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VISCOSITY, DENSITY AND COMPOSITION OF URANIUM HEXAFLUORIDE AND CHLOROTRIFLUOROETHYLENE LIQUID POLYMER SOLUTIONS

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ABSTRACT

A study of the solutions of uranium hexafluoride and chlorotrifluoroethylene liquid polymers was made with the purpose of relating the vapor pressure to the viscosity, density, and composition of the solution. The all metal apparatus consisted of an Ostwald viscosimeter, a pycnometer, a pressure transmitter, and a suitable mixing device. The measurements were made at 60°C. from 0 to 650 mm. mercury pressure. The viscosity and density were found to be parabolic functions of the vapor pressure of the solution. The addition of uranium hexafluoride decreases the viscosity and increases the density of the solution. The rate of decrease of the viscosity diminishes with increasing concentration of uranium hexafluoride while the rate of increase of the density increases. The solution was non-ideal and deviated from Raoult's law. The composition and vapor pressure were related by the Margules equation.

VISCOSITY, DENSITY AND COMPOSITION OF URANIUM HEXAFLUORIDE AND CHLOROTRIFLUOROETHYLENE LIQUID POLYMER SOLUTION

A study of the properties of solutions of uranium hexafluoride and chlorotrifluoroethylene liquid polymers has been made with the purpose of relating these properties to the vapor pressures of the solutions. These data should be of considerable value, as the largest single use of chlorotrifluoroethylene liquid polymers is as a confining liquid in pumps used for the compression of uranium hexafluoride. These data may also prove useful in making diffusion plant uranium inventories.

A limited amount of data on the solubility of uranium hexafluoride in chlorotrifluoroethylene liquid polymers was reported by A. D. Kirshenbaum[1] for pressures below 100 mm. mercury. Five observations of the viscosity of uranium hexafluoride and chlorotrifluoroethylene liquid polymers solutions were made by A. D. Kirshenbaum and J. S. Kasper[2] in glass apparatus.

Since the available data on the properties of uranium hexafluoride and chlorotrifluoroethylene liquid polymers solutions were of limited scope and accuracy, the properties of these solutions were investigated and correlated more thoroughly. In this report the viscosity, density and composition of solutions of uranium hexafluoride and chlorotrifluoroethylene liquid polymers are correlated with the vapor pressures of the solutions at 60°C.

APPARATUS AND MATERIALS

Apparatus

The apparatus, shown in figure 1, consisted essentially of a viscosimeter, a pressure indicator, a mixing chamber, a pycnometer, and auxiliary equipment. To minimize particles present due to corrosion, the system was fabricated, where practical, from monel or nickel; otherwise either copper or brass was used. Permanent connections were silver soldered while flare-type fittings were used for non-permanent joints.

Viscosimeter. The construction of the monel Ostwald viscosimeter with Fluorothene sight windows is shown in detail at the right in figure 1. The plunger type valve, released by a suitable mechanism, was adapted from a Kerotest valve bonnet. The nickel capillary, 0.055 inches in diameter, was protected from particles by filters of 100-mesh monel screen placed in all leads to the viscosimeter proper.

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1. Kirshenbaum, A. D., "Solubility of Uranium Hexafluoride in GD-727c and GD-727h". Columbia University, SAM Laboratories, A-572, March 20, 1943.

2. Kirshenbaum, A. D. and J. S. Kasper, "Viscosities of C-616-MFL Solutions". Carbide and Carbon Chemicals Corporation, SAM Laboratories, DE-M-6, July 19, 1945.

