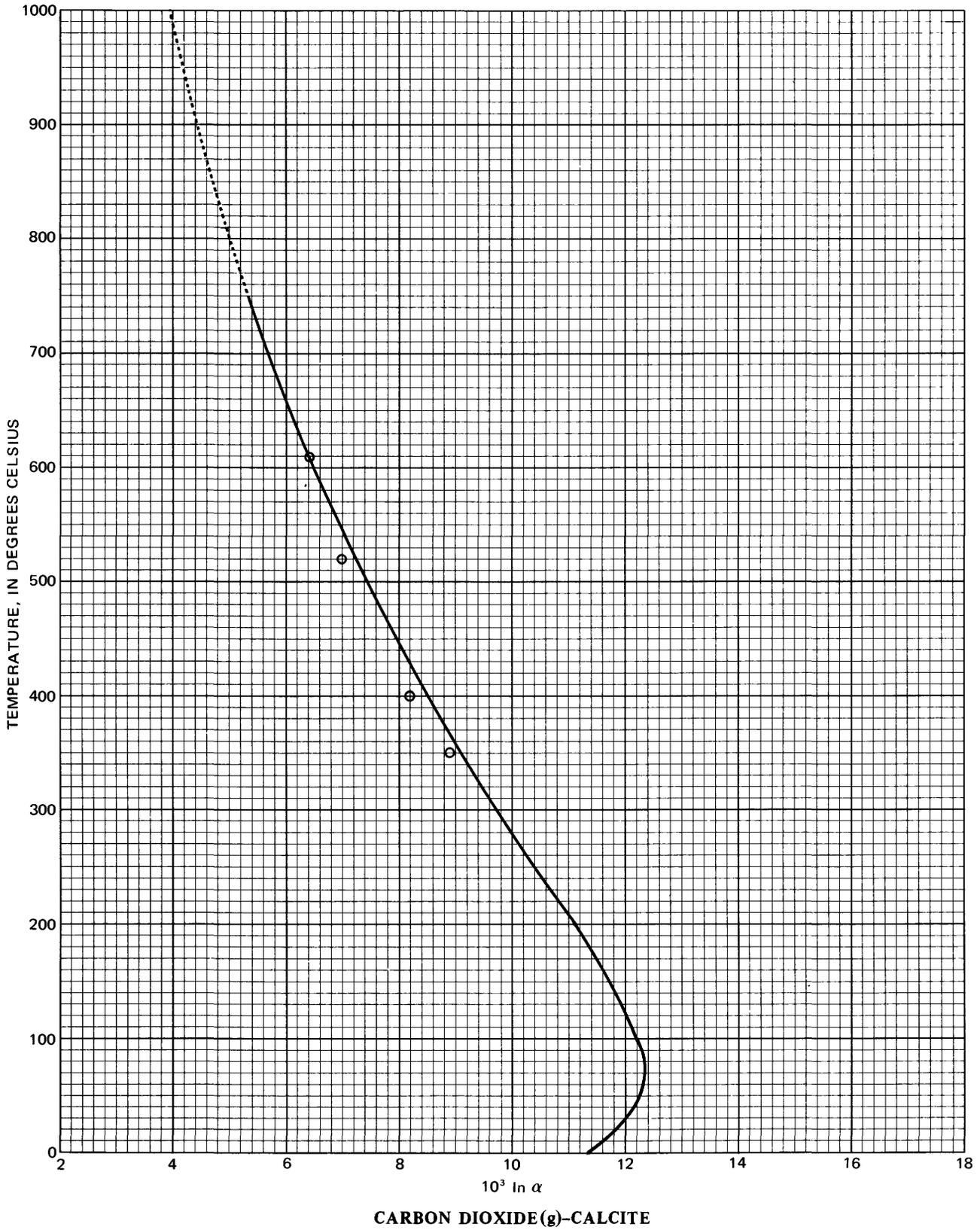
NH₄Cl, NaF, KCl, and CaCl₂ SOLUTIONS(l)-WATER(l)

FIGURE 12

Bottinga (1968a, b) calculation:

$$10^3 \ln \alpha = -1.8034(10^6 T^{-2}) + 10.611(10^3 T^{-1}) - 2.7798^*$$

Circles are data from O'Neil and Epstein (1966b).



O
X
Y
G
E
N

FIGURE 13

A, O'Neil, Clayton, and Mayeda (1969): (0° to 500°C).

$$(\text{CaCO}_3) 10^3 \ln \alpha = 2.78(10^6 T^{-2}) - 2.89^*$$

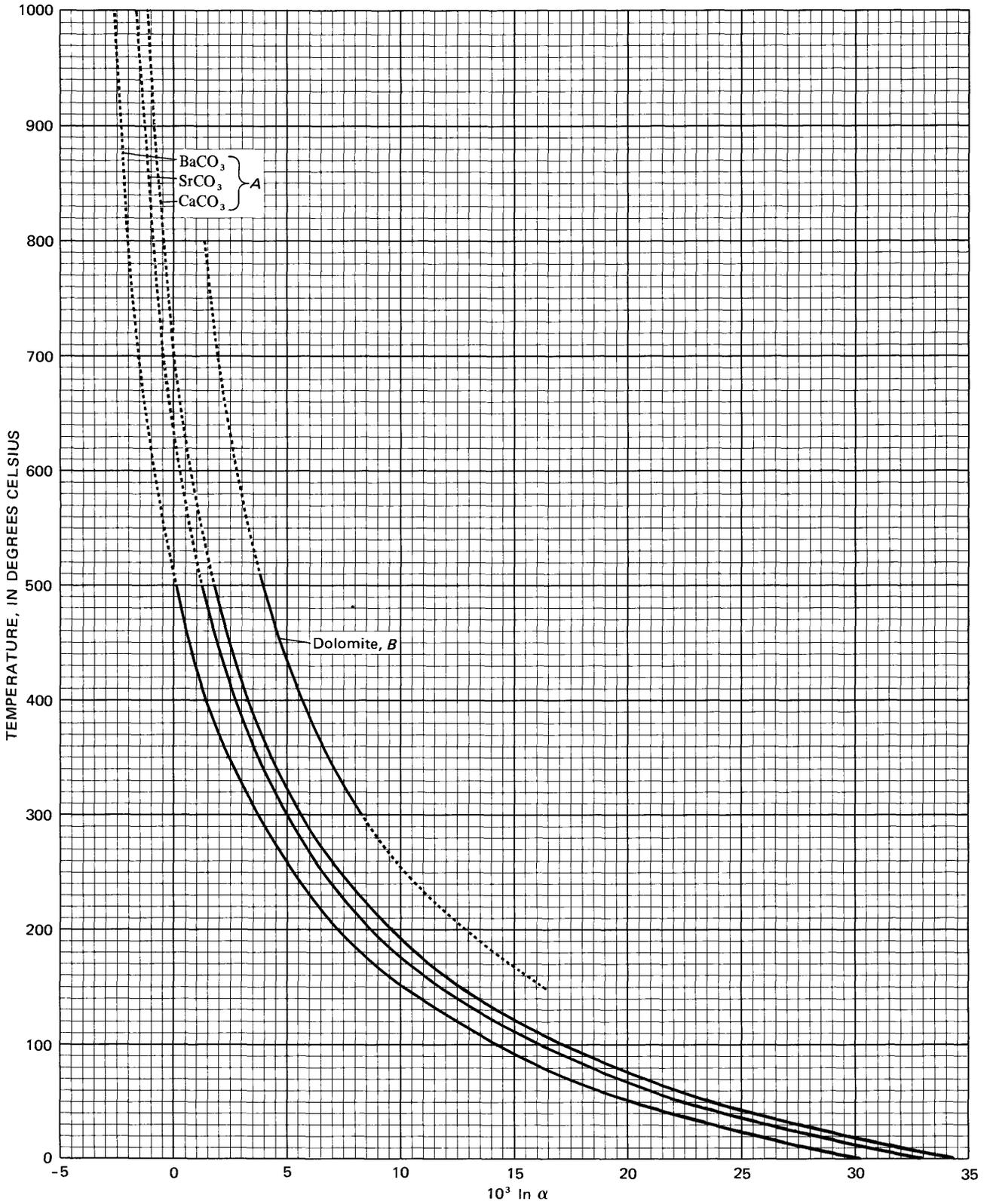
$$(\text{SrCO}_3) 10^3 \ln \alpha = 2.69(10^6 T^{-2}) - 3.24^*, \text{ and}$$

$$(\text{BaCO}_3) 10^3 \ln \alpha = 2.57(10^6 T^{-2}) - 4.23^*.$$

B, Northrop and Clayton (1966): (300° to 510°C).

$$\text{Dolomite. } 10^3 \ln \alpha = 3.20(10^6 T^{-2}) - 1.50^*.$$

This equation represents the average of two consistently different fractionation expressions for different dolomites.



O
X
Y
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ALKALINE EARTH CARBONATES-WATER

FIGURE 14

Lloyd (1968):

A, (Anhydrite)

B, (Dissolved sulfate)

Mizutani and Rafter (1969):

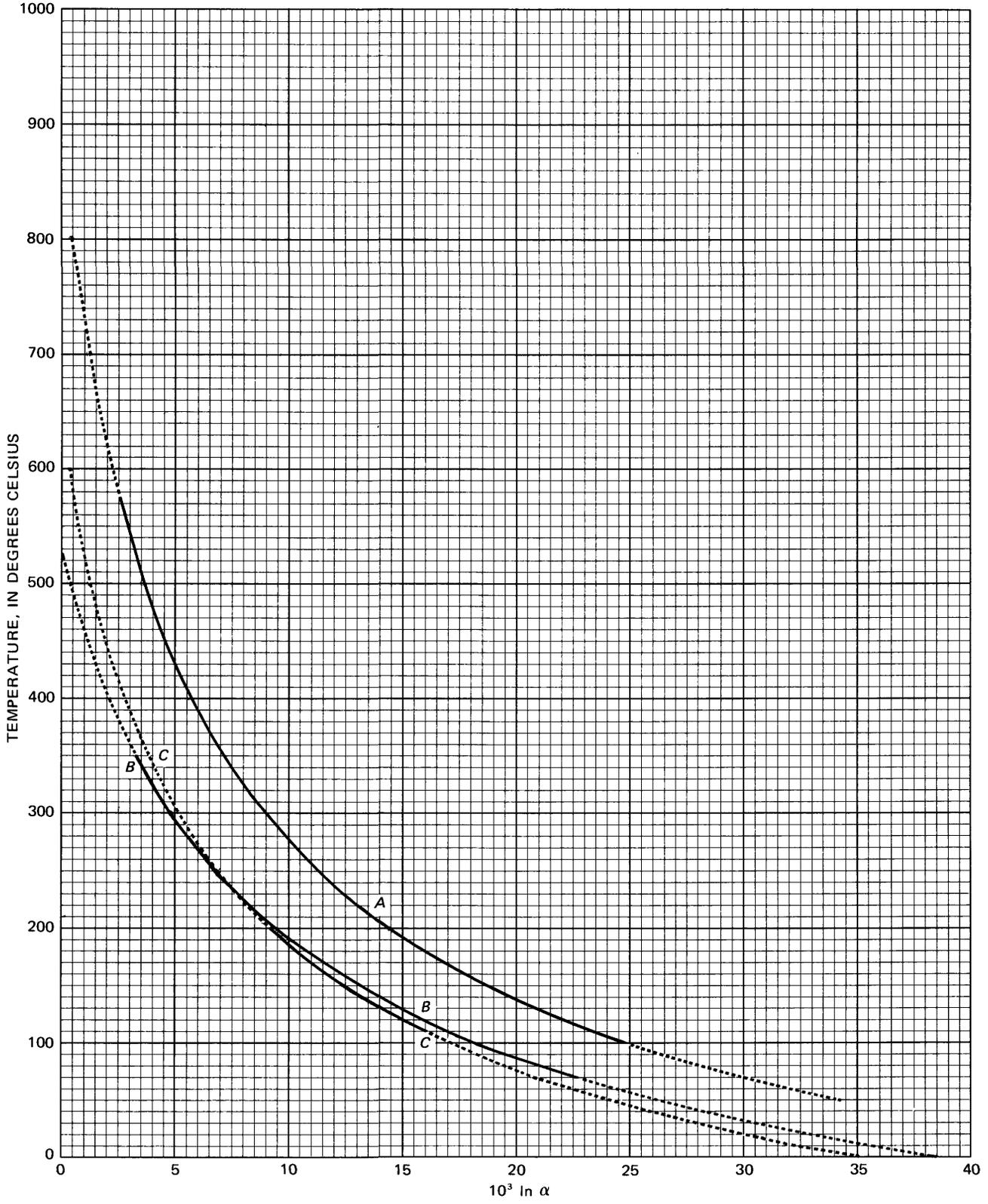
C, (Dissolved sulfate)

$$10^3 \ln \alpha = 3.88(10^6 T^{-2}) - 2.90^*$$

$$10^3 \ln \alpha = 3.25(10^6 T^{-2}) - 5.10^*$$

(110° to 200°C).

$$10^3 \ln \alpha = 2.88(10^6 T^{-2}) - 3.60^*$$



O
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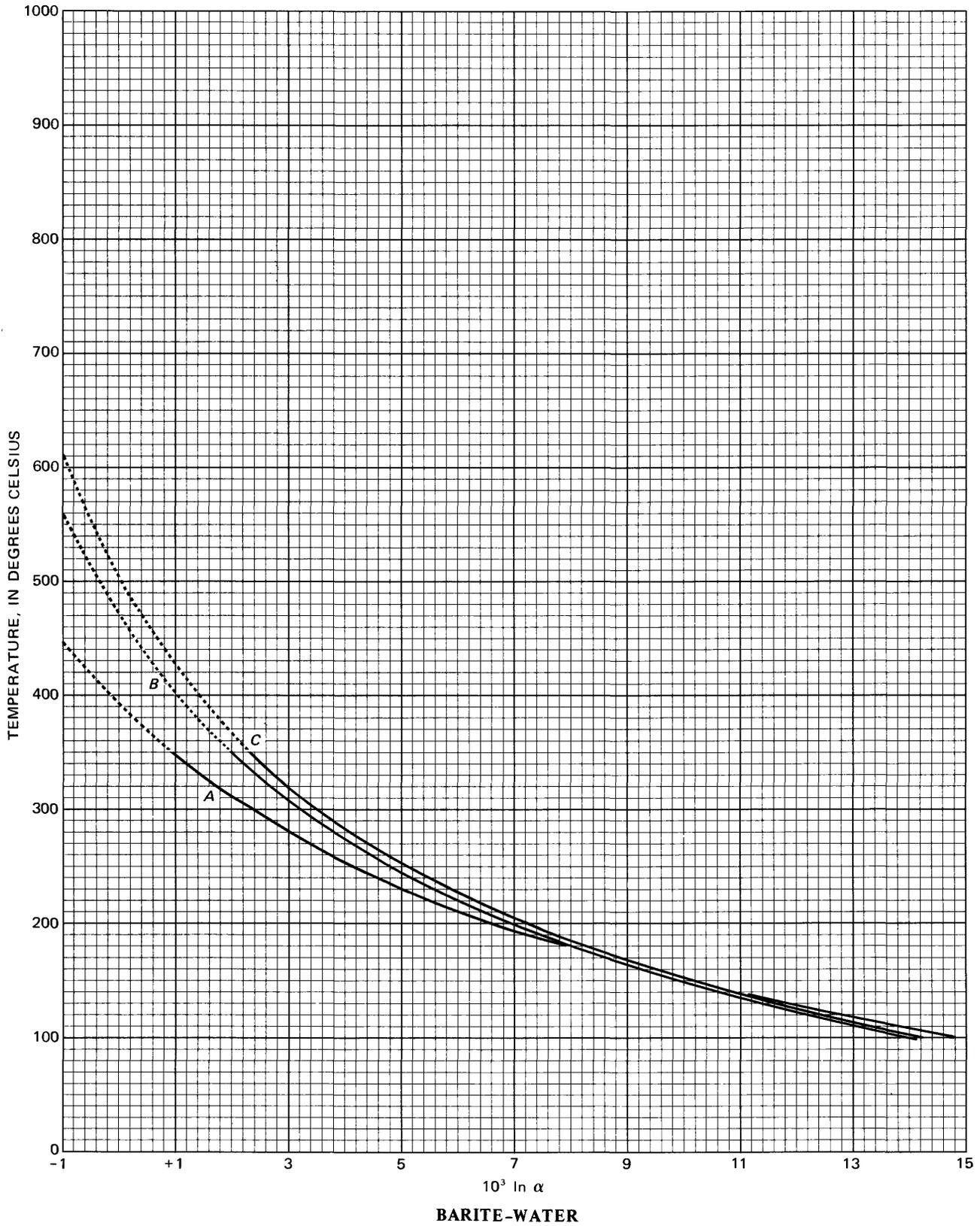
DISSOLVED SULFATE-WATER(I) AND ANHYDRITE-WATER

FIGURE 15

R. Robinson and M. Kusakabe (written commun., 1975):

- A, $\text{BaSO}_4\text{-H}_2\text{O}$ $10^3 \ln \alpha = 3.0(10^6 T^{-2}) - 6.79^*$.
B, $\text{BaSO}_4\text{-}1\text{ M NaCl}$ $10^3 \ln \alpha = 2.58(10^6 T^{-2}) - 4.3^*$.
C, $\text{BaSO}_4\text{-}1\text{ M NaCl} + 1\text{ M H}_2\text{SO}_4$ $10^3 \ln \alpha = 2.64(10^6 T^{-2}) - 4.8^*$.

The $\text{BaSO}_4\text{-}1\text{ M NaCl}$ and $1\text{ M NaCl} + 1\text{ M H}_2\text{SO}_4$ data have been corrected for hydration effects. In addition, the $\text{BaSO}_4\text{-}1\text{ M NaCl} + 1\text{ M H}_2\text{SO}_4$ data have been corrected for exchange with HSO_4^- at high temperature.



O
X
Y
G
E
N

FIGURE 16

A, Clayton, O'Neil, and Mayeda (1972):

$$10^3 \ln \alpha = 3.38(10^6 T^{-2}) - 2.90^*$$

(200° to 500°C), and

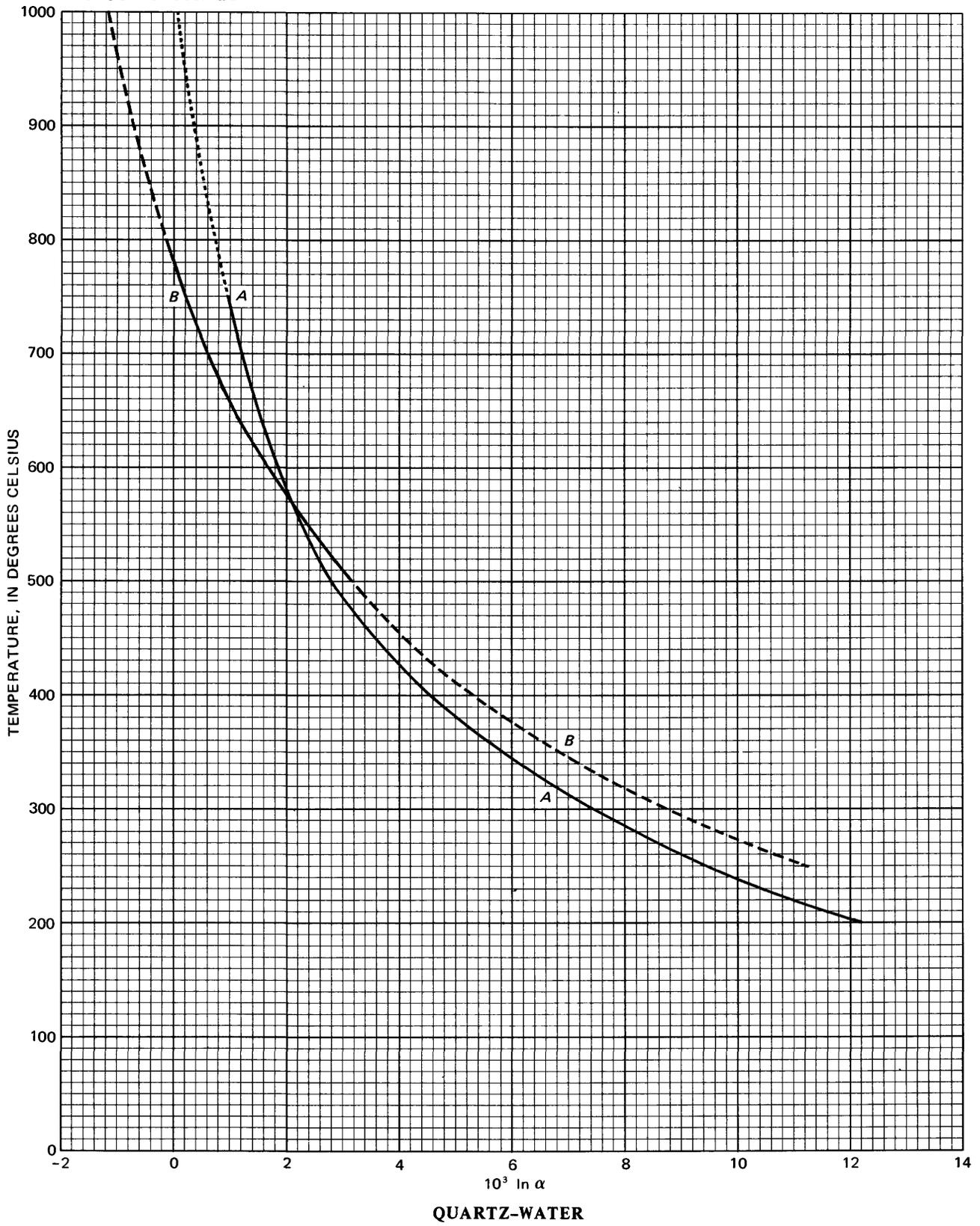
$$10^3 \ln \alpha = 2.51(10^6 T^{-2}) - 1.46^*$$

(500° to 750°C).

