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THE EQUATION OF STATE OF HYDROGEN FROM ONE TO A MILLION ATMOSPHERES PRESSURE

WORK DONE BY:

J. O. Hirschfelder

J. L. Magee

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By M. Ballegos 5-13-96

REPORT WRITTEN BY:

J. O. Hirschfelder

J. L. Magee

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ABSTRACT

The equation of state of hydrogen gas has been extended above the experimental range (3000 atmospheres) to the megabar region. For densities 0.10 to 0.30, the compressed liquid of Lennard-Jones and Devonshire has been used; for densities 0.30 to 0.50, the Einstein solid has been used. At the highest densities, the H_2 molecules lose their rotational degree of freedom.

According to the calculations, H_2 gas compressed from 1 atmosphere at room temperature to a density of 0.50 gm/cc develops a pressure of about 2,500,000 atmospheres; compressed from 1,000 atmospheres to a density of 0.50, it develops a pressure of 870,000 atmospheres. This density is below that of the metallic hydrogen of Wigner and Huntington (0.59) which Bowers predicts would require a pressure of seven megabars.

The theoretical pressures may be as much as a factor 3 too large. The uncertainties arise due to the difficulty in obtaining the intermolecular interactions. At the highest densities the transition of the molecules from the normal rotating variety to non-rotating molecules adds to the uncertainty.

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THE EQUATION OF STATE OF HYDROGEN FROM ONE TO A MILLION ATMOSPHERES PRESSURE

The experimental data for the equation of state of hydrogen only exists for pressures up to 3000 atmospheres and temperatures up to 400° C. We have made what we consider the most satisfactory extrapolation of the equation of state to the extreme conditions of interest. The process is as follows: first, we determine the intermolecular forces. Then we compute the potential wells in which the molecules move. From the potential wells it is a simple matter to calculate the partition function and hence the thermodynamic equation of state. There are three essential difficulties in carrying out this process. 1) At the extraordinarily high pressures in which we are interested, the energy of interaction of hydrogen molecules is so large that it cannot be determined accurately from a combination of first and second order quantum mechanical perturbations. 2) The energy of interaction is a function of the angular orientation of the molecules and this leads to hindered rotation at high densities. 3) Then there is an uncertainty of two entropy units (communal entropy) depending on whether we endow our high density system with the rigidity of a solid or the flexibility of a liquid.

At the highest densities, hydrogen is an Einstein solid. Apparently this solid changes smoothly from a molecular lattice to a metal with increase of density. We find a density of 0.5 gm/cm^3 at a pressure of around one megabar. According to Wigner and Huntington[1] the metallic hydrogen will have a density of 0.59 and Bowers estimates that this requires a pressure of around seven megabars. The most likely errors in both our calculations and the theory of metals are in the direction of giving the density too low at a given pressure.

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[1] E. Wigner and H. B. Huntington, J. Chem. Phys., 3, 764 (1935).

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INTERMOLECULAR FORCES

A. Intermolecular Forces from Experimental Second Virial Coefficients

Lennard-Jones[2] has studied the variation of the second virial coefficient with temperature and found that it is consistent with the assumption that the intermolecular potential between two hydrogen molecules is

$$\epsilon(r) = \epsilon_m \left[2(r^*/r)^9 - 3(r^*/r)^6\right] \text{kcal/mole} \tag{1}$$

Here ϵ_m = .0465 kcal/mole, r is the distance between the molecules and $r^* = 3.50 \times 10^{-8}$ cm is the separation for which the energy of interaction is a minimum. From theoretical considerations, it would seem preferable to express the energy of repulsion as an exponential rather than an inverse power. However, this has never been done for hydrogen. The inverse ninth power is a somewhat smaller power than required for most molecules. Hydrogen is unusually compressible because of its asymmetry (which means that hydrogen, in rotating, occupies an abnormally large volume and part of the compression is attained through a hindering of rotation) and because it does not contain any inner shells.

Henry Eyring[3] has developed a rough method for determining the energy of interaction of two diatomic molecules as a combination of first and second order quantum mechanical perturbation schemes. His calculations for hydrogen were repeated using atomic orbitals without screening constants and a slightly different proportionality constant for the energy of attraction. The calculations were made for these four configurations:

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2) Fowler and Guggenheim, "Statistical Mechanics" (Camb. Press 1939), Chap. VII.

3) Eyring, H., J.A.C.S., 54, 3191 (1932).