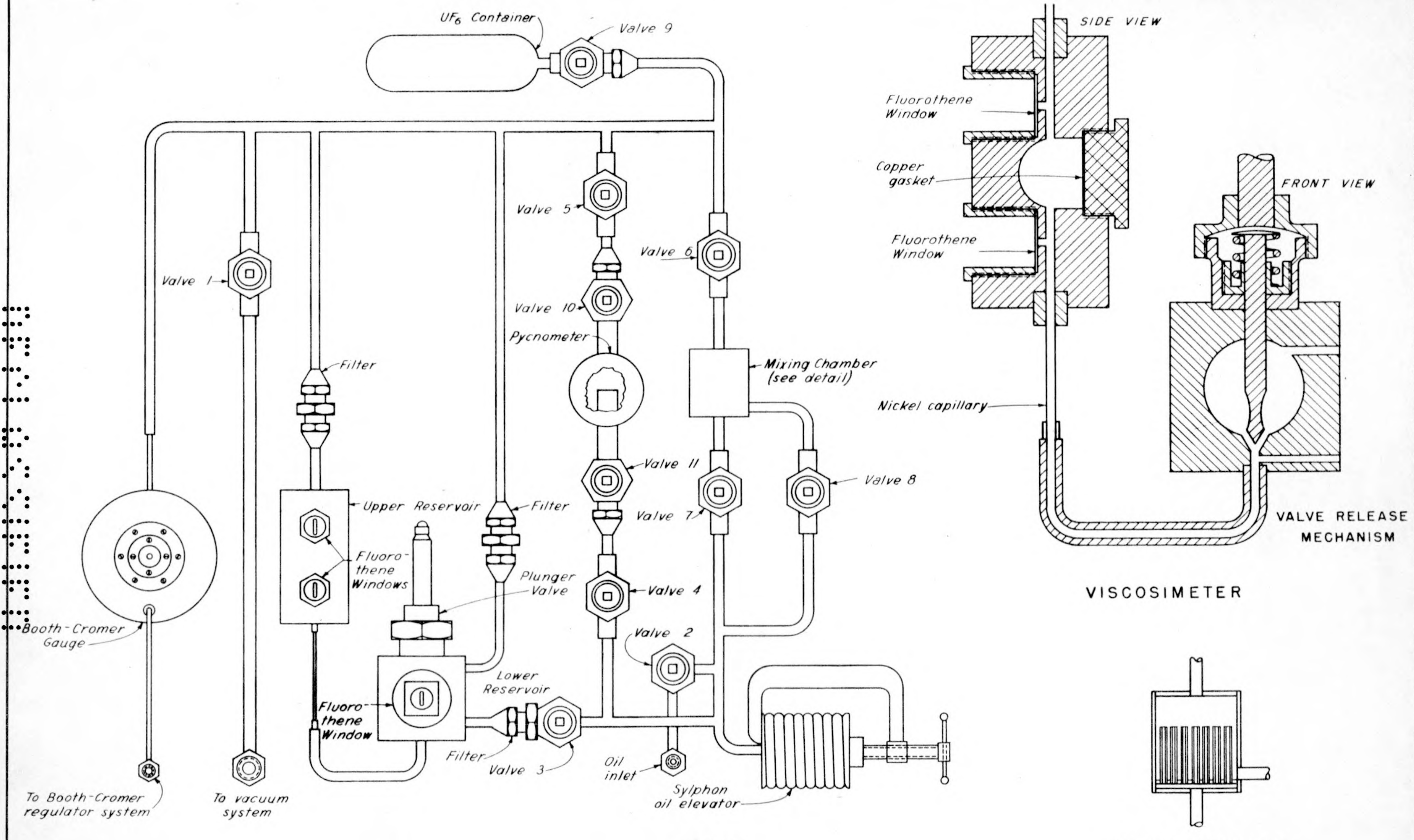

FIGURE I

METAL VISCOSIMETER SYSTEM

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Mixing Chamber and Oil Elevator. The mixing chamber is also shown in figure 1. A four-inch brass sylphon was used to displace the polymer to various parts of the system.

Pressure Indicator. A Booth-Cromer pressure transmitter and indicator[3] was used for measuring pressure.

Pycnometer. "H"-type Crane valves were used on the overflow type pycnometer. The seat sides of the valves were placed toward the inside of the pycnometer so that any sample remaining in the valve could be removed before weighing.