B, Bottinga and Javoy (1973):

$$10^3 \ln \alpha = 4.10(10^6 T^{-2}) - 3.70.$$

This expression was constructed from a combination of experimental determinations of other investigators, theoretical considerations, and consistencies in data from natural systems.



O
X
Y
G
E
N

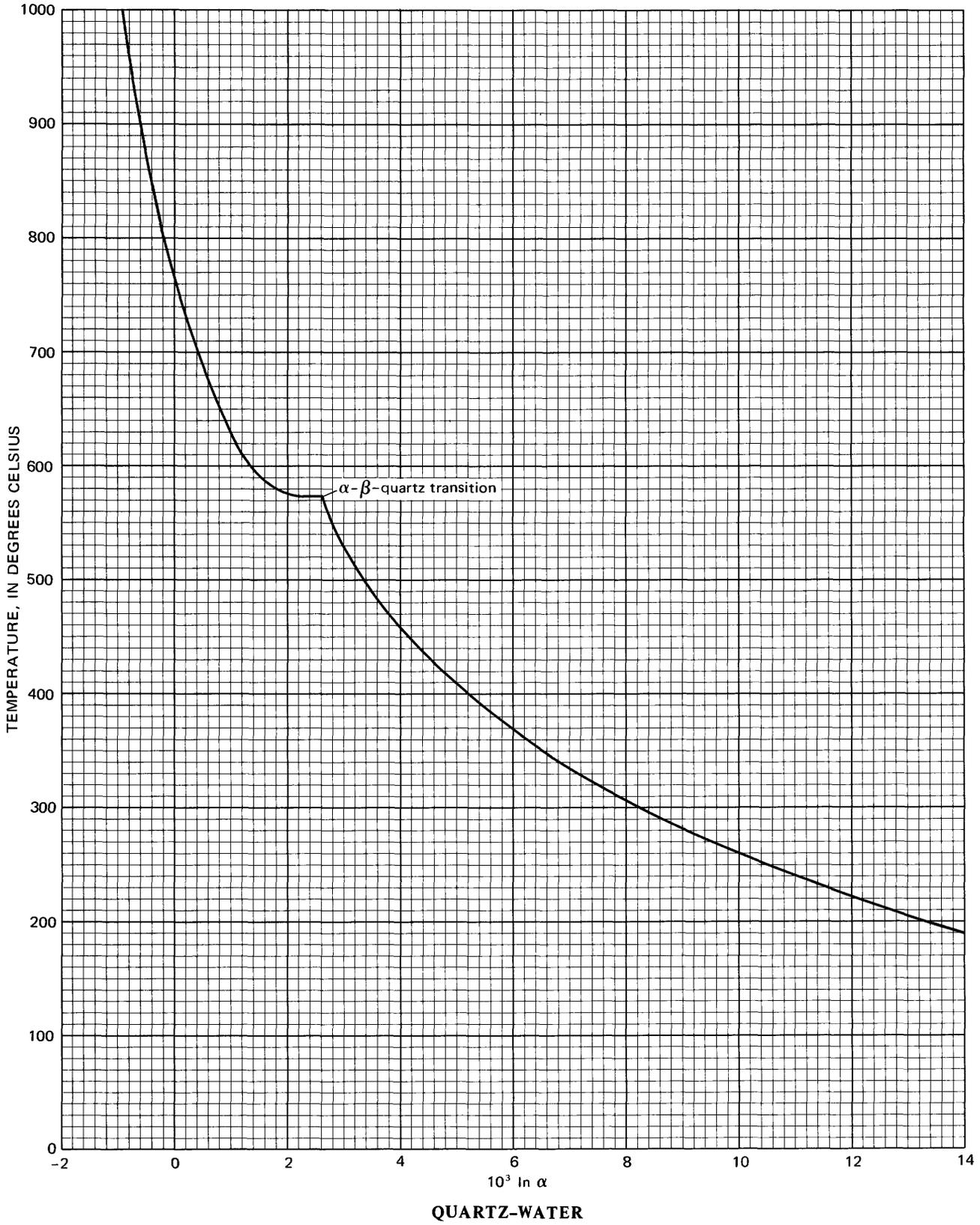
FIGURE 17

Shiro and Sakai (1972):

This curve results from a combination of Shiro and Sakai's calculation of the partition function ratios of α - and β -quartz, the partition function ratios of water derived from their calculated partition function ratios of calcite, and the experimental calcite-water fractionations of O'Neil, Clayton, and Mayeda (1969). A discontinuity occurs at the α to β transition temperature (573°C) of quartz.

$$10^3 \ln \alpha = 3.55(10^6 T^{-2}) - 2.57^* \quad (195^\circ \text{ to } 573^\circ \text{C}), \text{ and}$$

$$10^3 \ln \alpha = 3.23(10^6 T^{-2}) - 2.94^* \quad (573^\circ \text{ to } 1,000^\circ \text{C}).$$



O
X
Y
G
E
N

FIGURE 18

O'Neil and Taylor (1967):

A, (Alkali feldspars)

B, (Plagioclase)

where

B = mole fraction anorthite.

(350° to 800°C).

$$10^3 \ln \alpha = 2.91(10^6 T^{-2}) - 3.41.$$

$$10^3 \ln \alpha = (2.91 - 0.76B)(10^6 T^{-2}) - (3.41 - 0.14B),$$

Bottinga and Javoy (1973):

C, Alkali feldspar

D, (Plagioclase)

where

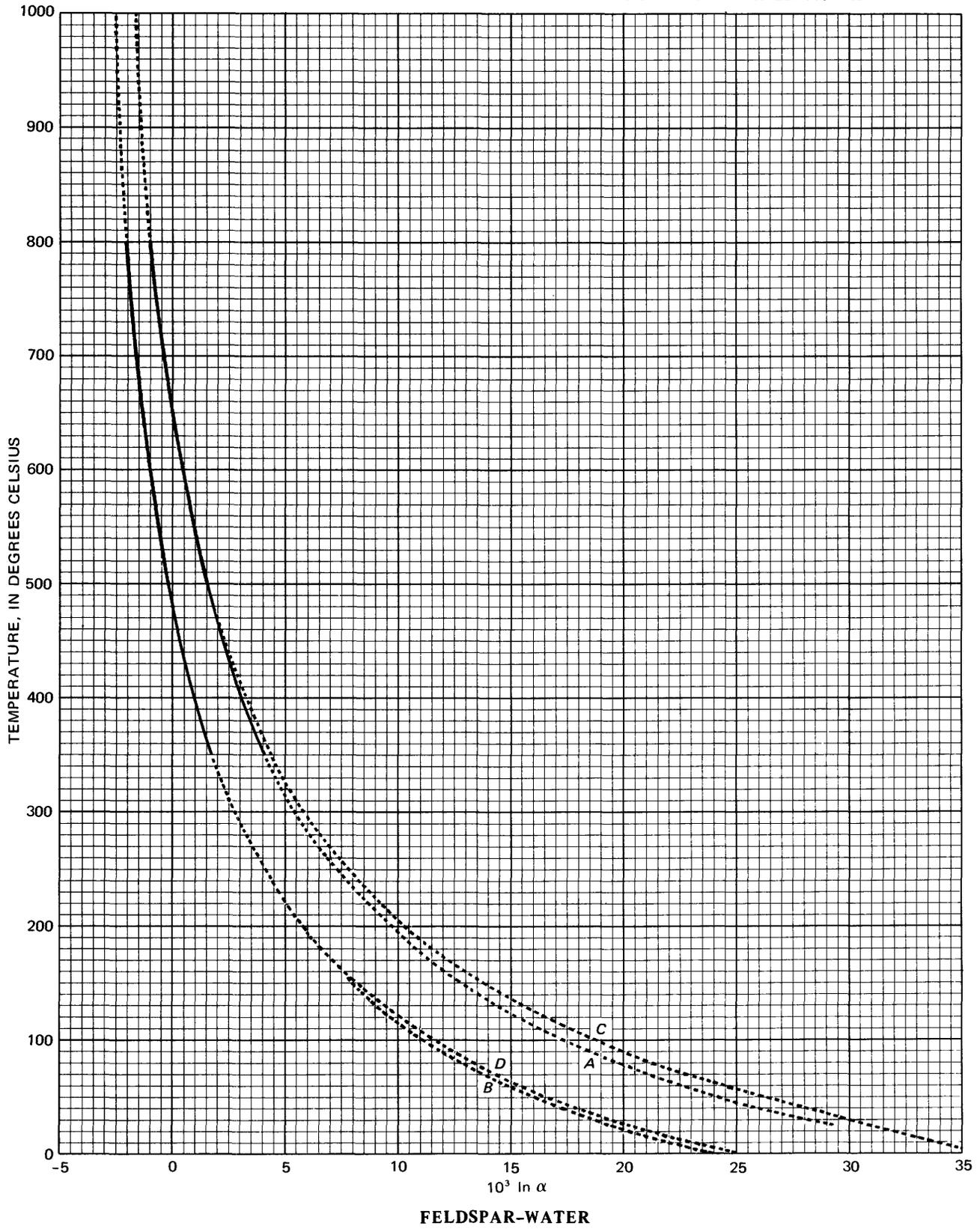
B = mole fraction anorthite.

(500° to 800°C).

$$10^3 \ln \alpha = 3.13(10^6 T^{-2}) - 3.70.$$

$$10^3 \ln \alpha = (3.13 - 1.04B)(10^6 T^{-2}) - 3.70,$$

NOTE.—Sodium and potassium feldspar have identical isotopic properties within the limits of analytical uncertainty.



O
X
Y
G
E
N

FIGURE 19

A, O'Neil and Taylor (1969): (400° to 650°C).

$$10^3 \ln \alpha = 2.38(10^6 T^{-2}) - 3.89.$$

B, Bottinga and Javoy (1973): (500° to 800°C).

$$10^3 \ln \alpha = 1.90(10^6 T^{-2}) - 3.10.$$

NOTE.—Muscovite and paragonite have identical isotopic properties within the limits of analytical uncertainty.

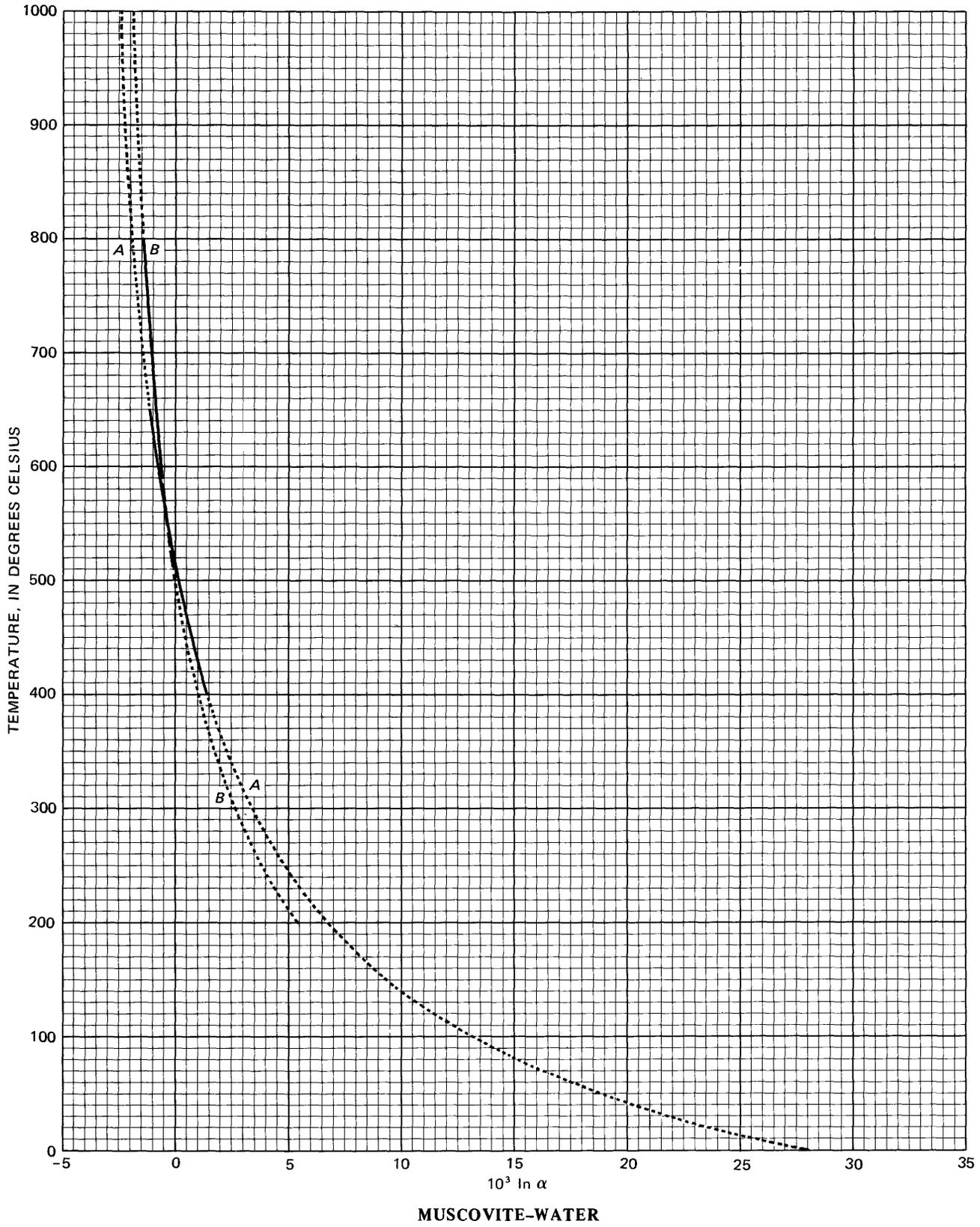
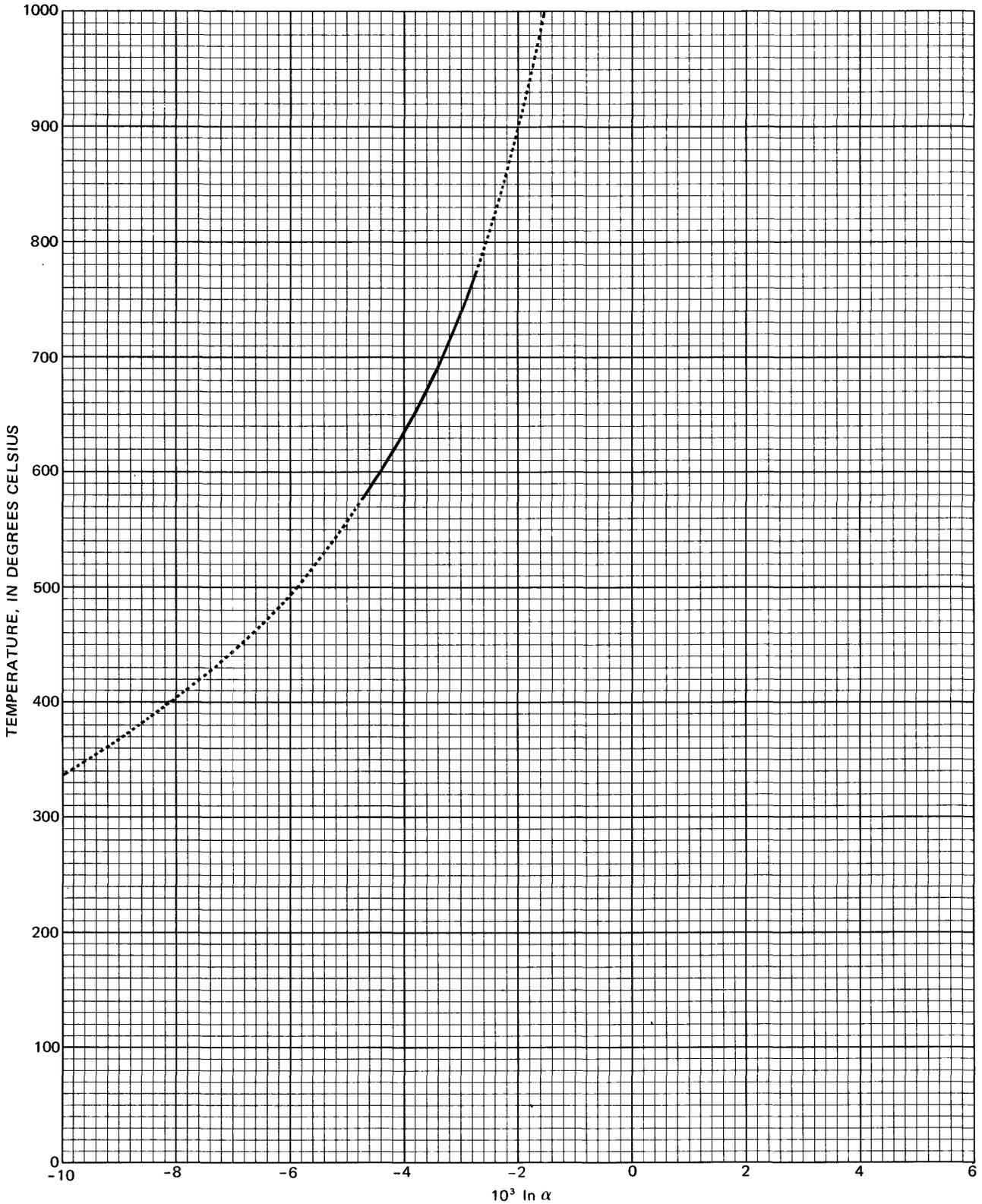


FIGURE 20

Addy and Garlick (1974): (575° to 775°C).

$$10^3 \ln \alpha = 4.1(10^6 T^{-2}) + 1.46^*$$

This curve should show a reversal of slope at low temperature similar to that shown by the magnetite-water system. (See fig. 21.)



O
X
Y
G
E
N

RUTILE-WATER

FIGURE 21

A, Becker (1971):

The curve was constructed from the partition function ratio of water derived from the experimental calcite-water fractionations and the calcite reduced partition function ratios of O'Neil, Clayton, and Mayeda (1969), and the average of Becker's maximum and minimum values for the reduced partition function ratio for magnetite. The latter was derived from corrected high temperature magnetite-water fractionations of O'Neil and Clayton (1964) and theoretical considerations. This curve has been recalculated, using the value of 1.0412 for the CO₂-H₂O fractionation.