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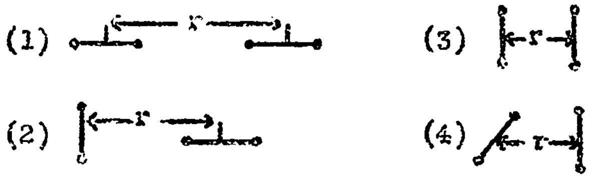

and the following energies obtained:

TABLE I

r (10^{-8} cms)	ϵ_1 (kcal/mole)	ϵ_2 (kcal/mole)	ϵ_3 (kcal/mole)	ϵ_4 (kcal/mole)
2.50	3.80	2.11	1.24	1.24
2.75	1.79	0.98	0.55	0.54
3.00	0.81	0.42	0.18	0.18
3.25	0.33	0.13	0.02	-0.01
3.50	0.10	-0.02	-0.09	-0.09

The absolute values of these energies are probably not correct but it is clear that if the hydrogen molecules always approached each other in the most favorable manner they could come approximately 0.35 Å closer to each other. Thus, for non-rotating molecules we take the interaction potential to be given by Eq. (1) with the exception that the separation for minimum energy is taken to be $r^* = 3.15 \times 10^{-8}$ cm.

II. EXPERIMENTAL EQUATION OF STATE DATA AT ROOM TEMPERATURE (300° K)

Deming and Shupe[4)] have measured the density of hydrogen gas at room temperatures up to a pressure of 1000 atmospheres. In order to obtain the corresponding entropies, it is convenient to express the equation of state of hydrogen

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[4)] Newitt, D.M., "High Pressure Plants and Fluids at High Pressure" (Oxford 1940), p. 467.

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In the Beattie-Bridgman form[5]:

$$P = \frac{RT^2}{v^2}\left[v + B_o\left(1 - (b/v)\right)\right]\left[1 - (c/vT^3)\right] - A_o\left[1 - (a/v)\right] \qquad (2)$$

Here v is the molar volume in liters, P is the pressure in atmospheres, T is the absolute temperature, and the constants are: $R = .08206$, $A_o = .1975$, $a = -.00506$, $B_o = .02096$, $b = -.04359$, $c = 504$. From this it follows that the entropy is given by the equation:

$$S = S_1^o + 1.987\left[\ln(.08206\ T) + \ln v - (B_o + 2c/T^3)/v \right.$$
$$\left. - B_o(-(1/2)b + c/T^3)/v^2 + 2cB_ob/(3T^3v^3)\right] \text{kcal/mole}$$

Here S_1^o is the entropy of hydrogen gas at one atmosphere pressure neglecting gas imperfection (omitting nuclear spin). The values of S_1^o have been tabulated[6] up to 5000° K. At 300° K, $S_1^o = 31.269$ and we obtain the values given in Table II.

TABLE II

T = 300° K

P atm.	V cc/mole	S kcal/mole
1	24,620	31.269
25	998.8	24.859
50	506.8	23.468
75	342.9	22.648
100	261.1	22.063
150	179.3	21.228
200	138.5	20.628
300	97.78	19.763
400	77.36	19.128
500	65.16	18.624
600	57.01	18.201
800	46.81	17.514
1000	40.61	16.960

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[5] Hougen and Watson, "Industrial Chemical Calculations" (Wiley 1936), p.391.

[6] Hirschfelder, McClure, Curtis and Osborne, "Thermochemical Properties of Propellant Gases", N.D.R.C. A-116, p.63.

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III. POTENTIAL ENERGY WELLS FOR MOTION OF HYDROGEN MOLECULE

The potential energy of an assembly may be estimated in the following manner. Most types of van der Waal's forces are additive and short ranged. The energy of interaction of the assembly with a particular molecule is therefore just a sum of the energy of interaction of this molecule with each of its nearest neighbors. The energy of interaction with the next layer of molecules is already negligible for the case of hydrogen. Lennard-Jones and Devonshire showed that the properties of a compressed gas can be determined by placing all of the molecules except one in their mean lattice positions and calculating the energy of this one molecule as a function of position. The potential energy well so formed is almost spherical in shape and it is convenient to average out the angular dependence. The energy of the assembly per molecule, w(R), as a function of R, the distance of the molecule from its lattice point, is:

$$w(R) = 6\int_0^\pi \epsilon\left[\sqrt{R^2 + a^2 - 2aR\cos\theta}\right]\sin\theta \, d\theta \qquad (3)$$

here the factor 6 is made up of the number of nearest neighbors, 12 (for spherical close packing) and 1/2 (because the energy of interaction of a pair of molecules must be charged equally to the two molecules). Also, $\underline{a}$ is the distance between nearest neighbors. The molar volume for hexagonal close packing is

$$V = a^3 \times 10^{-24} \times 6.023 \times 10^{23} \times (2)^{-(1/2)} = .4259\ a^3 \text{ cc/mole} \qquad (4)$$

and the density of hydrogen is

$$\Delta = 2.016/V = 4.734/a^3 \text{ gm/cc} \qquad (5)$$

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If the energy of interaction between two molecules is given by Eq. (1), it is easy to show that

$$w(R) = w(0) + 24\ \epsilon_m\ (r*/a)^9\ \ell_9 - 36\ \epsilon_m\ (r*/a)^6\ m_6 \qquad (6)$$