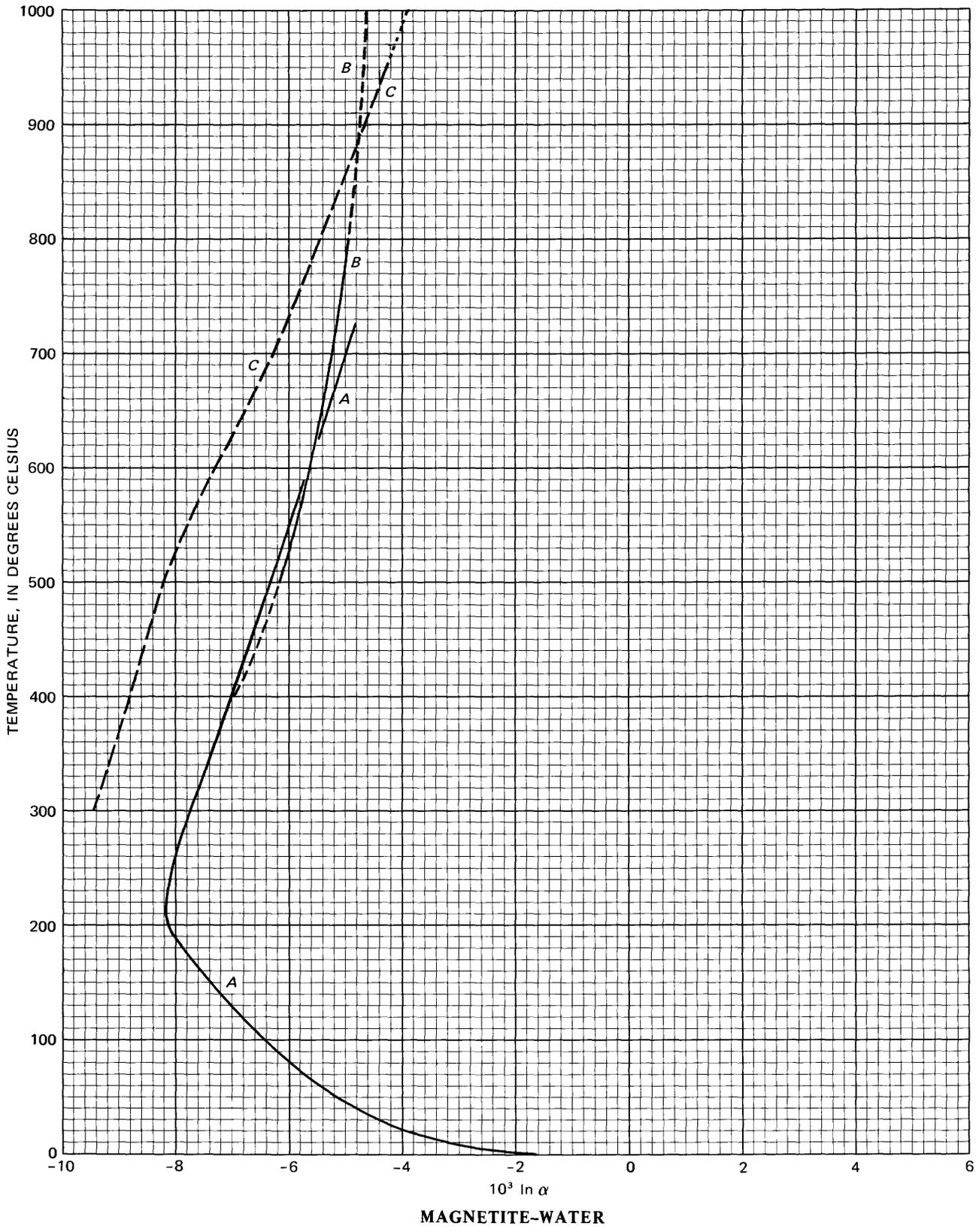
B, Bottinga and Javoy (1973): (500° to 800°C).

$$10^3 \ln \alpha = -1.47(10^6 T^{-2}) - 3.70.$$

C, Bertenrath, Friedrichsen, and Hellner (1972):

These fractionations are the results of experiments in the temperature range of 300° to 960°C in which hematite was reduced to magnetite in the presence of water at Ni-NiO buffered oxygen fugacities. This curve has been recalculated using the value of 1.0412 for the CO₂-H₂O fractionation.

NOTE.—Based on natural data, it is commonly assumed for purposes of geothermometry that $\Delta_{\text{quartz-illmenite}} = 0.95 \Delta_{\text{quartz-magnetite}}$. Also see Bottinga and Javoy (1974).



O
X
Y
G
E
N

FIGURE 22

A. Becker (1971):

This curve was obtained by combining the magnetite-water curve of figure 21 and the quartz-water curve of Clayton, O'Neil, and Mayeda (1972).

B. The two curves shown in the figure differ by only 20° or 30°C for per mil fractionations less than 14.0, but they were constructed from wholly different mineral-water curves.

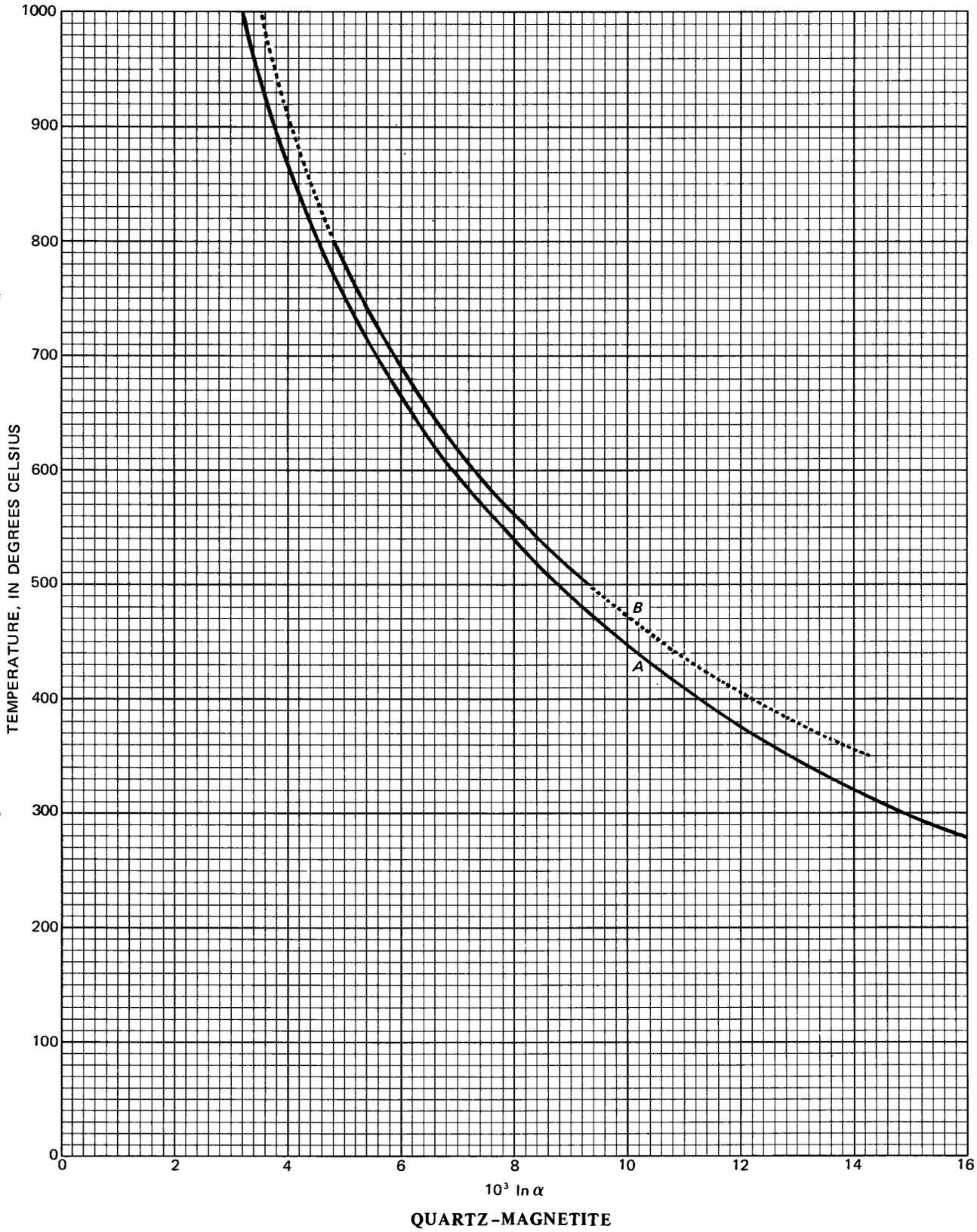
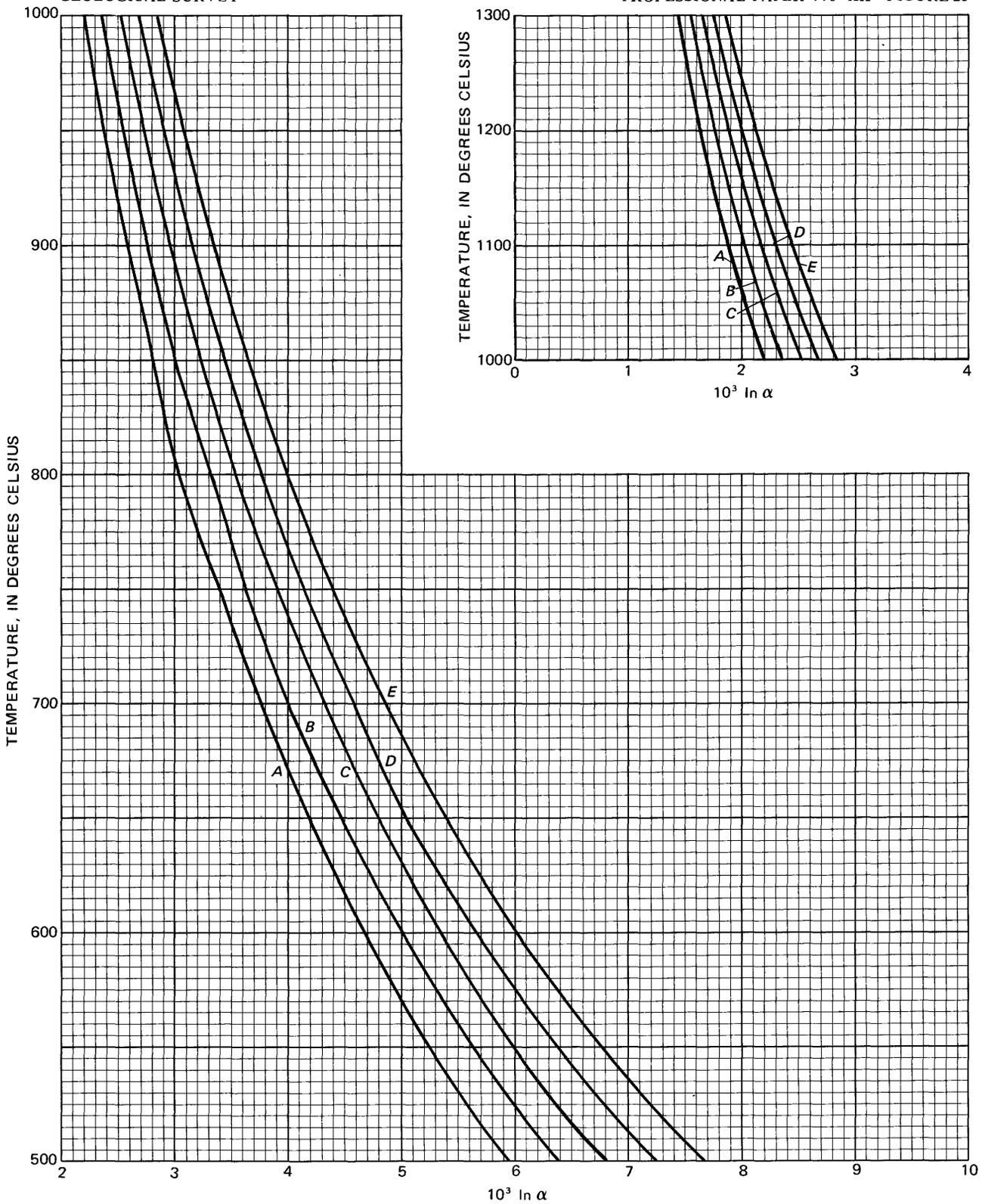


FIGURE 23

Bottinga and Javoy (1973):

- A*, Anorthite-magnetite
- B*, Anorthite(75)-magnetite.
- C*, Anorthite(50)-magnetite.
- D*, Anorthite(25)-magnetite.
- E*, Albite-magnetite.

Potassium feldspar has isotopic properties identical to albite within the limits of analytical error. The plagioclase-magnetite curves formulated by Anderson, Clayton, and Mayeda (1971) are virtually identical to those shown in the figure.



PLAGIOCLASE FELDSPAR-MAGNETITE

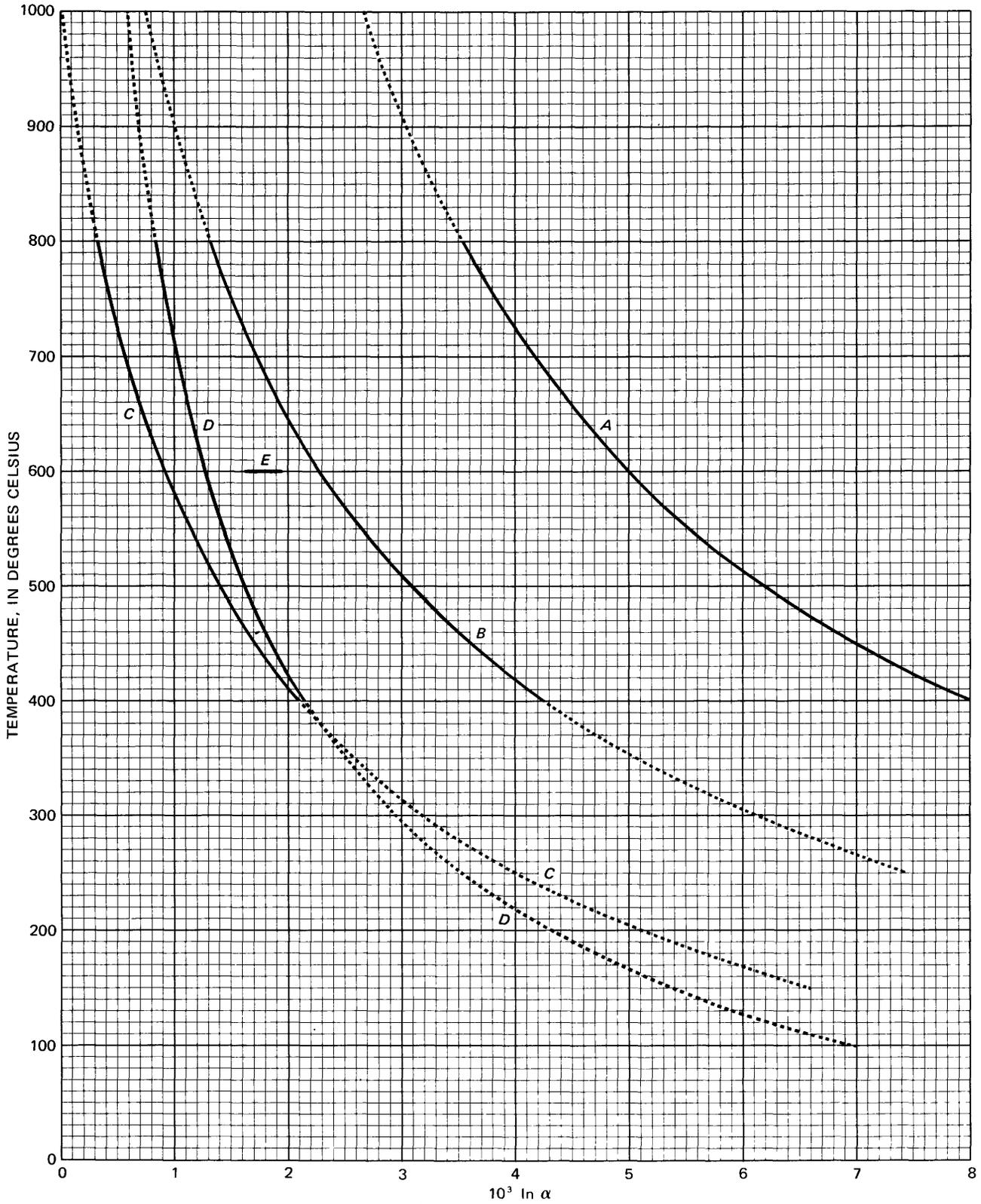
O
X
Y
G
E
N

FIGURE 24

- A*, Muscovite-magnetite.
- B*, Quartz-muscovite.
- C*, Quartz-calcite.
- D*, Quartz-alkali feldspar.
- E*, Quartz-alkali feldspar.

Experimental determination by Blattner and Bird (1974).

Expression of O'Neil, Clayton, and Mayeda (1969) for calcite-water was used in the quartz-calcite curve. All the other relationships in this and other curves, except *E*, are from Bottinga and Javoy (1973).



O
X
Y
G
E
N

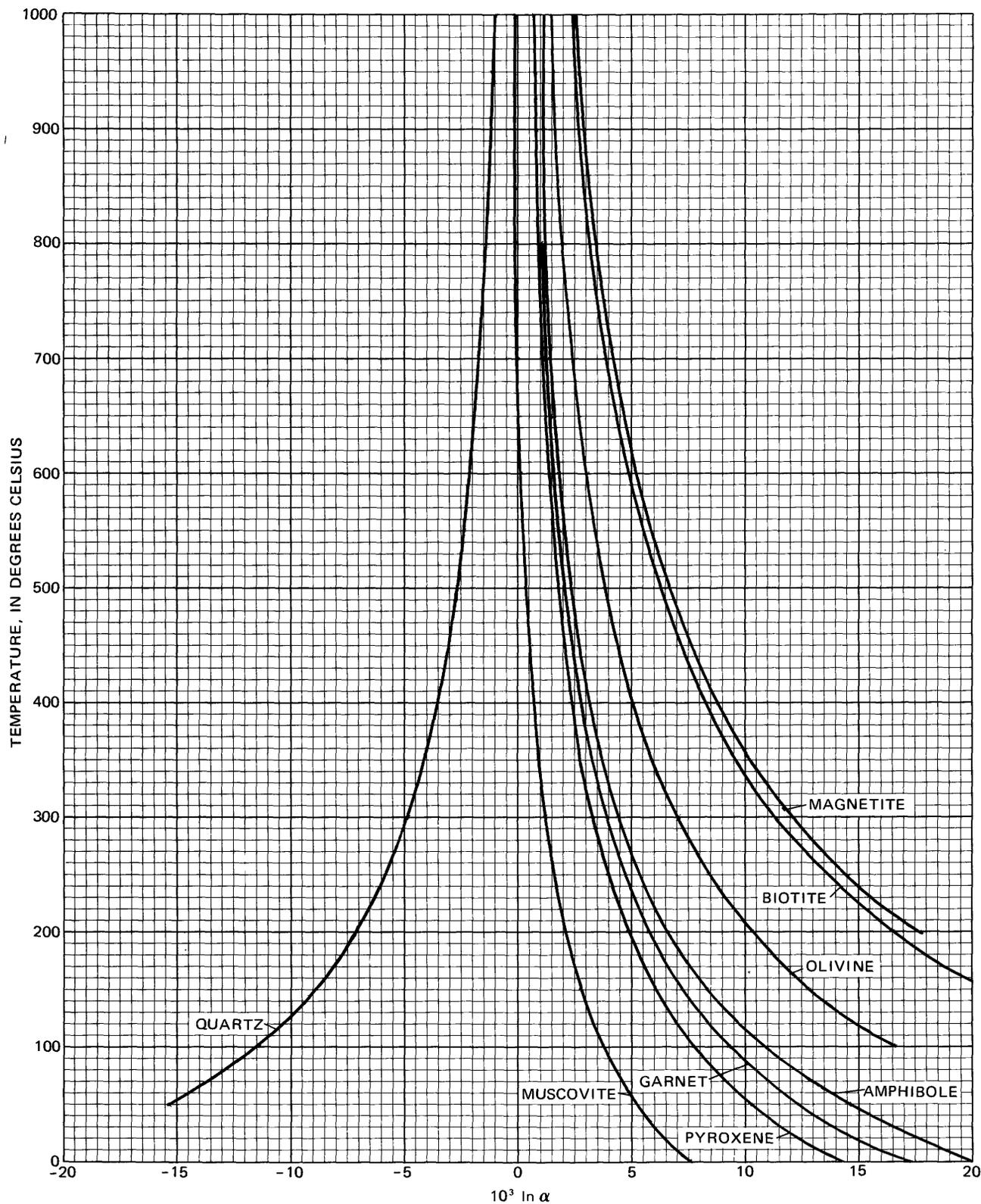
MUSCOVITE-MAGNETITE AND QUARTZ-MUSCOVITE, QUARTZ-CALCITE, AND QUARTZ-ALKALI FELDSPAR

FIGURE 25

Bottinga and Javoy (1974).