where

$$\ell_9 = \frac{1 + 5(R/a)^2 + 3(R/a)^4 + (1/7)(R/a)^6}{(1 - (R/a)^2)^7} - 1$$

$$m_6 = \frac{1 + (R/a)^2}{[1 - (R/a)^2]^4} - 1$$

$$w(0) = 12\ \epsilon(a)$$

Fig. 1 shows these potential energy wells for different densities of hydrogen. From the shape of these curves it would appear that the potential energy wells could be represented by the equation:

$$w(R) - w(0) = B_n(R/a)^n$$

Here n and B_n were constants chosen so as to make the potential correct when R has such values that w(R) - w(0) is either around 5 kcal/mole or 10 kcal/mole. For densities below .30 gm/cc, n varies from 3 to 2 and for higher densities n is approximately 2. The value of 2 for n is very convenient because it corresponds to the basic assumption in the Einstein solid. Similar potential energy wells were obtained for the case of hindered rotation. The values obtained are given in Table III and also the values of the Einstein θ.

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TABLE III

Unhindered Rotation				Hindered Rotation		
Δ	n	B_n	θ	n	B_n	θ
.10	6.652	1034.4				
.12	5.439	737.8				
.14	4.487	526.3				
.16	3.743	382.8				
.18	3.692	540.7				
.20	3.144	398.8				
.22	2.903	410.3				
.24	2.715	404.9				
.26	2.540	414.8				
.28	2.406	411.7				
.30	2	264.4	1009	2	125.2	694
.32	2	313.6	1122	2	143.9	760
.34	2	369.7	1243	2	165.2	830
.36	2	433.6	1372	2	188.8	905
.38	2	505.0	1508	2	215.6	985
.40	2	584.8	1651	2	245.8	1070
.42	2	673.6	1800	2	278.8	1158
.44	2	772.0	1957	2	315.4	1251
.46	2	880.3	2122	2	355.9	1350
.48	2	999.1	2293	2	400.4	1451
.50	2	1128.4	2468	2	449.1	1558

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IV. LENNARD-JONES AND DEVONSHIRE EQUATION OF STATE FOR COMPRESSED GAS

Lennard-Jones and Devonshire showed that the properties of a gas can be expressed in terms of the potential wells discussed in the preceding paragraph. The boiling points, Boyle point, critical point, etc. as well as the properties of liquids can be calculated accurately on this basis. It is to be expected that this method becomes better as the material becomes more compressed.

The free volume, J, is given by the integral:

$$J = 4\pi a^3 \int_0^\infty (r/a)^2 \, e^{-(B/RT)(r/a)^n} \, d(r/a) = 4\pi a^3 \, (RT/B)^{3/n} (1/n) \, \Gamma(3/n) \qquad (8$$

It is easy to determine the properties of the assembly in terms of the free volume. The equations are given in Fowler and Guggenheim. If we let

$$D = 2.30259 \left[1.07710 - (3/n)(\log_{10} B + 2.70182) + \log_{10} \Gamma\left(1 + (3/n)\right) \right] \qquad (9)$$

the properties of the system are:

$$S = S_1^o + 1.987 \left[-\ln\Delta + (3/n) \ln T - \ln 82.06\,T + (3/n) + D \right] \qquad \text{kcal/mole deg.} \quad (1$$

$$P = -\frac{6\Delta^2}{2.016} \frac{d\varepsilon(a)}{d\Delta} + \frac{\Delta RT}{2.016} \left[1 + \Delta \frac{dD}{d\Delta} \right] \frac{3 \times 82.06\, T \ln T}{2.016} \frac{\partial(1/n)}{\partial(1/\Delta)} \qquad \text{atm.} \qquad (11)$$

$$E = 6\varepsilon(a) + \frac{3 \times .08206\, T}{n} + E_1^o \qquad \text{kcal/mole} \qquad (12)$$

V. EINSTEIN SOLIDS

When the matter becomes very dense it becomes rigid and loses the communal entropy which characterizes the liquid and gaseous phases. At densities above 0.30 gm/cc we assume that this communal entropy is lost. The Lennard-Jones and Devonshire compressed gas then becomes an Einstein solid. At the high temperatures considered here, the difference between the Einstein and Debye treatments is negligible. In this theory the properties of the assembly are:

[redacted]

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$$S = S_1^0 + 0.209 - 11.438 \log_{10} T - 13.725 \log_{10} (1 - e^{-\Theta/T}) + 5.961(\Theta/T)\, e^{-\Theta/T}/(1 - e^{-\Theta/T}) \quad \text{kcal/mole deg.} \tag{13}$$

$$P = -\frac{6\Delta^2}{2.016}\frac{d\epsilon(a)}{d\Delta} + 61.06\,\Delta^2 \frac{d\Theta}{d\Delta}\left[\frac{1 + e^{-\Theta/T}}{1 - e^{-\Theta/T}}\right] \quad \text{atm.} \tag{14}$$

$$E = E_1^0 + 6\epsilon(a) + .002980\,\Theta\left[\frac{1 + e^{-\Theta/T}}{1 - e^{-\Theta/T}}\right] \quad \text{kcal/mole} \tag{15}$$

VI. HINDERED ROTATION

It is convenient to idealize the hindering of rotation of the molecules by supposing that there are only two possibilities. If the molecules rotate they rotate freely and occupy the large amount of space characterized by their intermolecular potential. However, the molecules can completely stop rotating in which case they lose the entropy of rotation but gain the advantage of a lower potential energy. It is easy to form the equilibrium constant for the ratio of the number of hindered molecules, N_h, to the number of rotating molecules, N_r. The subscript r will refer to rotating and h to hindered.

$$N_h/N_r = \exp\left[\left(-(E_h - E_r) - (T/1000)(S_r - S_h)\right)/RT\right] \tag{16}$$

The entropy difference due to the rotation is

$$S_{\text{rotation}} = R \ln \frac{8\pi^2 IkT}{2h^2} = R \ln \frac{T}{170.8} \tag{17}$$

This is not the total entropy difference between the hindered and non-hindered forms since the potentials are different for the two cases.

We have assumed that the transition from the rotating to the hindered molecules occurs when $N_h = N_r$. This transition occurs at densities of the order of 0.25 gm/cc when T = 1000° K and at higher densities for higher temperatures.

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Using the Einstein solid energies and entropies, the transition points have been calculated. They are given in Table IV.

TABLE IV

T	$\Delta_{trans.}$	E_r	S_r	E_h	S_h	$E_{trans.}$	$S_{trans.}$
2000	0.320	29.50	16.96	24.30	14.37	26.90	15.66
3000	0.380	48.34	19.04	38.83	15.86	43.59	17.45
4000	0.431	68.85	20.59	54.31	16.94	61.58	18.77
5000	0.474	90.51	21.84	70.43	17.81	80.47	19.83

The transition for T = 1000 occurs at a density below 0.30 and is thus not in our Einstein solid.

$E_{trans.}$ and $S_{trans.}$ are respectively $(E_r + E_h)/2$ and $(S_r + S_h)/2$. They are the E and S which have been assigned to the transition points.

VII. RESULTS OF CALCULATIONS

The calculated adiabatics are given in Fig. 2. The curves shown have been made up as follows: Einstein solid for densities 0.30 to 0.60; Lennard-Jones and Devonshire compressed gas for densities 0.10 to 0.30; and the last low density point for each curve is experimental (Table II).

The rotation hindering transition lowers the pressure for the low entropy curves at the higher densities. These curves have been drawn rather arbitrarily and the actual pressures probably do not change as abruptly as indicated. The centers of the transitions are given in Table IV; the slope of the curve in this region is not known at all.

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The errors in the pressure calculations are all in the direction to make the calculated values too high. The actual pressures may be as much as a factor 8 lower than those given in Fig. 2 in the megabar region.

The pressure isothermals are given in Fig. 3. The same data are used, of course, in this plot as in the previous one. Again the transitions for the hindering of rotation are drawn arbitrarily except for position.

Entropies and energies are given in Figs. 4 and 5.