These curves represent the following fractionations:

Feldspar(An_{60})-quartz,
feldspar(An_{60})-muscovite,
feldspar(An_{60})-pyroxene,
feldspar(An_{60})-garnet,
feldspar(An_{60})-amphibole,
feldspar(An_{60})-olivine,
feldspar(An_{60})-biotite, and
feldspar(An_{60})-magnetite.



O
X
Y
G
E
N

LDSPAR (An₆₀)-QUARTZ, -MUSCOVITE, -PYROXENE, -GARNET,
-AMPHIBOLE, -OLIVINE, -BIOTITE, AND -MAGNETITE

FIGURE 26

A, Sheppard and Schwarcz (1970): (100° to 650°C).

$$10^3 \ln \alpha = 0.45(10^6 T^{-2}) - 0.40.$$

This curve is constructed from fractionations between coexisting calcite and dolomite in marbles, calibrated by the Mg-calcite solvus thermometer.

B, Northrop and Clayton (1966).

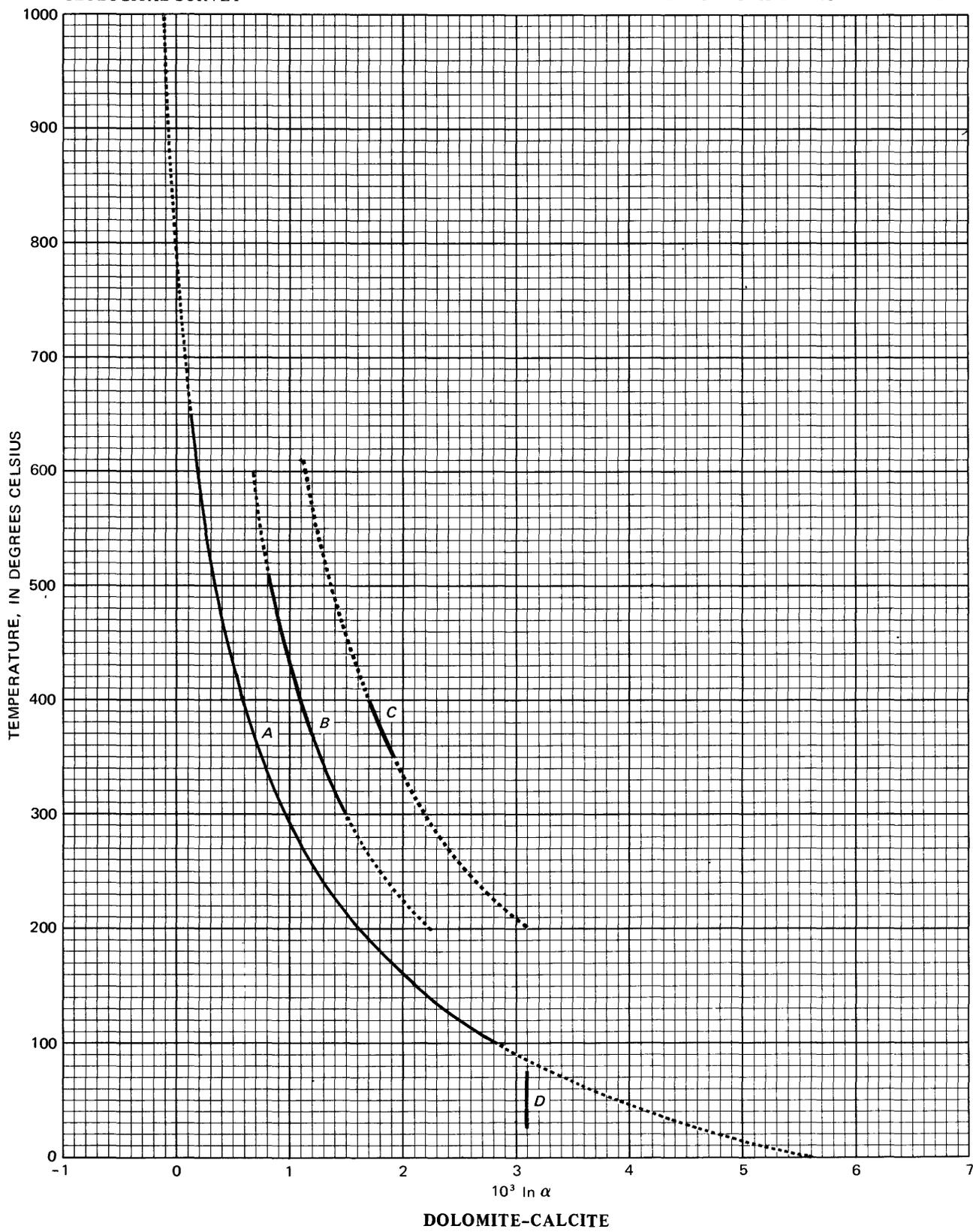
C, O'Neil and Epstein (1966b):

$$10^3 \ln \alpha = 0.56(10^6 T^{-2}) - 0.45.$$

This curve is based on measurements at only two temperatures, 350° and 400°C.

D, Fritz and Smith (1970):

The constant dolomite-calcite fractionation of +3.1 in the temperature range 25° to 79°C is calculated from data on synthesized protodolomites, using the acid fractionation factor of 1.01025 for both carbonates. If the acid fractionation factor of 1.01109 is used for dolomite, this value becomes +2.3.



O
X
Y
G
E
N

FIGURE 27

A, Malinin, Kropotova, and Grinenko (1967): (23° to 286°C).

This curve is a least-squares fit to the authors' data.

B, Mook, Bommerson, and Staverman (1974): (5° to 125°C).

$$10^3 \ln \alpha = 9.552(10^3 T^{-1}) - 24.10.$$

C, Emrich, Ehhalt, and Vogel (1970):

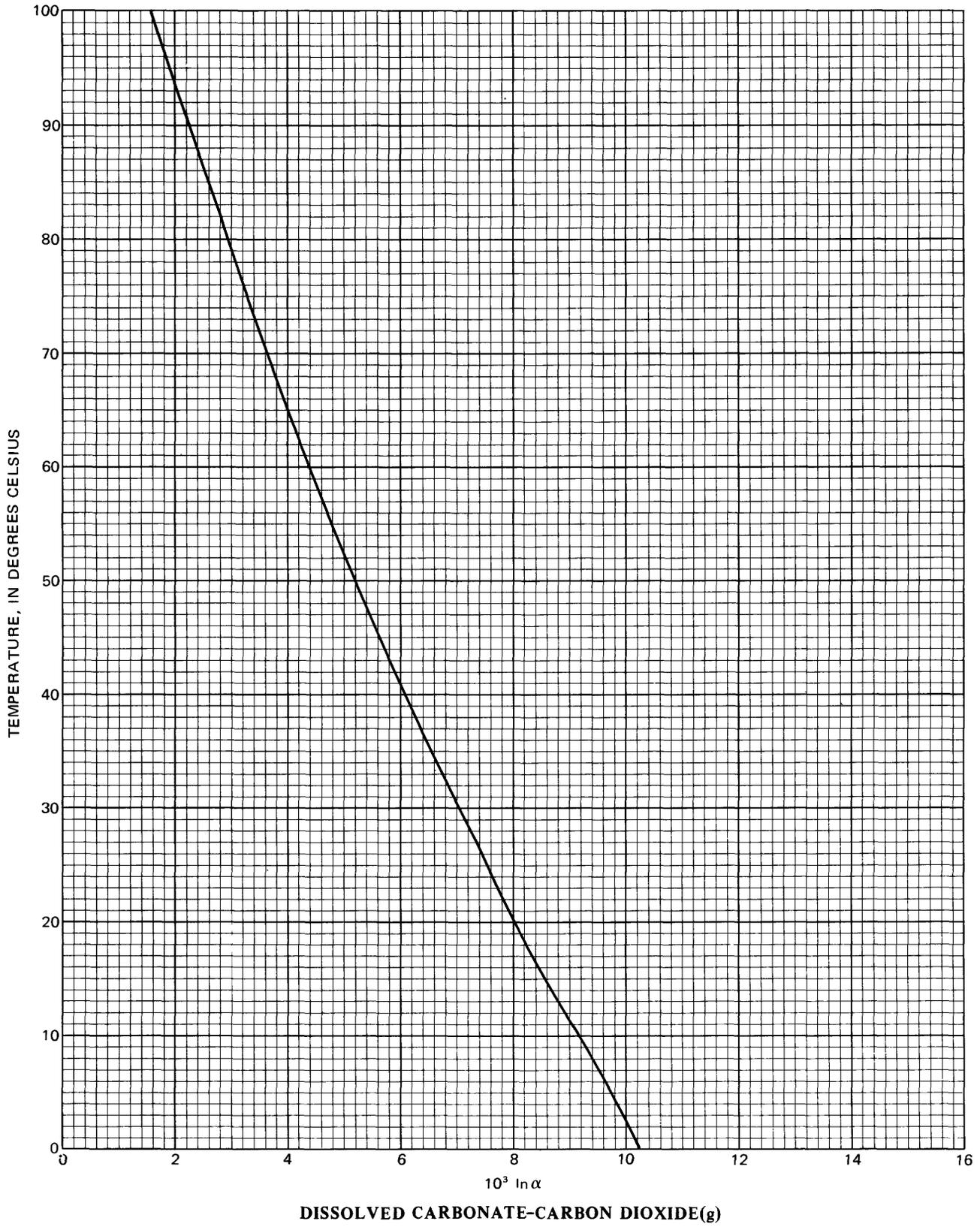
NOTE.—Data in the insert are given in the following table:

T(°C)	10 ³ ln α	Reference
0	9.3±0.4	Deuser and Degens (1967).
7	9.7±0.4	Wendt, Stahl, Geyh, and Fauth (1966).
10	8.4±0.4	Deuser and Degens (1967).
14	9.4±0.4	Wendt (1968).
20	8.4±0.1	Emrich, Ehhalt, and Vogel (1970).
20	7.6±0.4	Deuser and Degens (1967).
22	7.7±0.3	Vogel (1961).
25	7.7	Thode, Shima, Rees, and Krishnamurty (1965).
25	8.3	Abelson and Hoering (1961).
28	8.5±0.4	Wendt (1968).
30	6.9±0.4	Deuser and Degens (1967).

FIGURE 28

Thode, Shima, Rees, and Krishnamurty (1965) calculation:

The crossover point ($10^3 \ln \alpha = 0$) occurs at 130°C, and there is a reversal at 425°C
 $10^3 \ln \alpha = -48$).



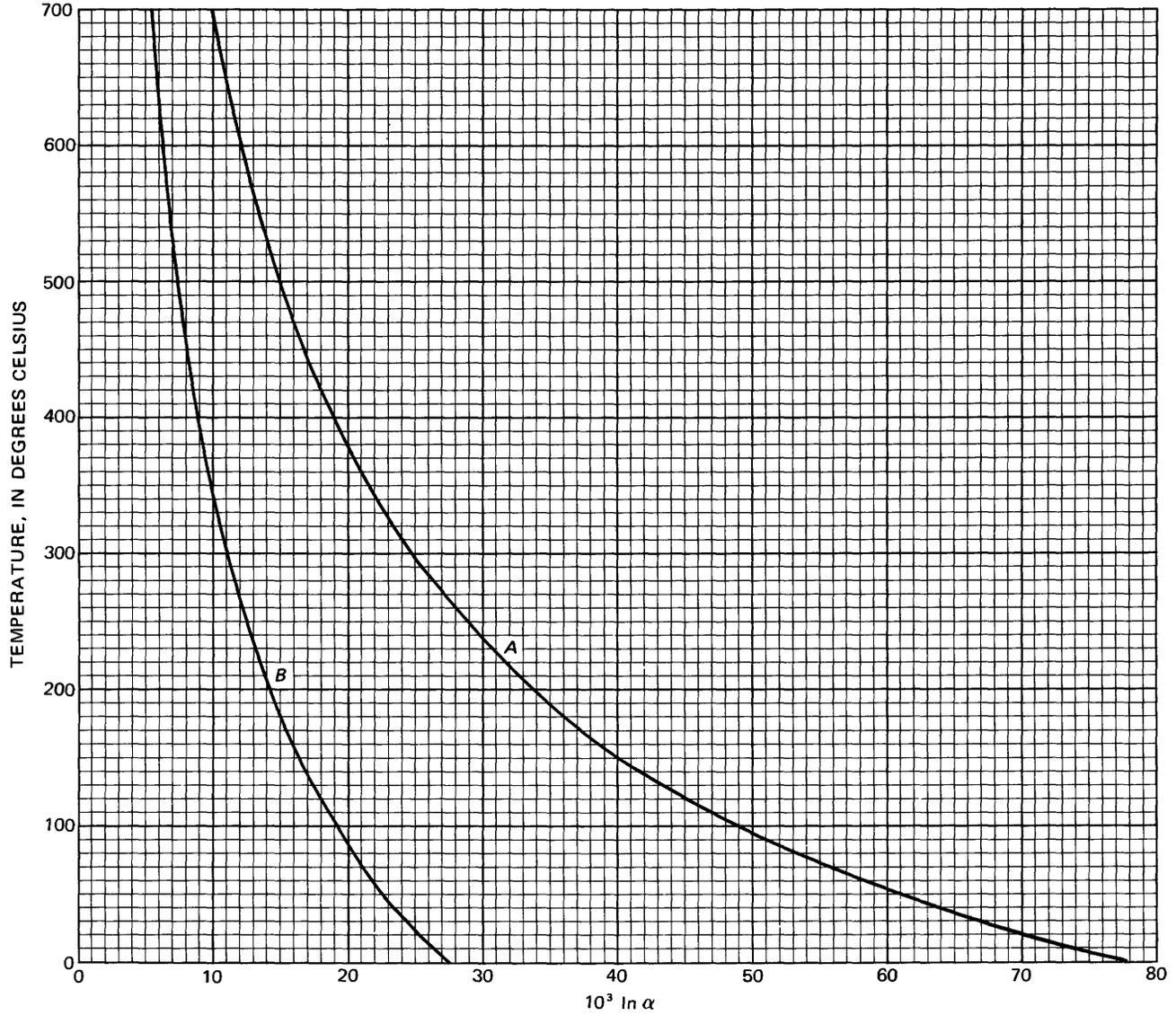
C
A
R
B
O
N

FIGURE 29

Bottinga (1969a):

A, Carbon dioxide(g)-methane(g).

B, Calcite-graphite.



CARBON DIOXIDE(g)-METHANE(g) AND CALCITE-GRAPHITE

C
A
R
B
O
N

FIGURE 30

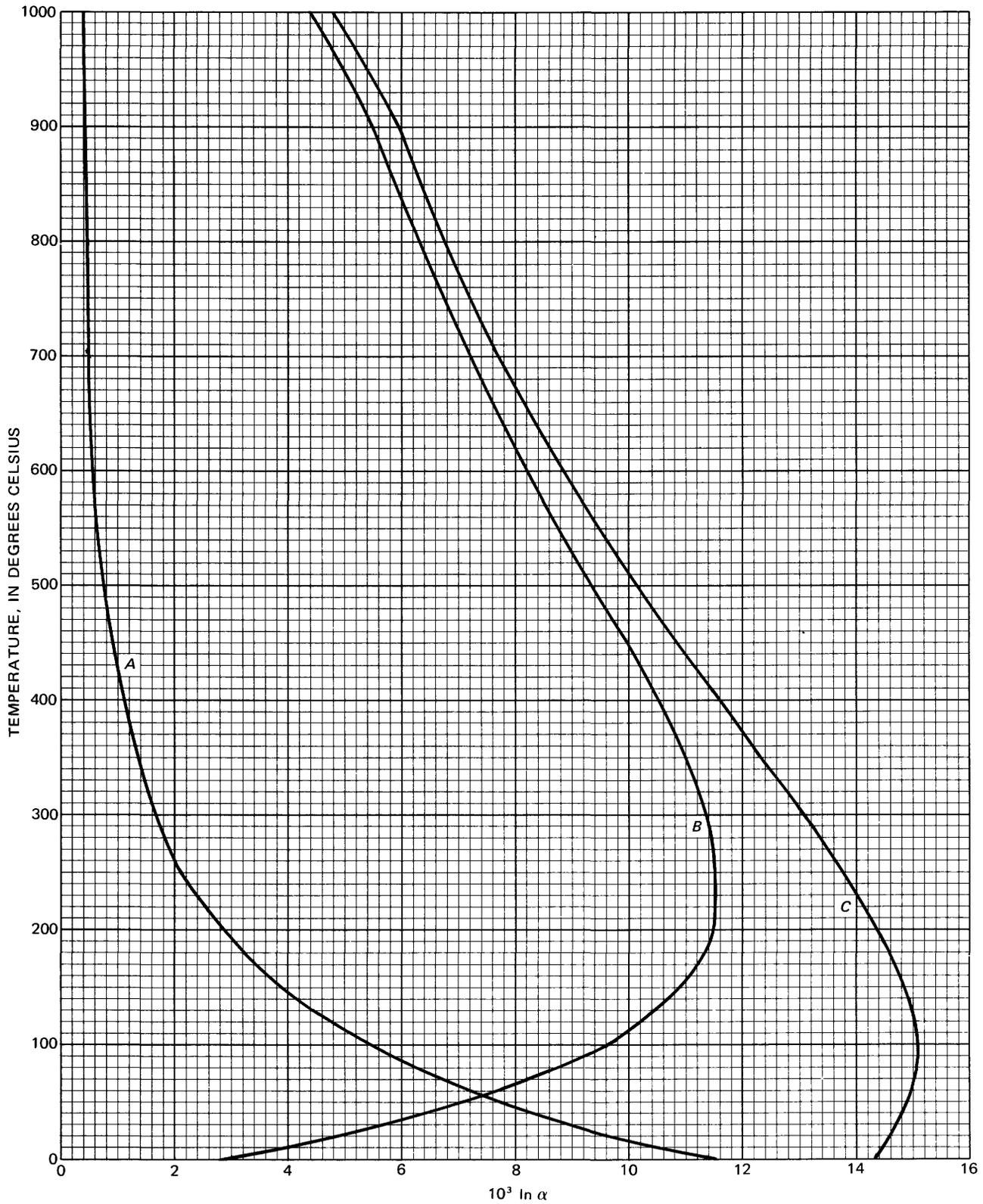
A, Bottinga (1969b):

Diamond-graphite.

B, Bottinga (1969b):

Carbon dioxide(g)-diamond.

C, Although carbon dioxide(g)-graphite is given in Bottinga (1969b), the data given in Bottinga (1968a) has more internal consistency; therefore, the latter data have been plotted from 0° to 700°C, and the former from 700° to 1,000°C.



C
A
R
B
O
N

DIAMOND-GRAPHITE, CARBON DIOXIDE(g)-DIAMOND, AND CARBON DIOXIDE(g)-GRAPHITE

FIGURE 31

A, Bottinga (1968b) calculation: (curve).

$$10^3 \ln \alpha = -2.9880(10^6 T^{-1}) + 7.6663(10^3 T^{-1}) - 2.4612.$$

Note the crossover point at 192°C.

B, Northrop and Clayton (1966): (●).

The values shown at 225°, 300°, and 400°C are interpolated values from partial exchange experiments where the percentages of exchange were 7, 20, and 43, respectively.

C, Vogel (1959): (x).

A value of -9.3 ± 0.5 at 20°C is not shown but is in agreement with the value of Emrich, Ehhalt, and Vogel (1970).