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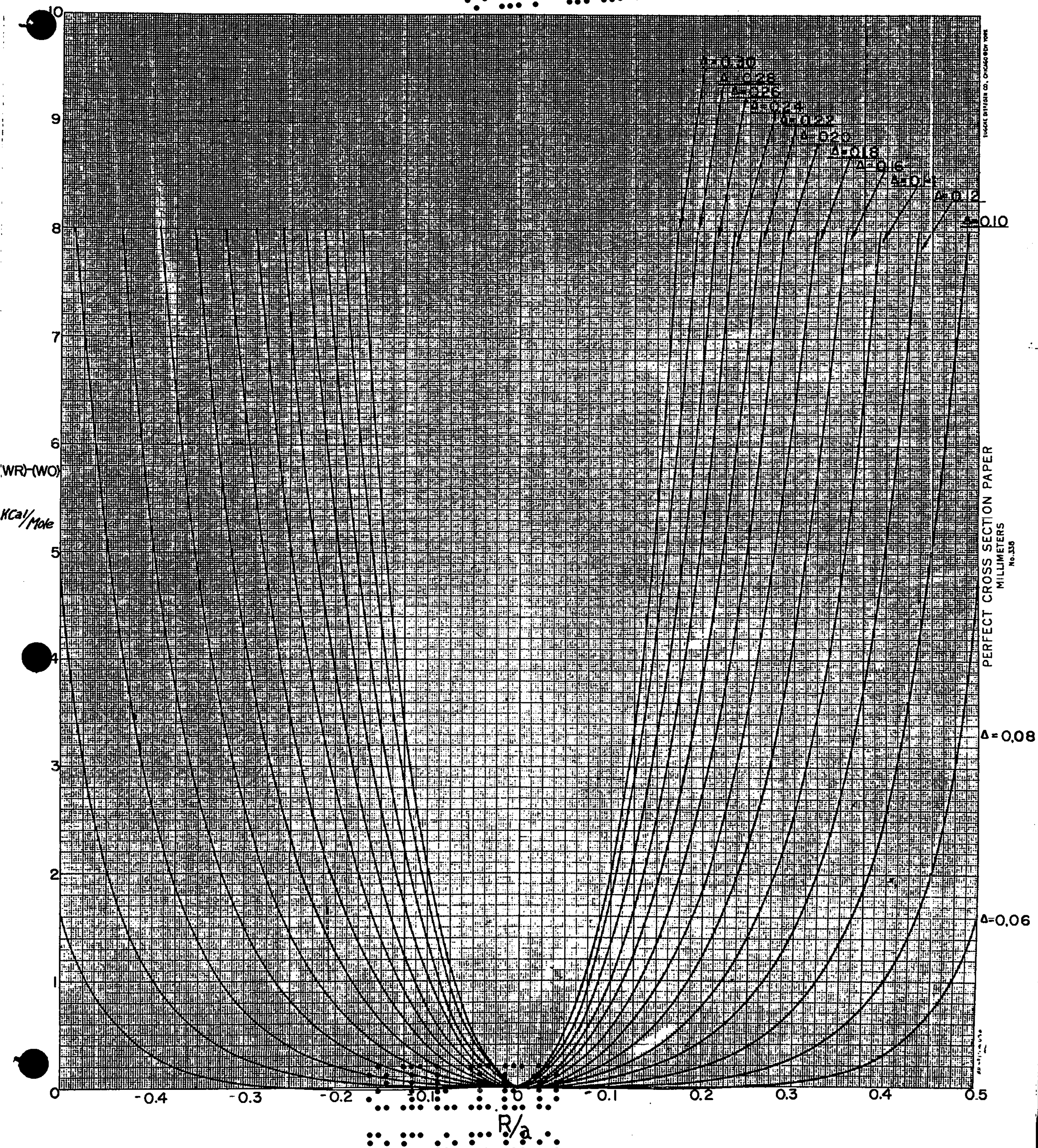
10
9
8
7
6
5
4
3
2
1
0
(WR)-(WO)
KCal/Mole
-0.4
-0.3
-0.2
-0.1
0
0.1
0.2
0.3
0.4
0.5
R/a
Δ=0.30
Δ=0.28
Δ=0.26
Δ=0.24
Δ=0.22
Δ=0.20
Δ=0.18
Δ=0.16
Δ=0.14
Δ=0.12
Δ=0.10
Δ=0.08
Δ=0.06
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FIG. 1

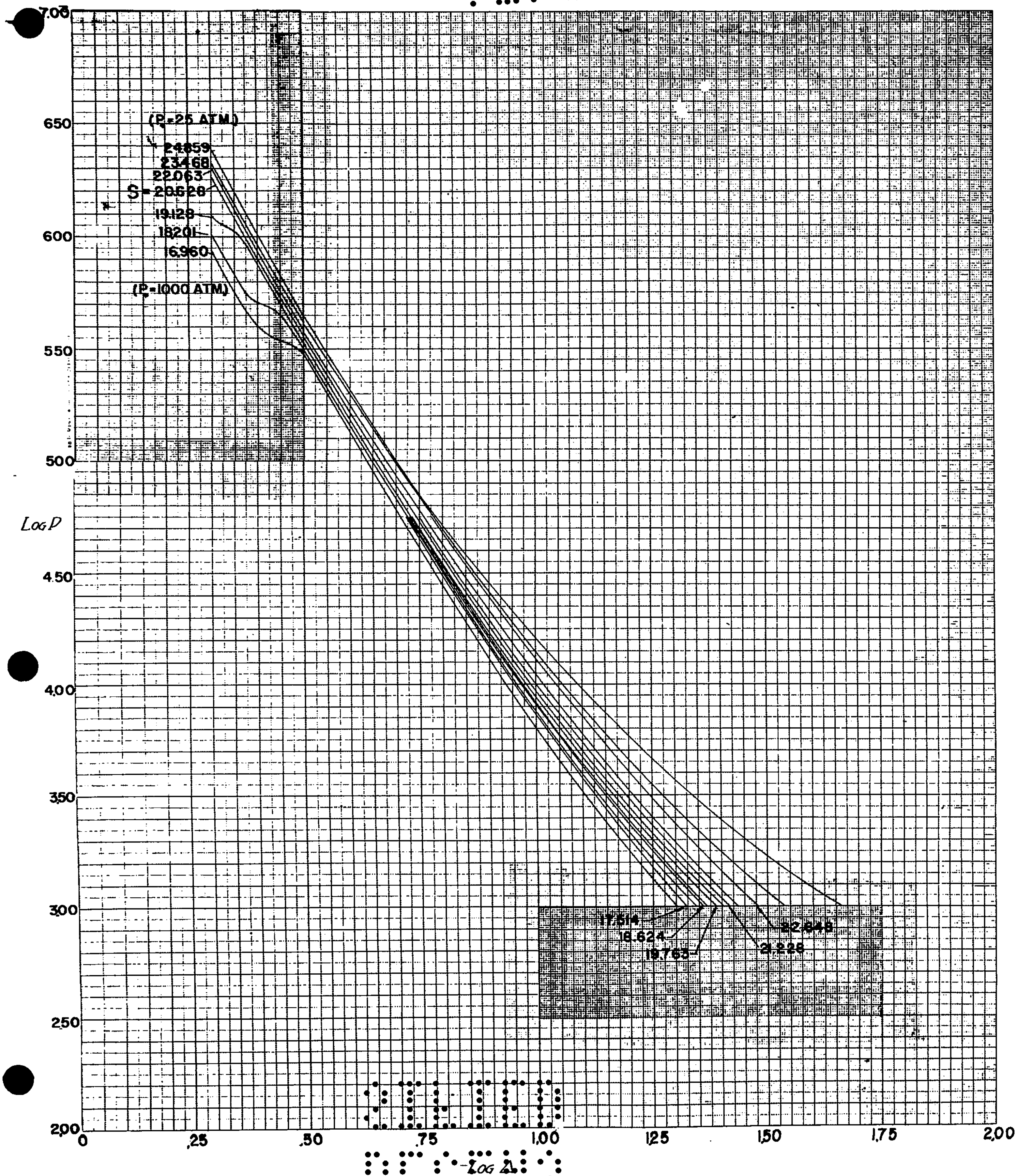
(P=25 ATM.)
24.859
23.468
22.063
S=20.628
19.128
18.201
16.960
(P=1000 ATM.)
17.514
18.624
19.763
21.228
22.848
Log P
7.00
650
600
550
500
4.50
4.00
3.50
3.00
250
2.00
0
.25
.50
.75
1.00
1.25
1.50
1.75
2.00
Log Δ

FIG 3

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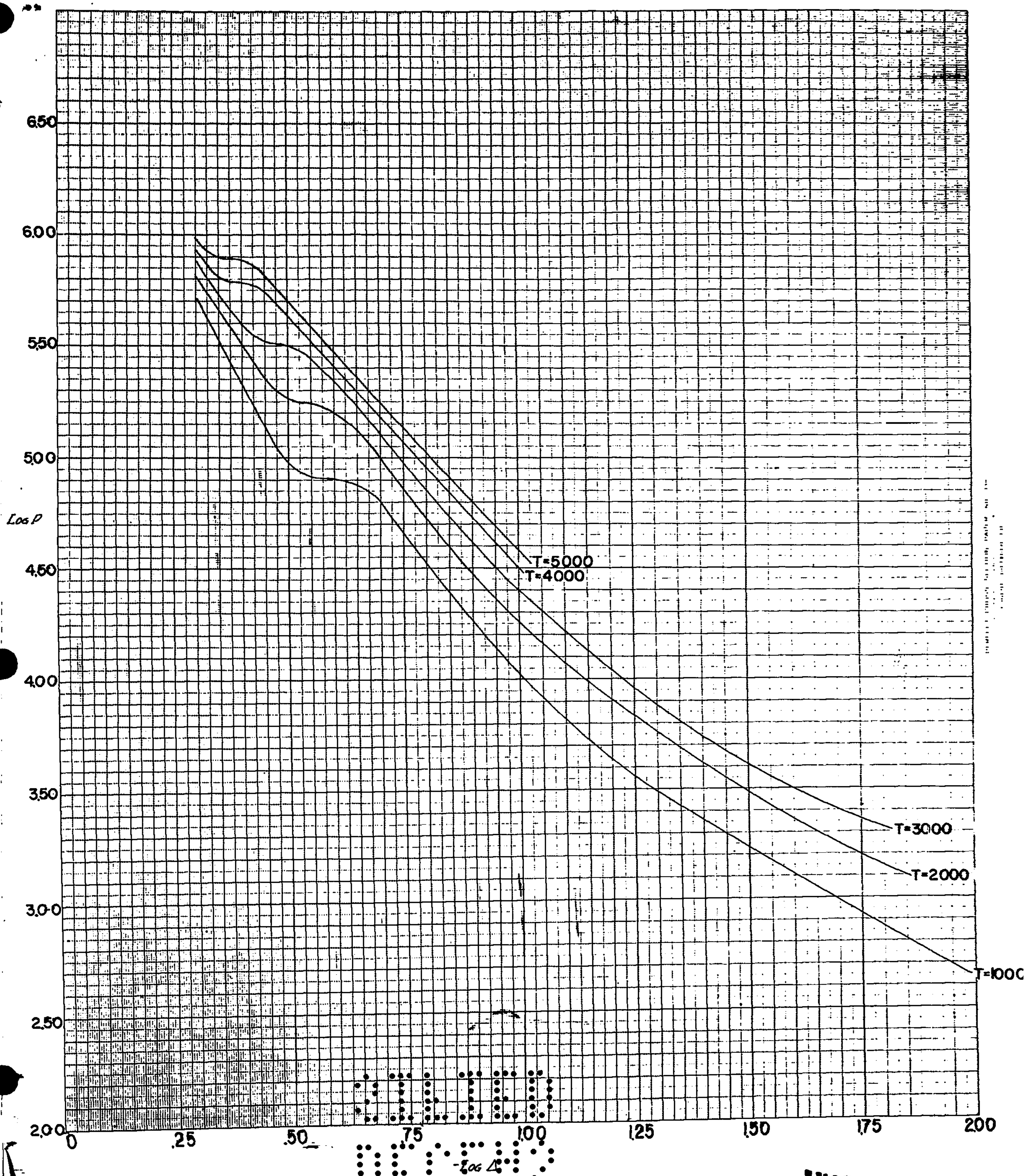