D, Baertschi (1957): (Δ).

E, Emrich, Ehhalt, and Vogel (1970): (o).

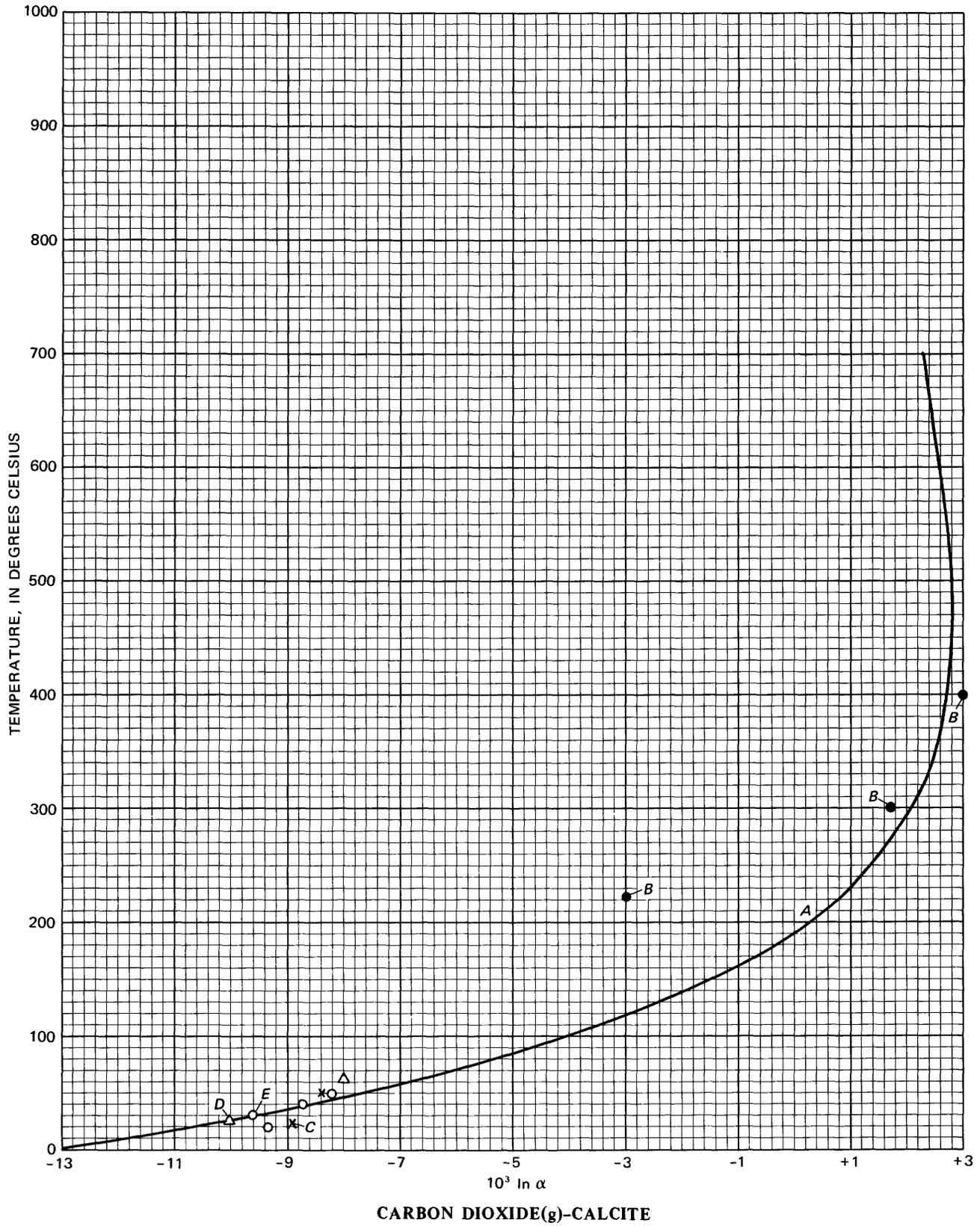
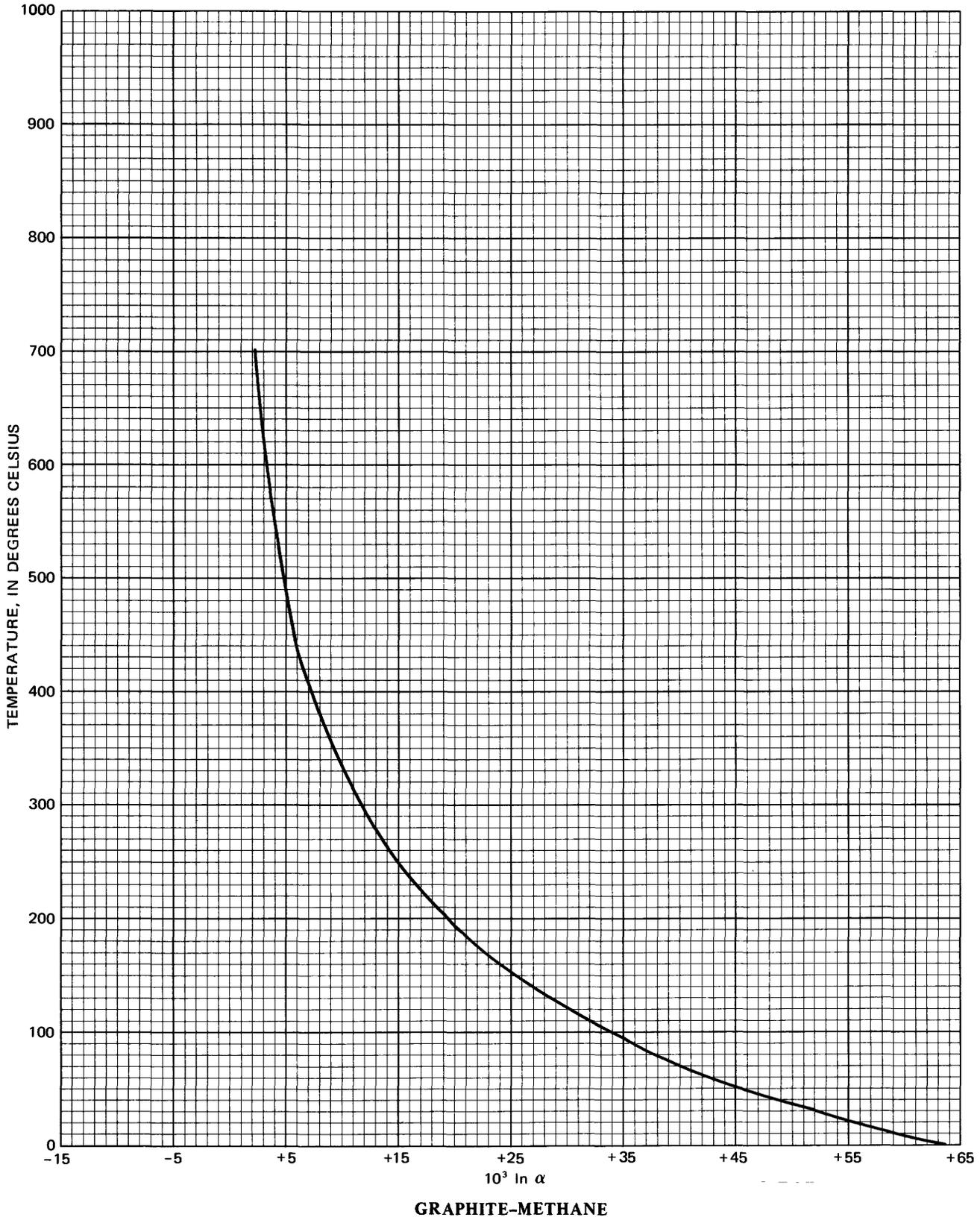


FIGURE 32

Bottinga (1969a).



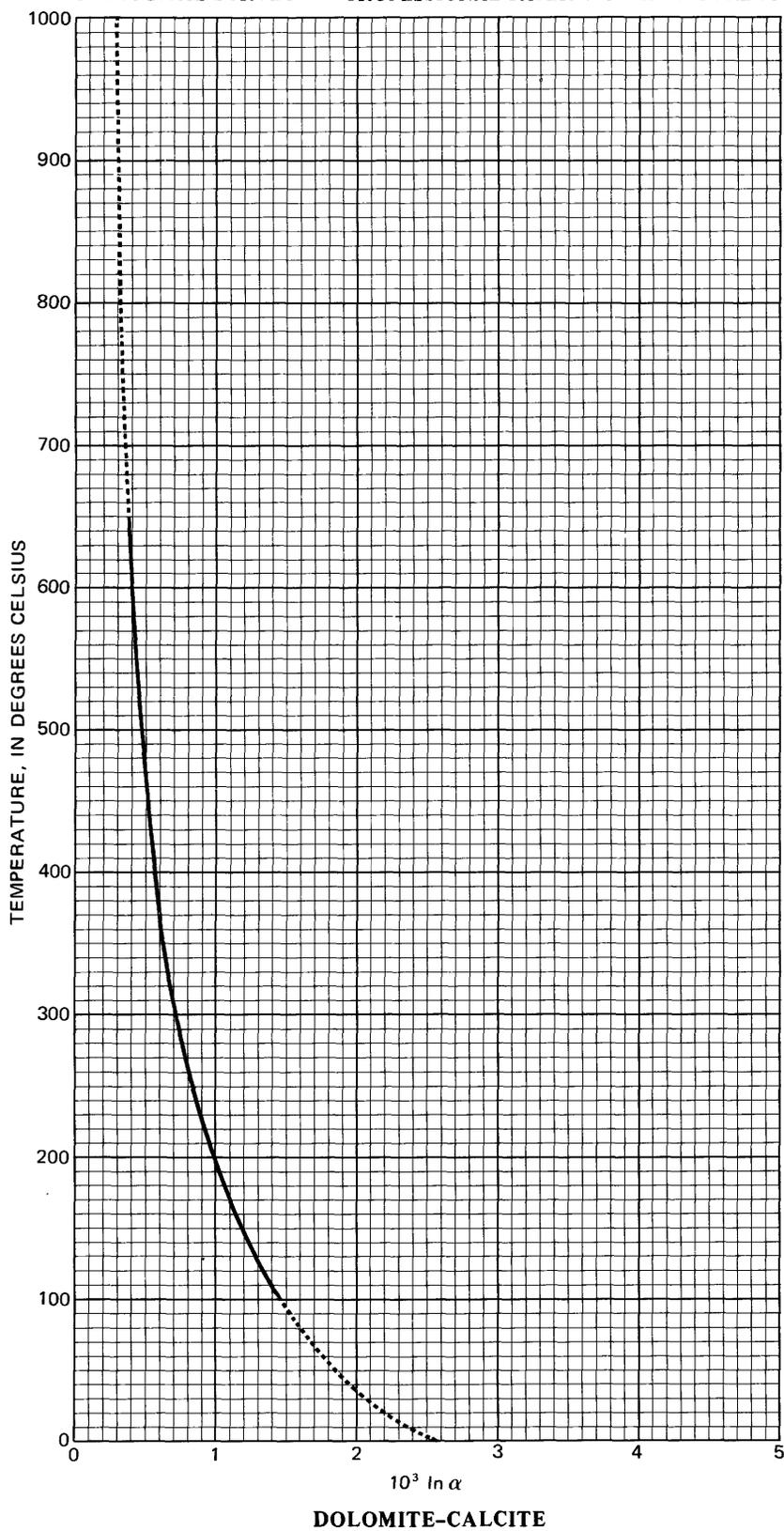
C
A
R
B
O
N

FIGURE 33

Sheppard and Schwarcz (1970): (100° to 650°C).

$$10^3 \ln \alpha = 0.18(10^6 T^{-2}) + 0.17.$$

This curve is constructed from fractionations between coexisting calcite and dolomite in marbles, calibrated by the Mg-calcite solvus thermometer.



C
A
R
B
O
N

FIGURE 34

A, Majzoub (1971):

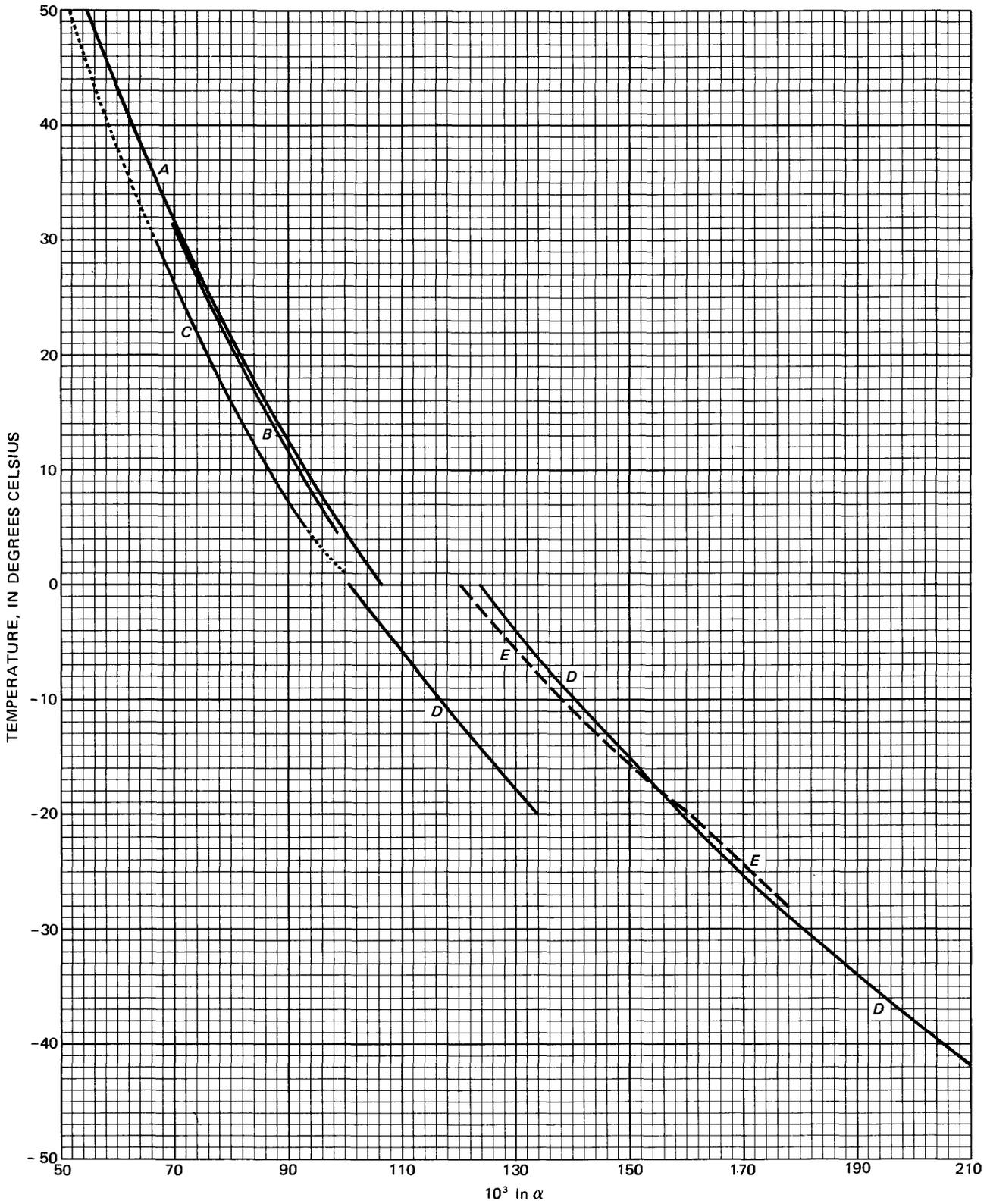
$$10^3 \ln \alpha = 24.844(10^6 T^{-2}) - 76.248(10^3 T^{-1}) + 52.612.$$

B, Because of internal consistency, one curve has been constructed from the data of Stewart and Friedman (1975), Ehhalt and Knott (1965), and Rennow (1970).

C, Merlivat, Botter, and Nief (1963).

D, Merlivat and Nief (1966).

E, Matsuo, Kuniyoshi, and Miyake (1964).



H
Y
D
R
O
G
E
N

WATER(l)-WATER(v) BETWEEN -20° AND $+50^{\circ}$ C
AND WATER(s)-WATER(v) BETWEEN -42° AND 0° C

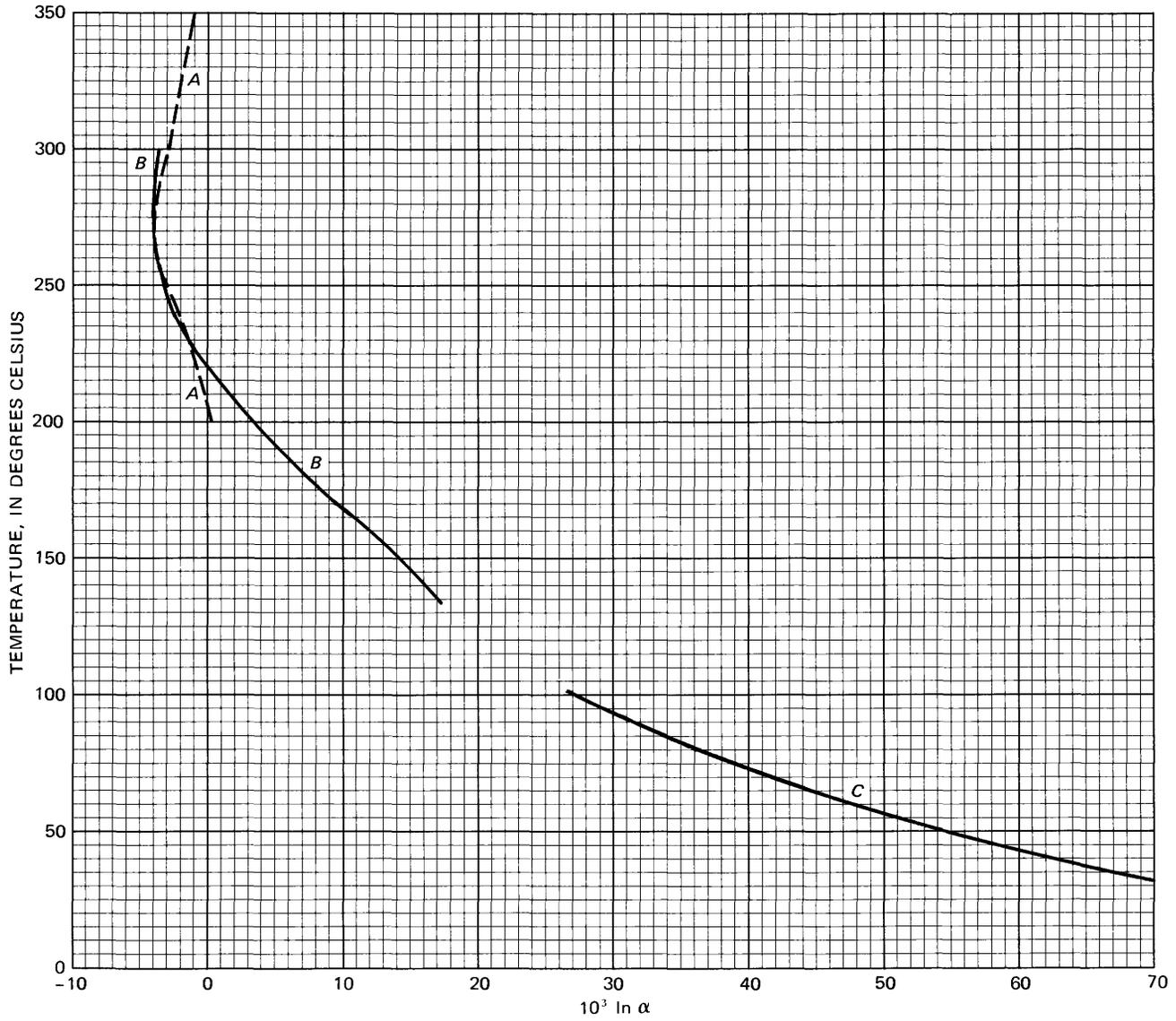
FIGURE 35

A, Merlivat, Botter, and Nief (1963).

B, Bottinga (1968a).

C, Majzoub (1971).