FIG 3

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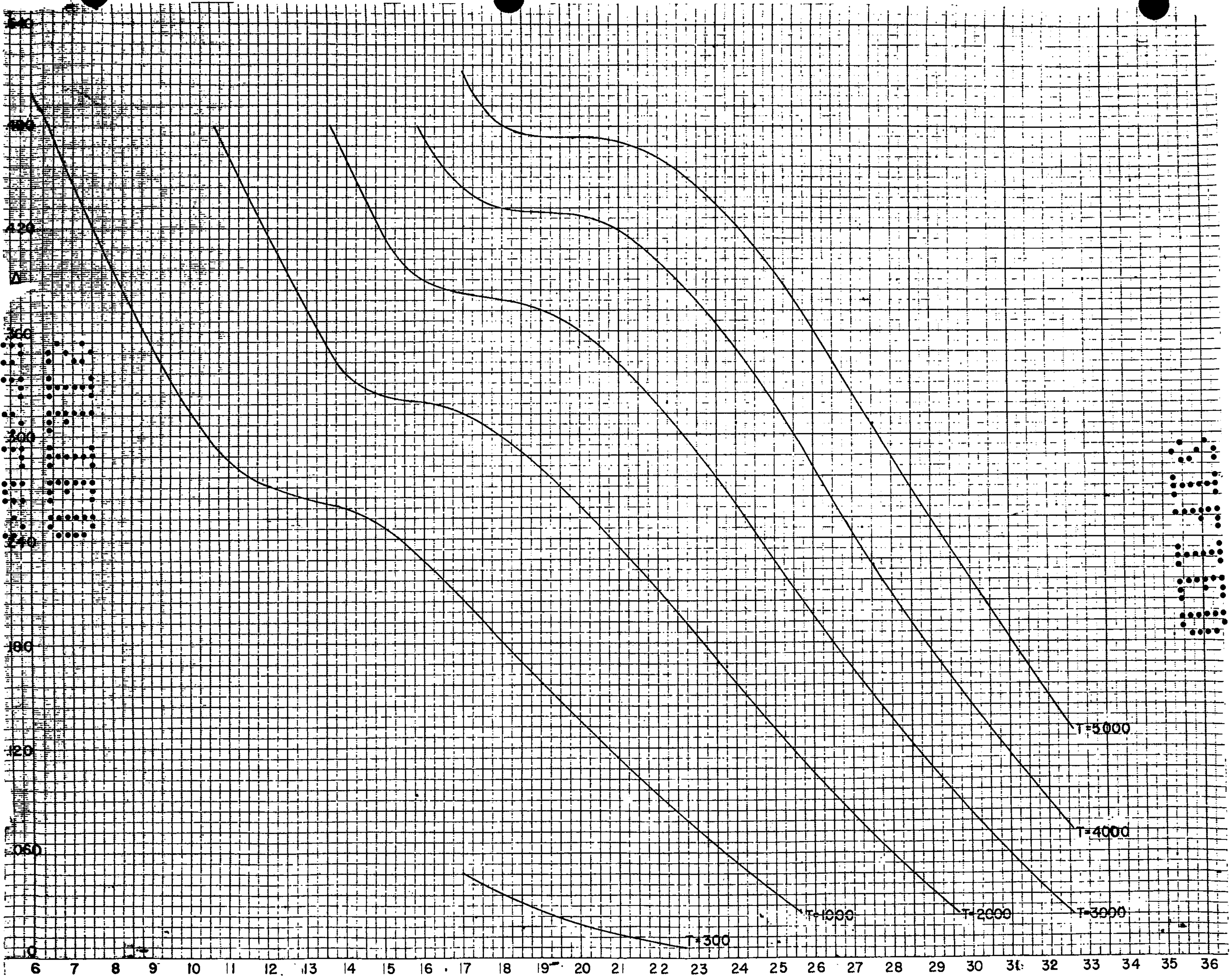

540
480
420
360
300
240
180
120
060
0
6
7
8
9
10
11
12
13
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15
16
17
18
19
20
21
22
23
24
25
26
27
28
29
30
31
32
33
34
35
36
T=300
T=1000
T=2000
T=3000
T=4000
T=5000

FIG 4 S

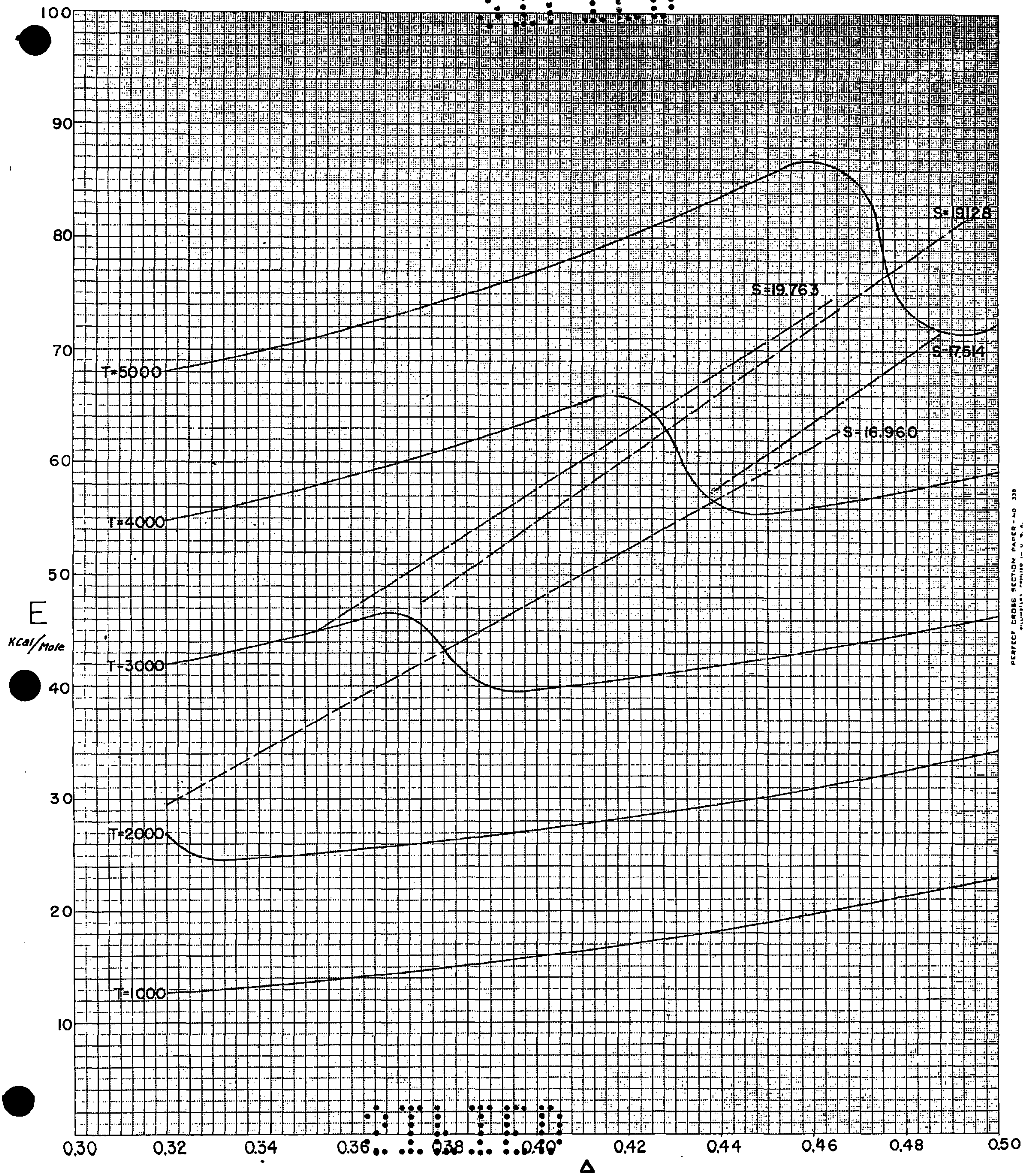
100
90
80
70
60
50
40
30
20
10
E
Kcal/Mole
T=5000
T=4000
T=3000
T=2000
T=1000
S=19.128
S=19.763
S=17.514
S=16.960
0.30
0.32
0.34
0.36
0.38
0.40
0.42
0.44
0.46
0.48
0.50
Δ
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FIG. 5