The data from 0° to 100°C of Merlivat, Botter, and Nief (1963) as corrected by Merlivat in Majzoub (1971) agrees very closely with that of Majzoub.

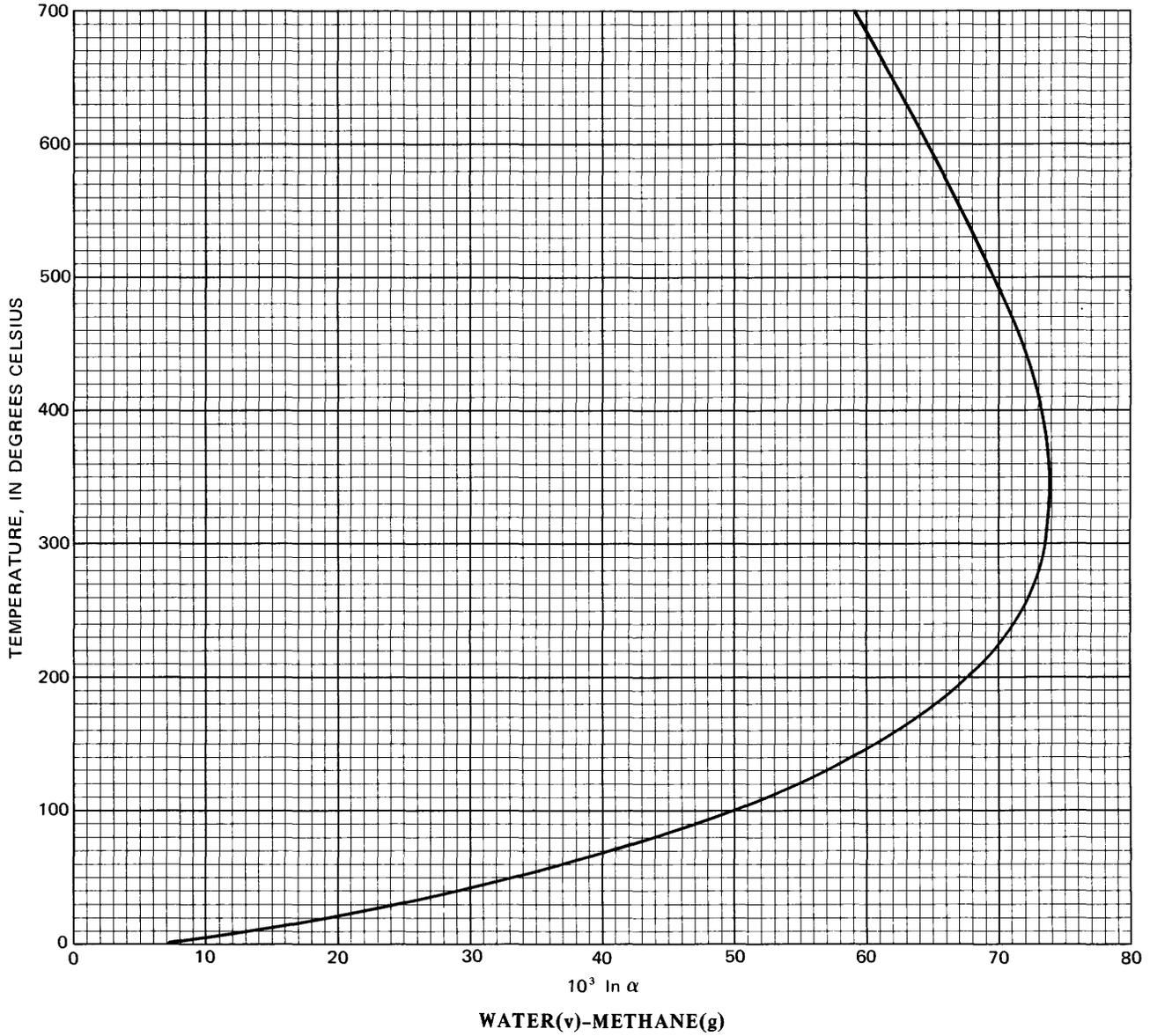


WATER(l)-WATER(v) BETWEEN 30° AND 350°C

H
Y
D
R
O
G
E
N

FIGURE 36

Bottinga (1969a).



H
Y
D
R
O
G
E
N

FIGURE 37

A, Suess (1949):

Water(v)-hydrogen fractionation.

$$10^3 \ln \alpha = 467.6(10^3 T^{-1}) - 303.9 \quad (\text{experimental}).$$

B, Bottinga (1969a):

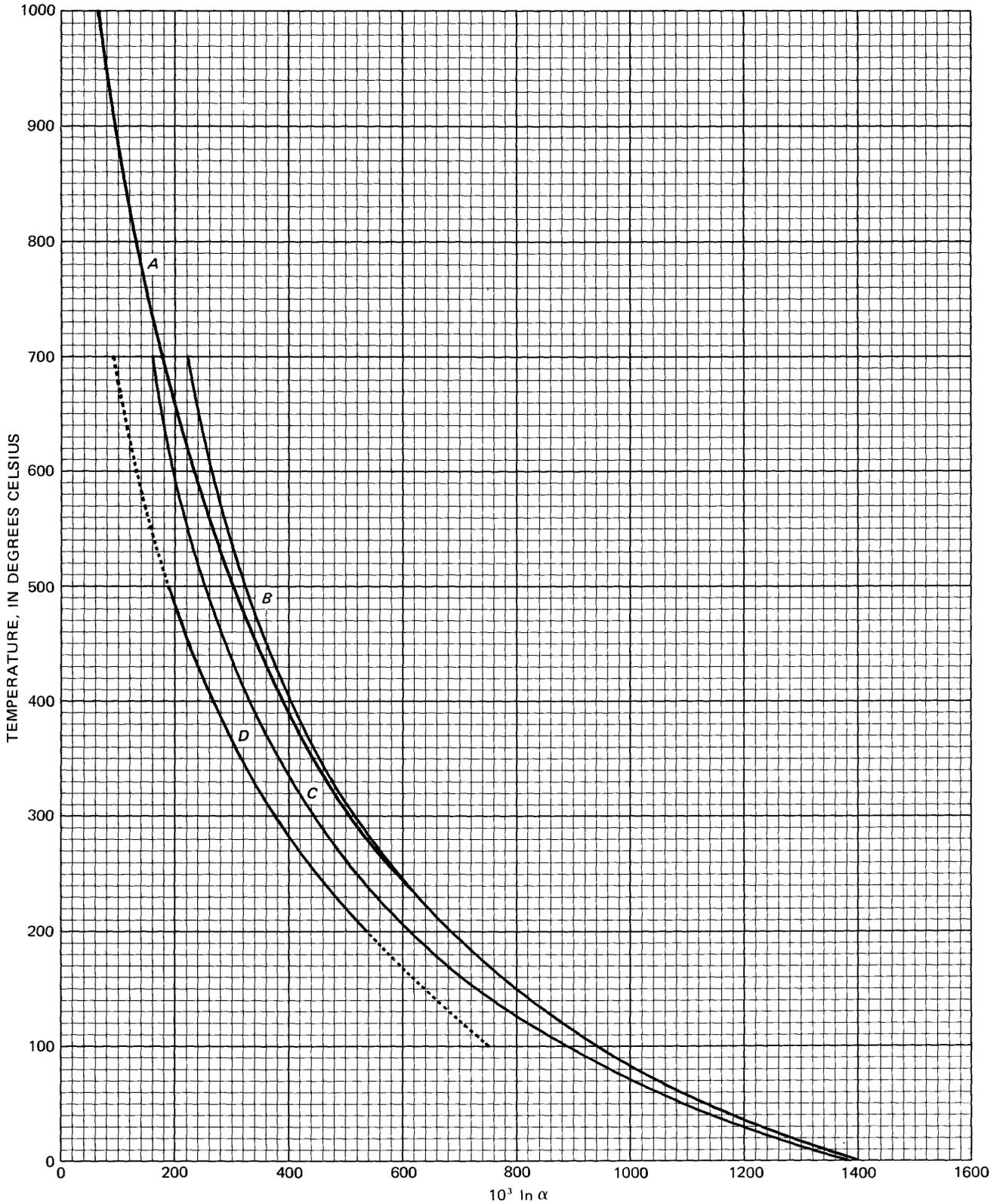
Water(v)-hydrogen(g) (calculated).

C, Bottinga (1969a):

Methane(g)-hydrogen(g) (calculated).

D, Y. Horibe and H. Craig (written commun., 1975).

$$10^3 \ln \alpha = -90.888 + 181.264(10^6 T^{-2}) - 8.949(10^{12} T^{-4}).$$

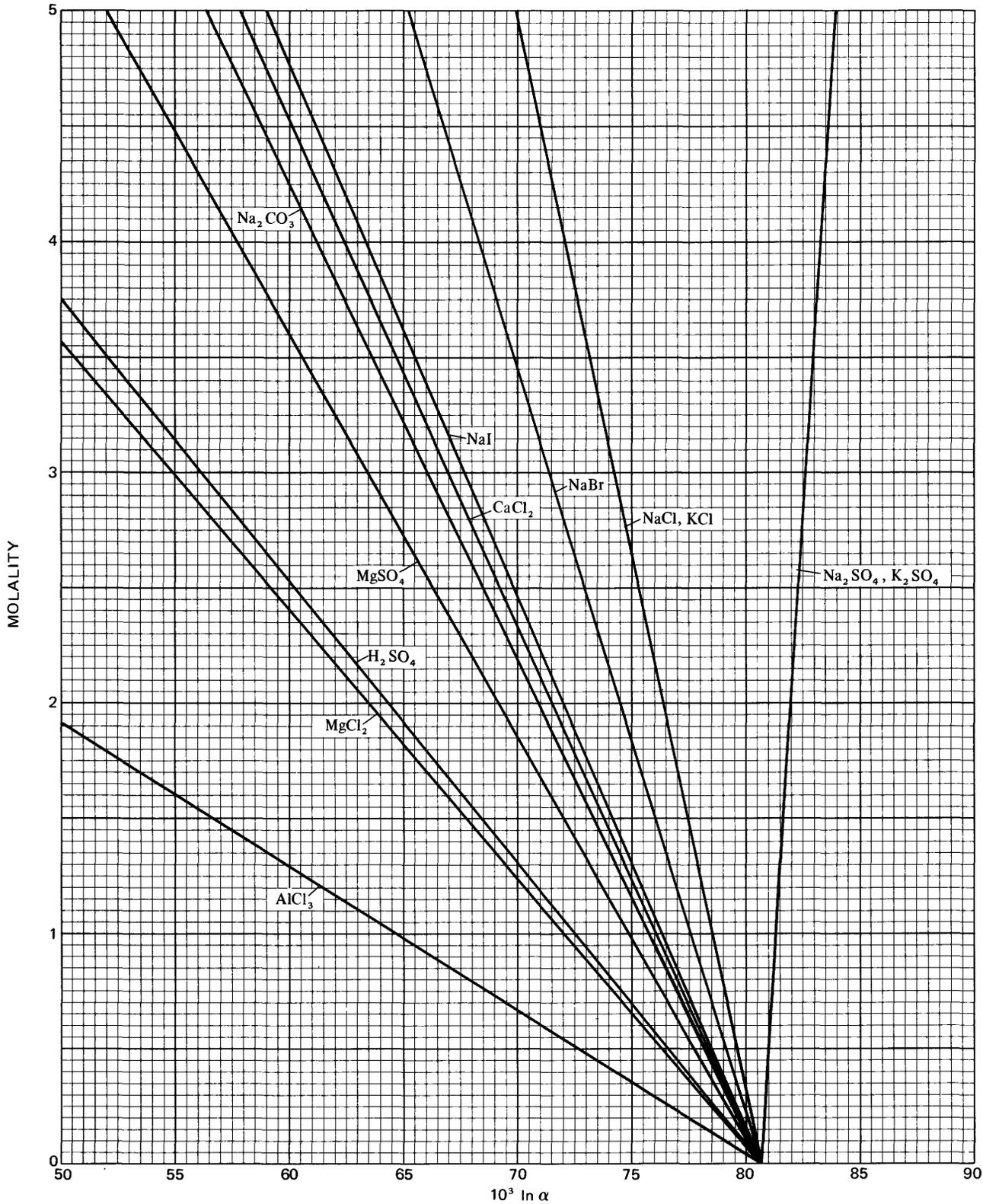


WATER(v)-HYDROGEN(g) AND METHANE(g)-HYDROGEN(g)

H
Y
D
R
O
G
E
N

FIGURE 38

Stewart and Friedman (1975).

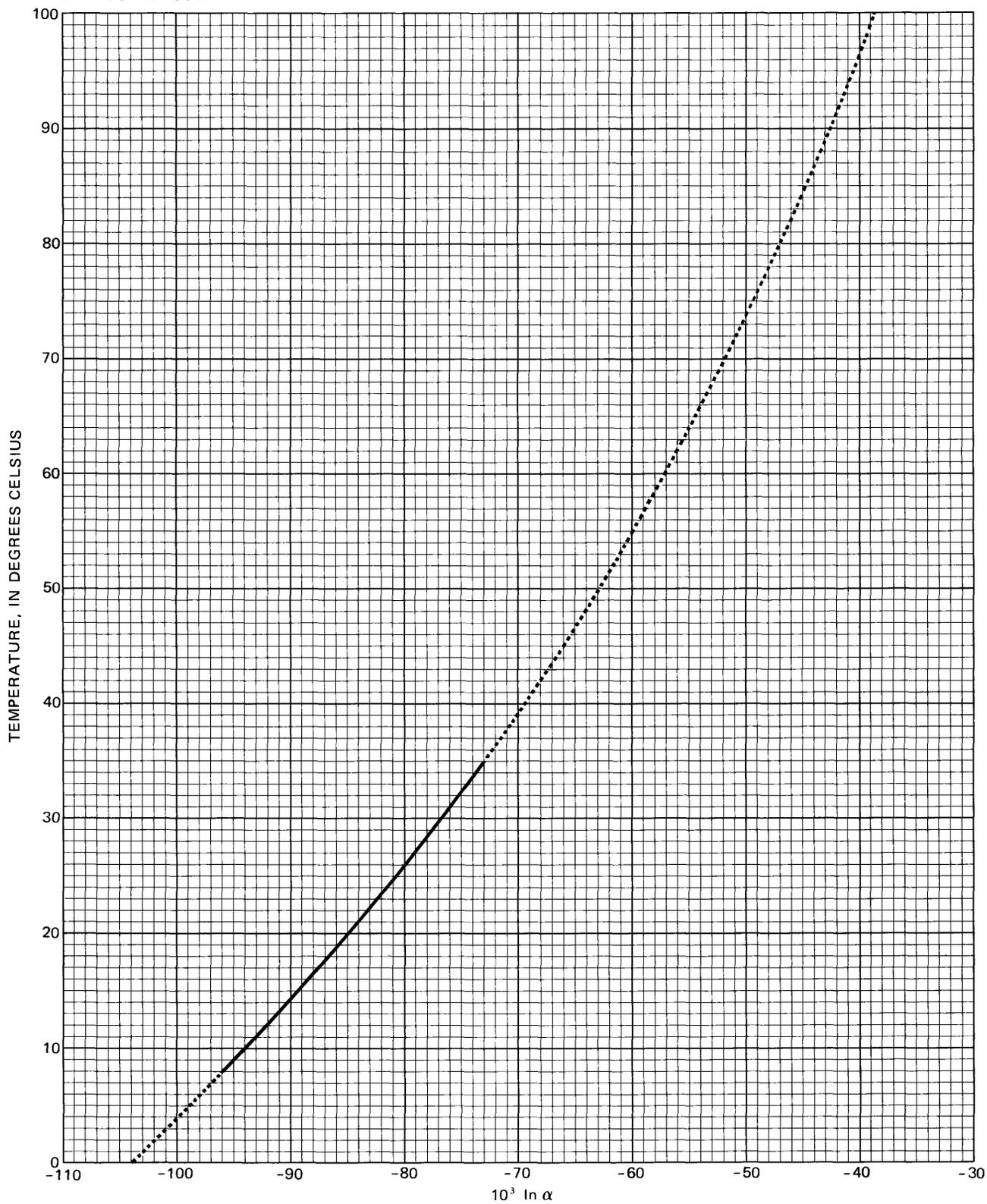


H
Y
D
R
O
G
E
N

WATER(l)-WATER(v), SOLUTE EFFECTS AT 20°C

FIGURE 39

Matsuo, Friedman, and Smith (1972): (8° to 35°C).
 $10^3 \ln \alpha = -14.20(10^6 T^{-2}) + 2.356(10^4 T^{-1})$.



TRONA-WATER (I)

H
Y
D
R
O
G
E
N

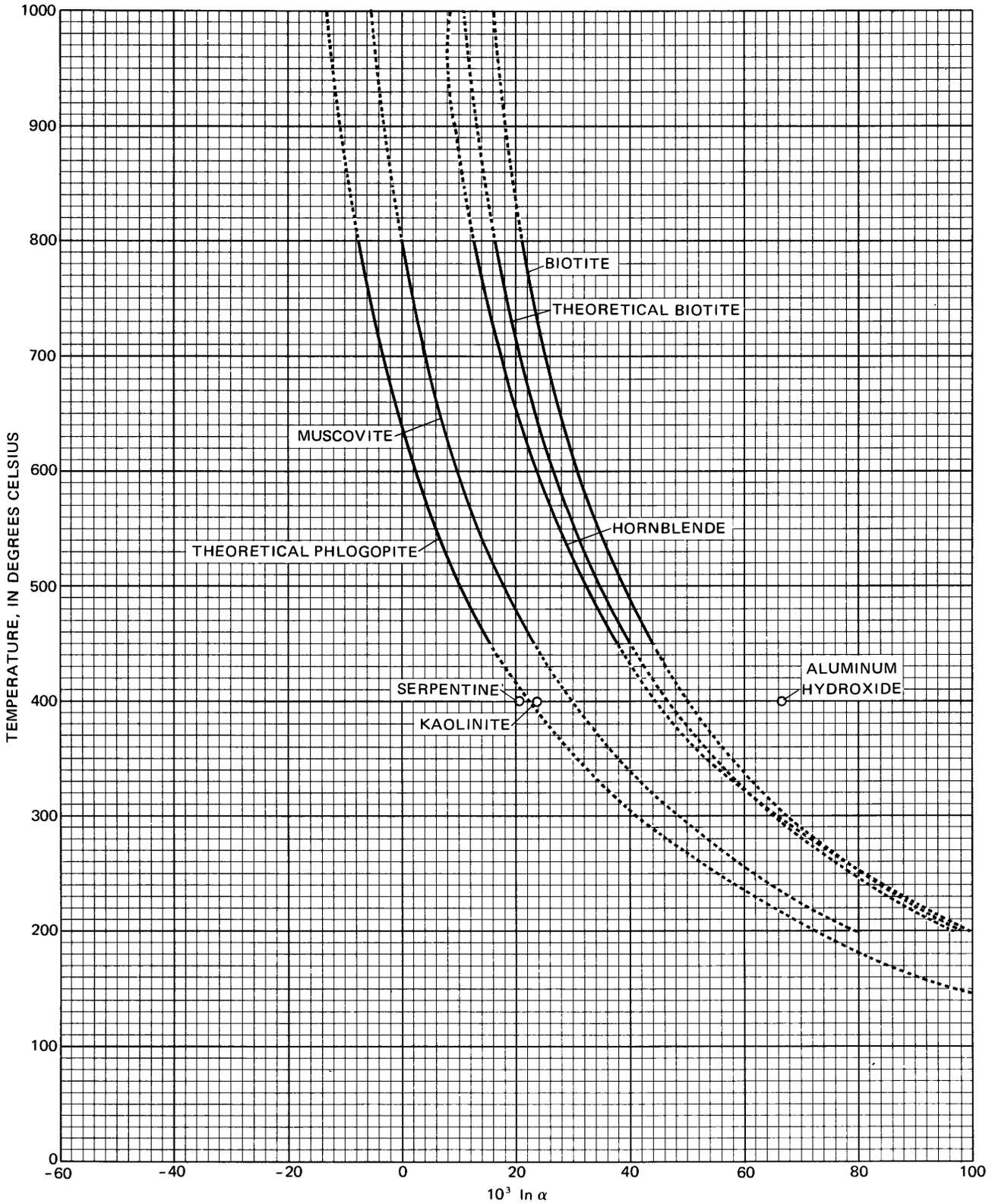
FIGURE 40

Suzuoki and Epstein (1976):

(Biotite)	$10^3 \ln \alpha = 21.3(10^6 T^{-2}) + 2.8;$
(Hornblende)	$10^3 \ln \alpha = 23.9(10^6 T^{-2}) - 7.9;$
(Muscovite)	$10^3 \ln \alpha = 22.1(10^6 T^{-2}) - 19.1;$
(Theoretical phlogopite)	$10^3 \ln \alpha = 22.4(10^6 T^{-2}) - 27.1;$ and
(Theoretical biotite)	$10^3 \ln \alpha = 22.4(10^6 T^{-2}) - 2.9.$

For the mica-water and the amphibole-water systems, the hydrogen isotope fractionations from 450° to 850°C are a function of temperature and molar fractions of the sixfold coordinated cations, regardless of mineral species. The fractionations can be expressed as:

$10^3 \ln \alpha_{(\text{mineral water})} = -22.4(10^6 T^{-2}) + 28.2 + (2x_{\text{Al}} - 4x_{\text{Mg}} - 68x_{\text{Fe}})$, where x is the molar fraction of the cations.



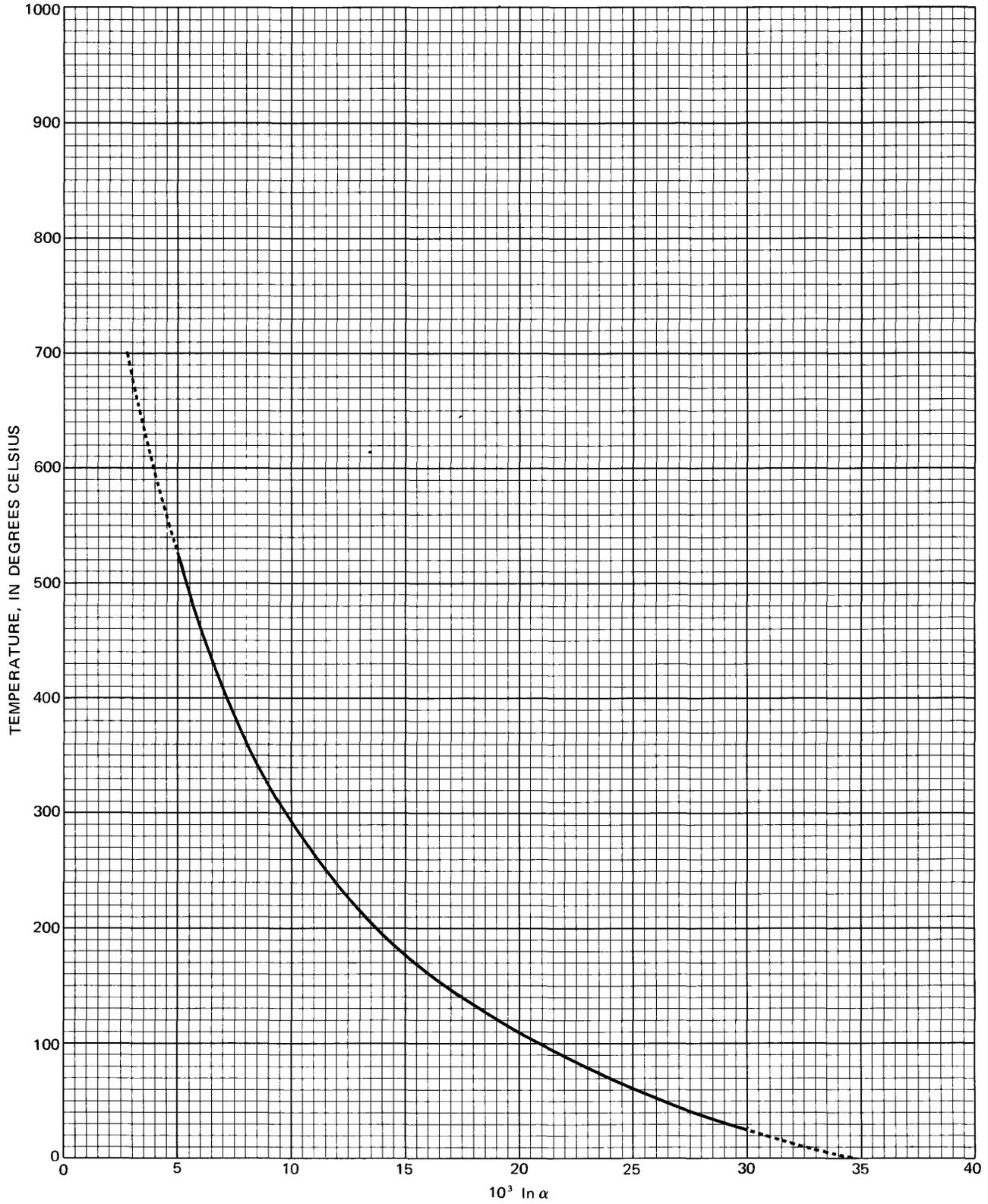
H
Y
D
R
O
G
E
N

WATER-BIOTITE, -THEORETICAL BIOTITE, -HORNBLENDE, -MUSCOVITE, -THEORETICAL PHLOGOPITE, -ALUMINUM HYDROXIDE, -KAOLINITE, AND -SERPENTINE

FIGURE 41

Saiki (1957): (27° to 527°C).

The partition function ratios of $\text{H}_2\text{S}(\text{g})$ and $\text{H}_2\text{S}(\text{aq})$ were assumed to be equal.

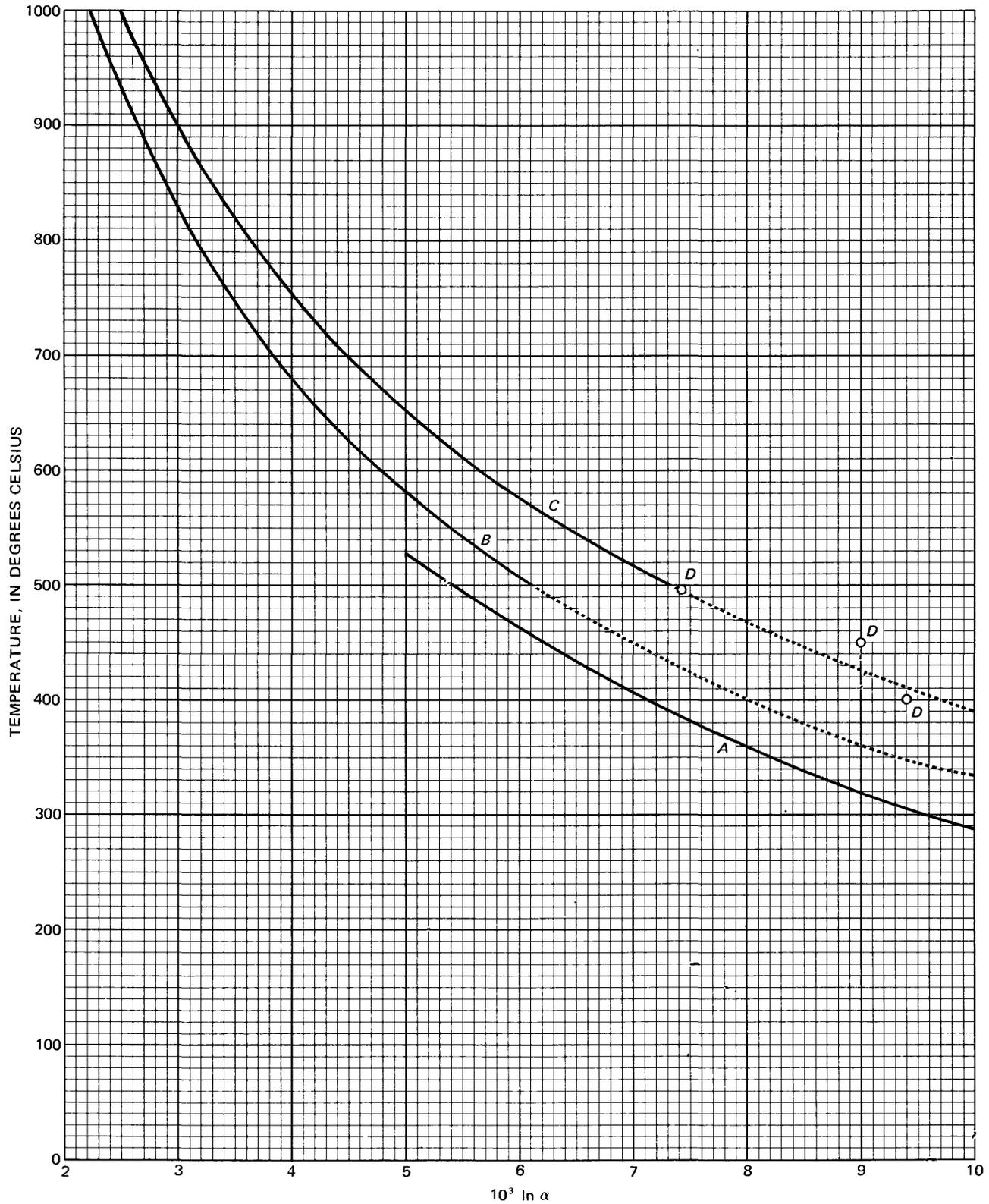


S
U
L
F
U
R

SULFUR DIOXIDE(g)-HYDROGEN SULFIDE(aq AND g) BETWEEN 27° AND 527° C

FIGURE 42

- A*, Sakai (1968): (287° to 527°C).
B, Thode, Cragg, Hulston, and Rees (1971):
 $10^3 \ln \alpha = 3.65(10^6 T^{-2})$ (calculated).
C, Thode, Cragg, Hulston, and Rees (1971):
 $10^3 \ln \alpha = 4.54(10^6 T^{-2}) - 0.30$ (experimental).
D, Grinenko and Thode (1970): (o).

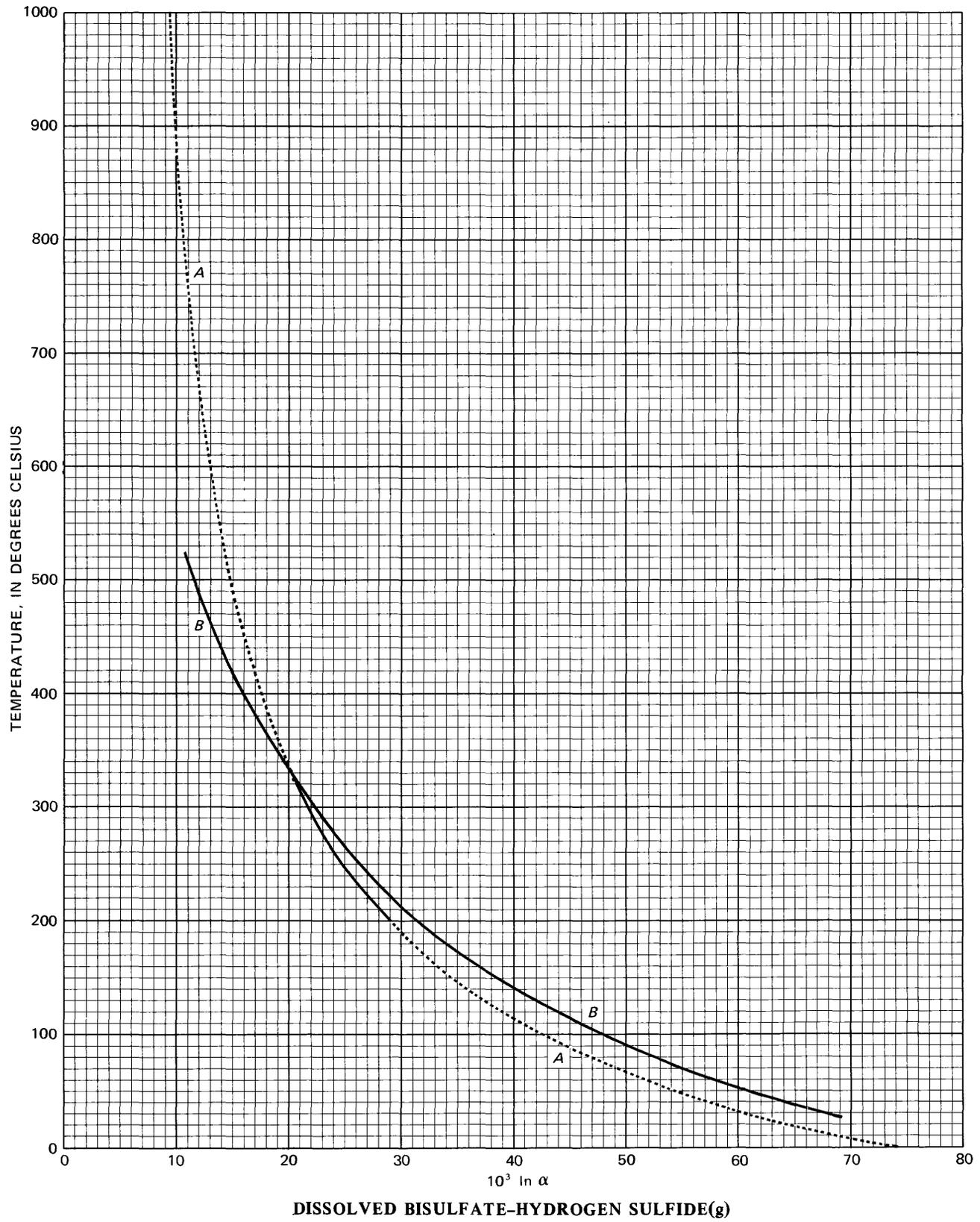


S
U
L
F
U
R

SULFUR DIOXIDE(g)-HYDROGEN SULFIDE(g) BETWEEN 287° AND 1,000°C

FIGURE 43

- A*, Robinson (1973): (200° to 320°C).
 $10^3 \ln \alpha = 5.1(10^6 T^{-2}) + 6.3.$
- B*, Sakai (1968): (27° to 527°C).

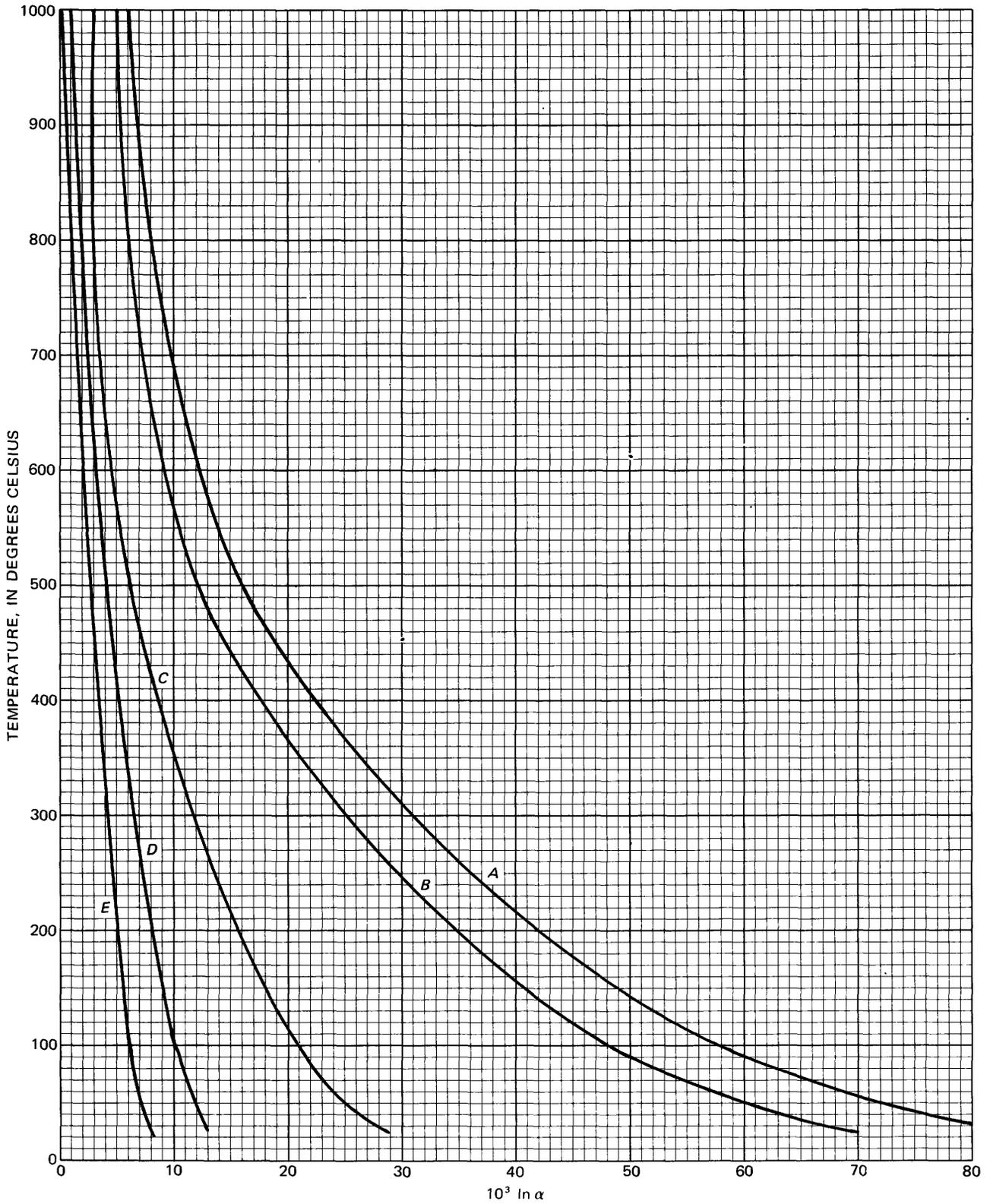


S
U
L
F
U
R

FIGURE 44

Sakai (1968):

- A*, Dissolved sulfate-dissolved sulfide.
- B*, Dissolved sulfate-hydrogen sulfide(g).
- C*, Dissolved sulfate-sulfur dioxide(g).
- D*, Hydrogen sulfide(g)-dissolved sulfide.
- E*, Dissolved sulfate-dissolved sulfide.



S
U
L
F
U
R

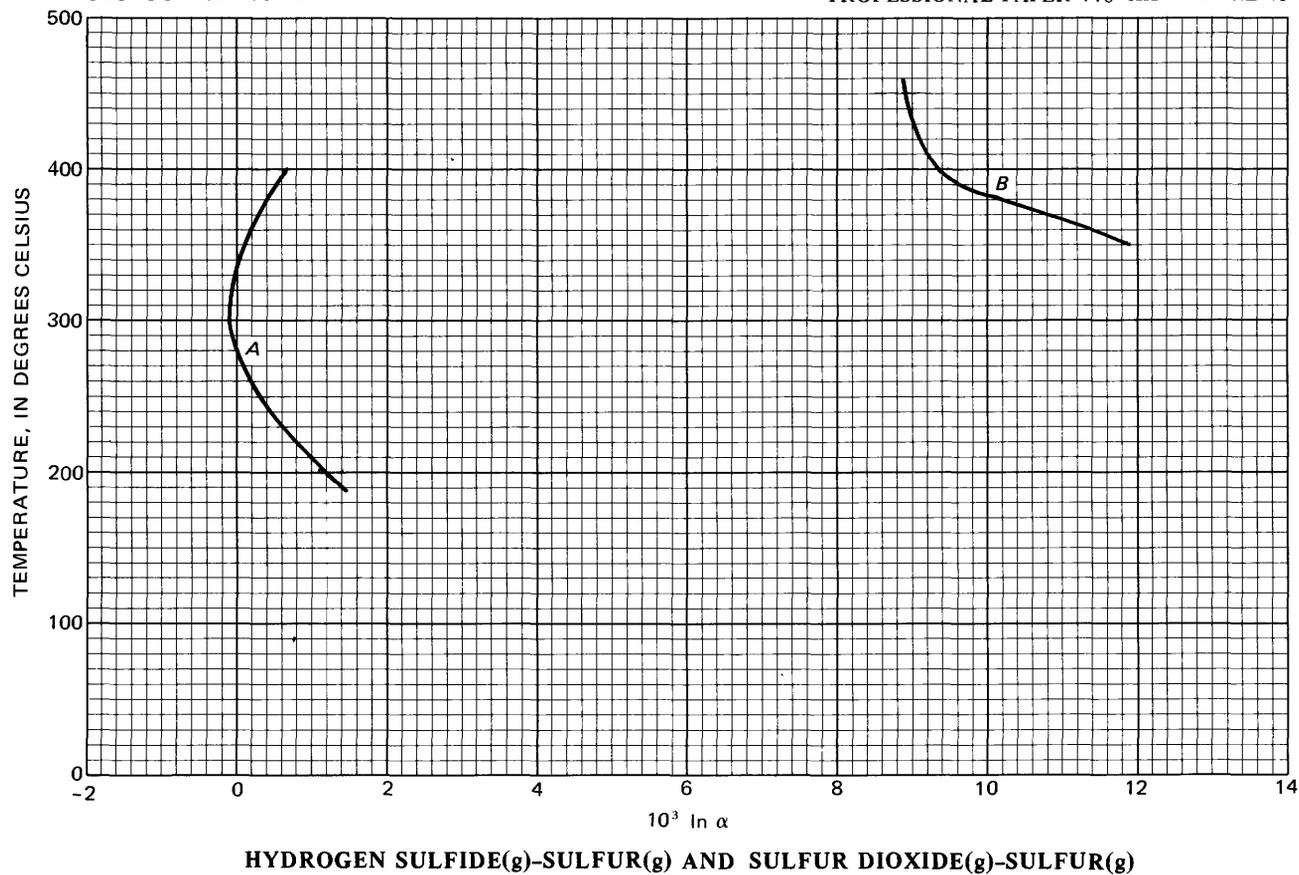
DISSOLVED SULFATE-DISSOLVED SULFIDE, -HYDROGEN SULFIDE(g), AND -SULFUR DIOXIDE(g);
HYDROGEN SULFIDE(g) -DISSOLVED SULFIDE AND DISSOLVED SULFATE-DISSOLVED SULFIDE

FIGURE 45

Grinenko and Thode (1970):

A, Hydrogen sulfide(g)-sulfur(g).

B, Sulfur dioxide(g)-sulfur(g).

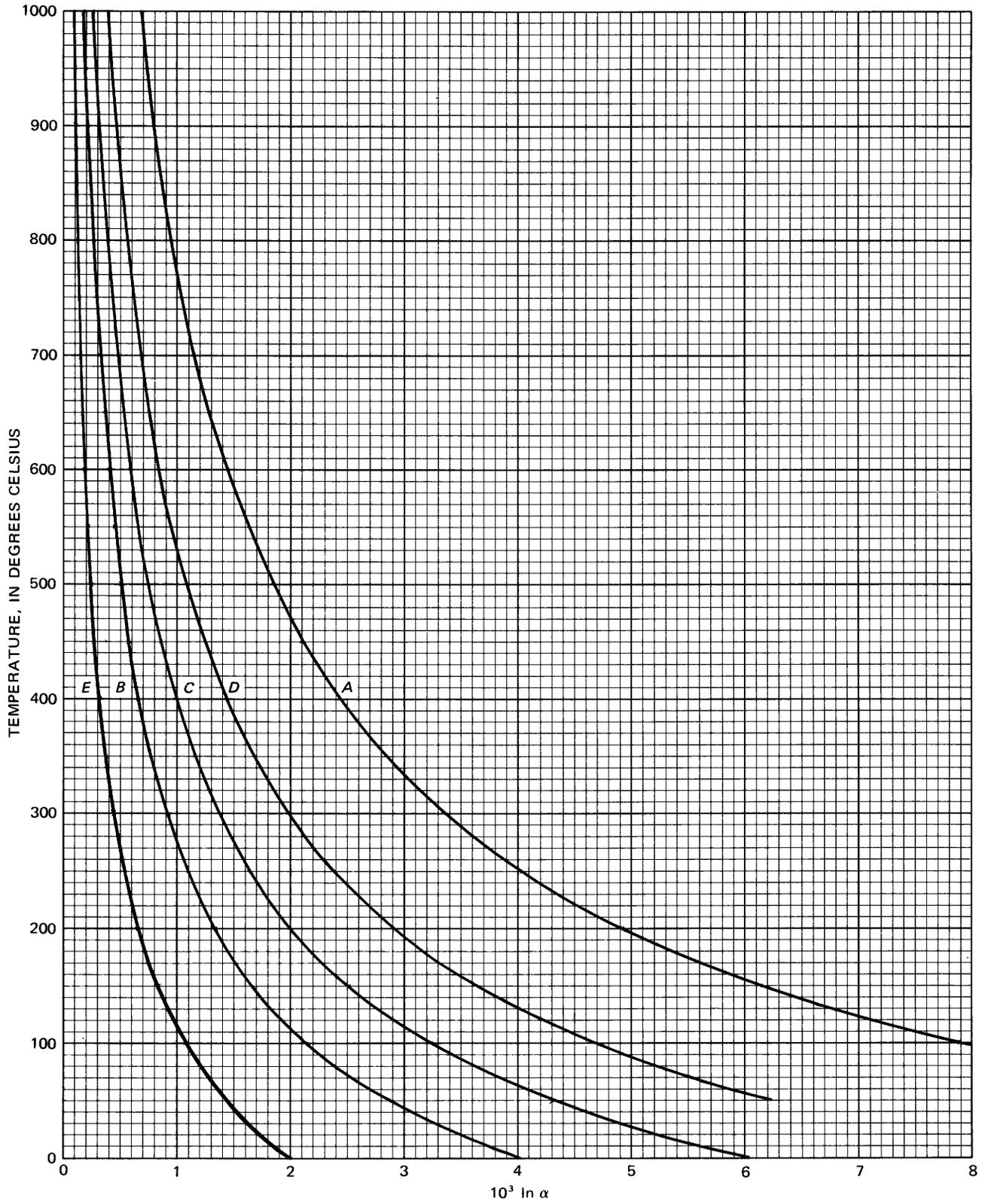


S
U
L
F
U
R

FIGURE 46

Kajiwara and Krouse (1971):

<i>A</i> , Pyrite-galena	$10^3 \ln \alpha = 1.1(10^6 T^{-2})$.
<i>B</i> , Pyrite-sphalerite (pyrite-pyrrhotite)	$10^3 \ln \alpha = 3.0(10^5 T^{-2})$.
<i>C</i> , Pyrite-chalcocopyrite	$10^3 \ln \alpha = 4.5(10^5 T^{-2})$.
<i>D</i> , Chalcocopyrite-galena	$10^3 \ln \alpha = 6.5(10^5 T^{-2})$.
<i>E</i> , Sphalerite-chalcocopyrite (pyrrhotite-chalcocopyrite)	$10^3 \ln \alpha = 1.5(10^5 T^{-2})$.



S
U
L
F
U
R

PYRITE-GALENA, -CHALCOPYRITE, AND -SPHALERITE; SPHALERITE-CHALCOPYRITE;
AND CHALCOPYRITE-GALENA

FIGURE 47

Sphalerite-galena:

<i>A</i> , Kiyosu (1973):	$10^3 \ln \alpha = 8.91(10^5 T^{-2}) - 0.57.$
<i>B</i> , Kajiwara and Krouse (1971):	$10^3 \ln \alpha = 8.0(10^5 T^{-2}).$
<i>C</i> , Czamanske and Rye (1974):	$10^3 \ln \alpha = 7.0(10^5 T^{-2}).$
<i>D</i> , Groctenboer and Schwarcz (1969):	$10^3 \ln \alpha = 6.6(10^5 T^{-2}) - 0.1.$

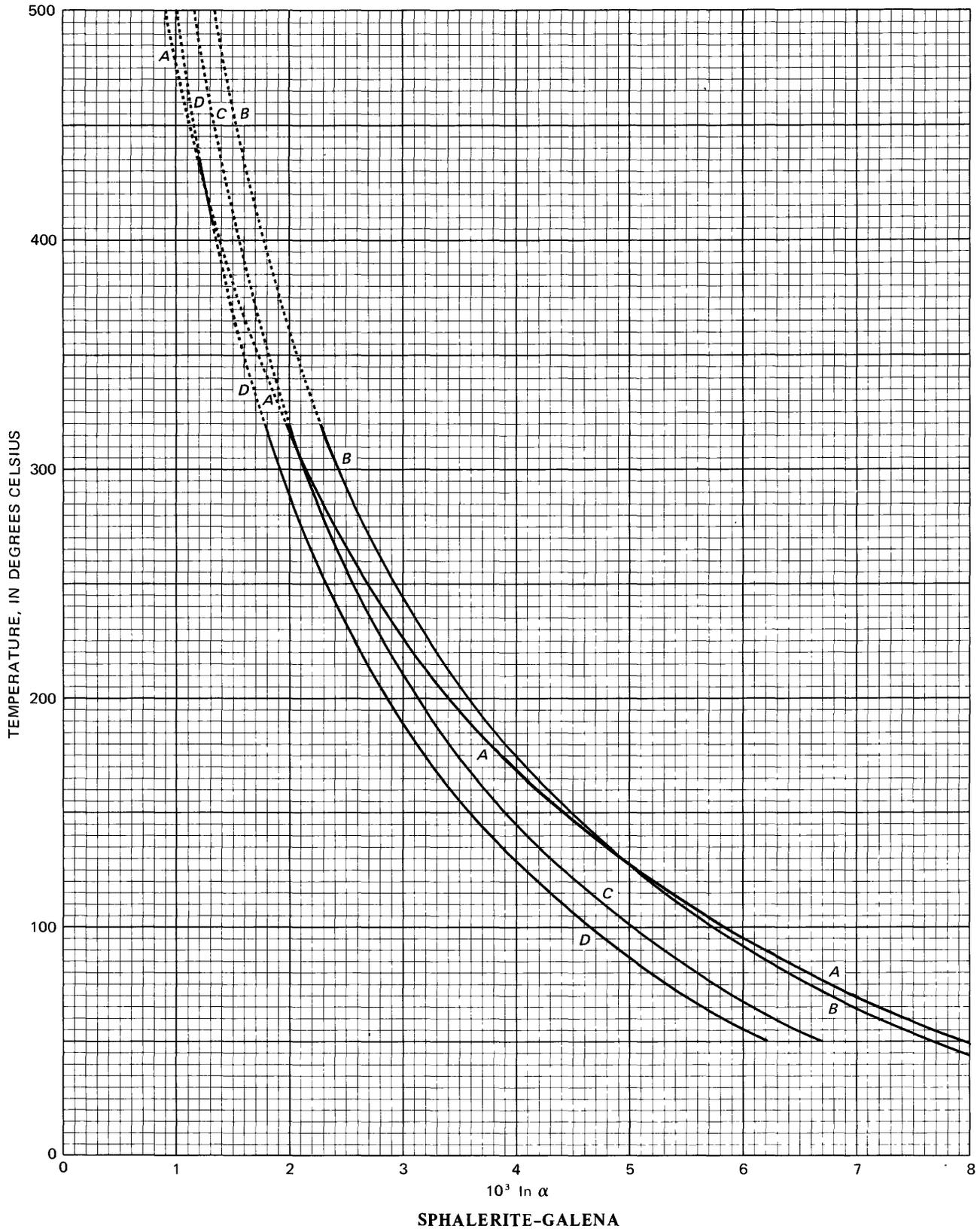
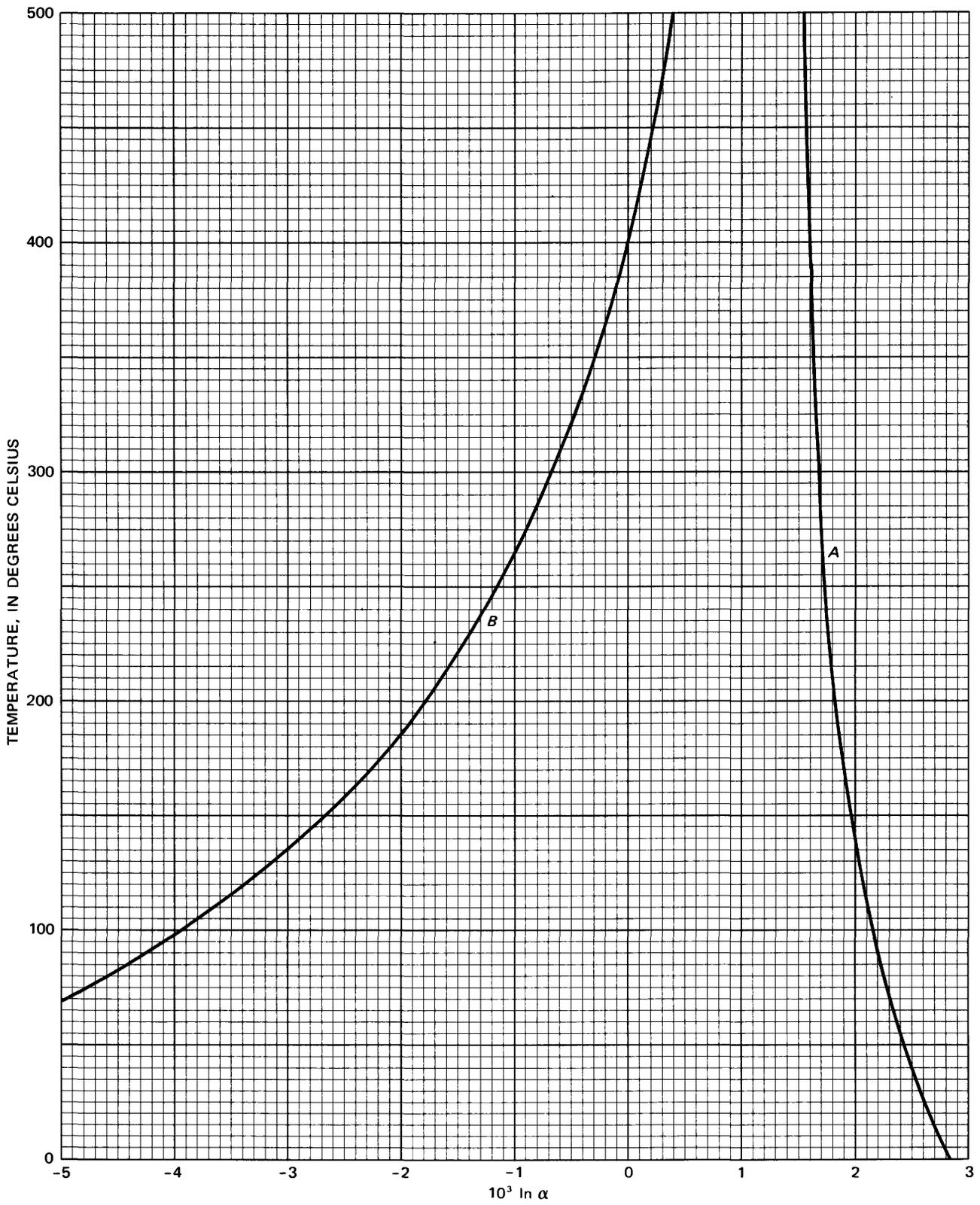


FIGURE 48

Kiyosu (1973): 50° to 340°C.
A, Sphalerite-HS⁻
B, Galena-HS⁻

$$10^3 \ln \alpha = 1.11(10^5 T^{-2}) + 1.36.$$
$$10^3 \ln \alpha = 7.82(10^5 T^{-2}) + 1.7.$$



S
U
L
F
U
R

SPHALERITE-HS⁻ AND GALENA-HS⁻

FIGURE 49

Suvorova (1974).

Experimental:

A, Molybdenite-galena

$$10^3 \ln \alpha = 1.3(10^6 T^{-2}) - 0.80.$$

B, Molybdenite-sphalerite

$$10^3 \ln \alpha = 0.71(10^6 T^{-2}) - 0.15.$$

Calculated: (400° to 750°C).

C, Molybdenite-pyrite

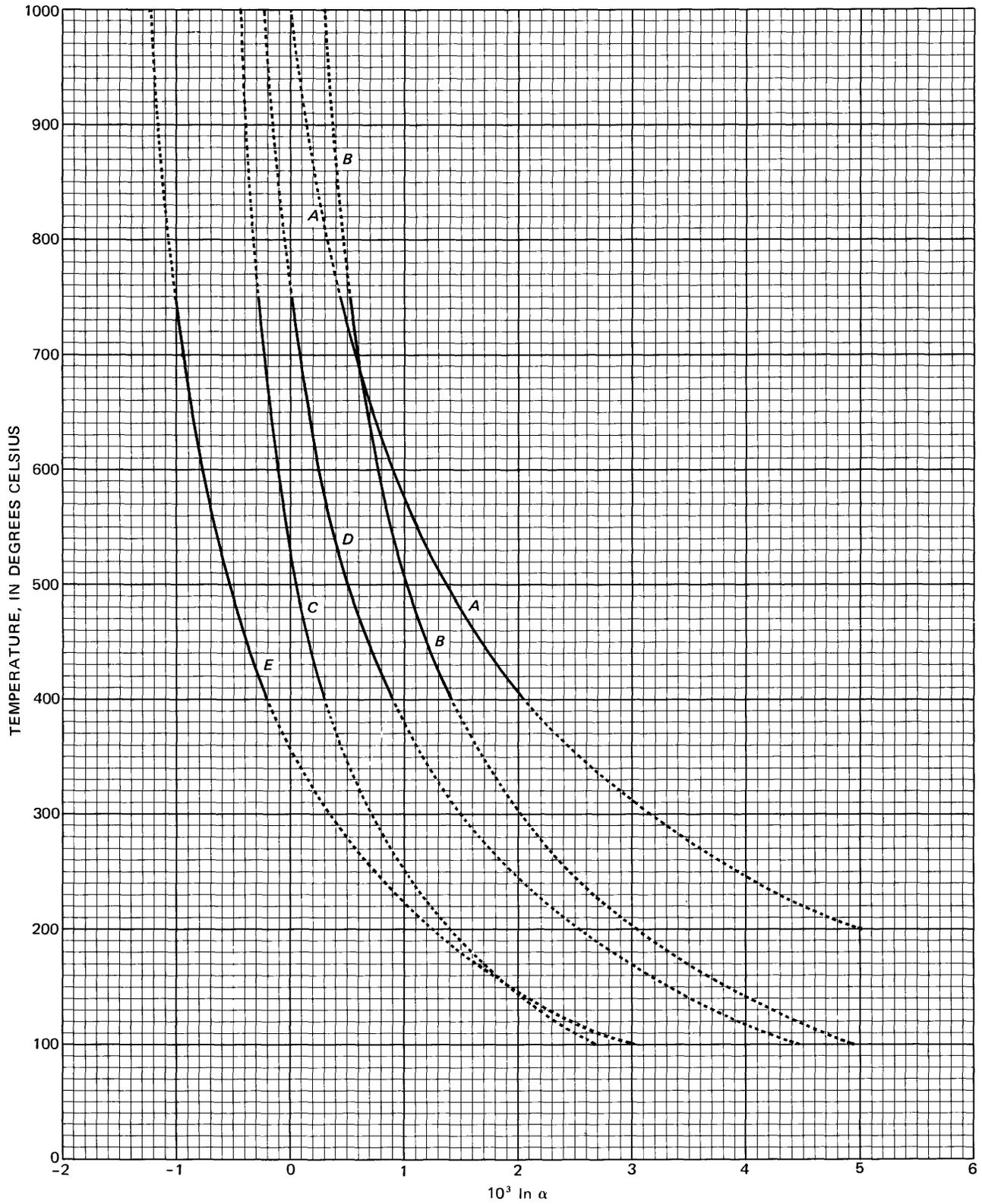
$$10^3 \ln \alpha = 0.48(10^6 T^{-2}) - 0.75.$$

D, Molybdenite-chalcocopyrite

$$10^3 \ln \alpha = 0.72(10^6 T^{-2}) - 0.70.$$

E, Molybdenite-pyrrhotite

$$10^3 \ln \alpha = 0.65(10^6 T^{-2}) - 1.65.$$



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MOLYBDENITE-SPHALERITE, -GALENA, -CHALCOPYRITE, -PYRITE, AND -PYRRHOTITE