Auxiliary Equipment. A vacuum system was used for evacuating the apparatus and for removing the uranium hexafluoride by condensation in a liquid nitrogen trap. A constant temperature air bath controlled by a sensitive mercury regulator and relay was used to maintain the temperature within the range 59.99 to 60.01°C.

Materials

The chlorotrifluoroethylene polymers used in this study had the following properties at 60.0°C.:

Molecular weight[4]	846
Density, gm./cc.[4]	1.909
Viscosity, cs.[4]	56.7
Vapor pressure[5], μ Hg	10.4

EXPERIMENTAL PROCEDURE

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[3] Cromer, S., "Pressure Transmitter and Relay". Columbia University, A-1286, 1947.

[4] Gabbard, J. L., et al, "Physical Properties of Chlorotrifluoroethylene Polymers as a Function of Molecular Weight. II. Molecular Fractionation, Density, Viscosity, Molecular Weights and the Correlation of these Properties of Chlorotrifluoroethylene Polymers". Carbide and Carbon Chemicals Corporation, K-25 Plant, K-124 (MDDC-1624), Jan. 15, 1948.

[5] Gabbard, J. L., et al, "Physical Properties of Chlorotrifluoroethylene Polymers. V. The Vapor Pressure of Chlorotrifluoroethylene Polymers as a Function of Temperature and Number Average Molecular Weight". Carbide and Carbon Chemicals Corporation, K-25 Plant, K-401, May 20, 1949.

Uranium hexafluoride was added to the apparatus through valves 6 and 9. The mixing of the uranium hexafluoride and the polymer sample were accomplished by raising the oil through a number of small tubes in the mixing chamber. The solution was then drained into the elevator through valve 8. This was repeated until equilibrium at the desired pressure was attained. The sample was usually saturated to a pressure higher than desired and uranium hexafluoride pumped from the solution to a lower pressure. This tended to remove any partial pressure of hydrogen fluoride that might have been present.

To load the viscosimeter, valves 4, 7, and 8 (see figure 1) were closed and the sample was raised to the crosswire in the upper reservoir. Valve 3 was closed, the plunger valve released and the efflux time measured. Valves 3, 7, and 8 were opened and the sample was allowed to drain into the elevator. The pycnometer was loaded similarly with valve 3 closed and 4 open. The sample was raised above the overflow tube inside the pycnometer and the excess oil was allowed to drain into the elevator. The pycnometer was removed then cleaned and weighed and the sample analyzed for uranium content.

The concentration of uranium in the solution was lowered by pumping a portion of the uranium hexafluoride into a liquid nitrogen trap. Equilibrium was again attained and additional measurements were made.

The calibration constants for the apparatus were determined using the liquid polymer as a standard.

DATA AND DISCUSSION

Viscosity and Pressure

The viscosities of uranium hexafluoride and chlorotrifluoroethylene liquid polymers solutions were measured at 60.0°C. between the partial pressures of uranium hexafluoride of 0 to 650 mm. mercury. These data are shown plotted in figure 2 and tabulated in table I. The viscosity was related to the vapor pressure of the solution by the empirical equation:

$$\eta_{cs.} = 56.73 - 0.16020p + 0.0001265p^2 \qquad (1)$$

where $\eta_{cs.}$ = the viscosity in centistokes

p = vapor pressure in mm. mercury.

The above equation was derived by a method of least squares. The range of the data from the curve is less than 4% for 99% of the data.

Figure 3 is a curve for the absolute viscosity in centipoises as a function of the vapor pressure of the solution. The equation,

$$\eta_{cp.} = 108.3 - 0.30096p + 0.002388p^2 \qquad (2)$$

where $\eta_{cp.}$ = viscosity in centipoises

p = vapor pressure of the solution in mm. mercury, was derived by combining calculated points from equations 1 and 5.

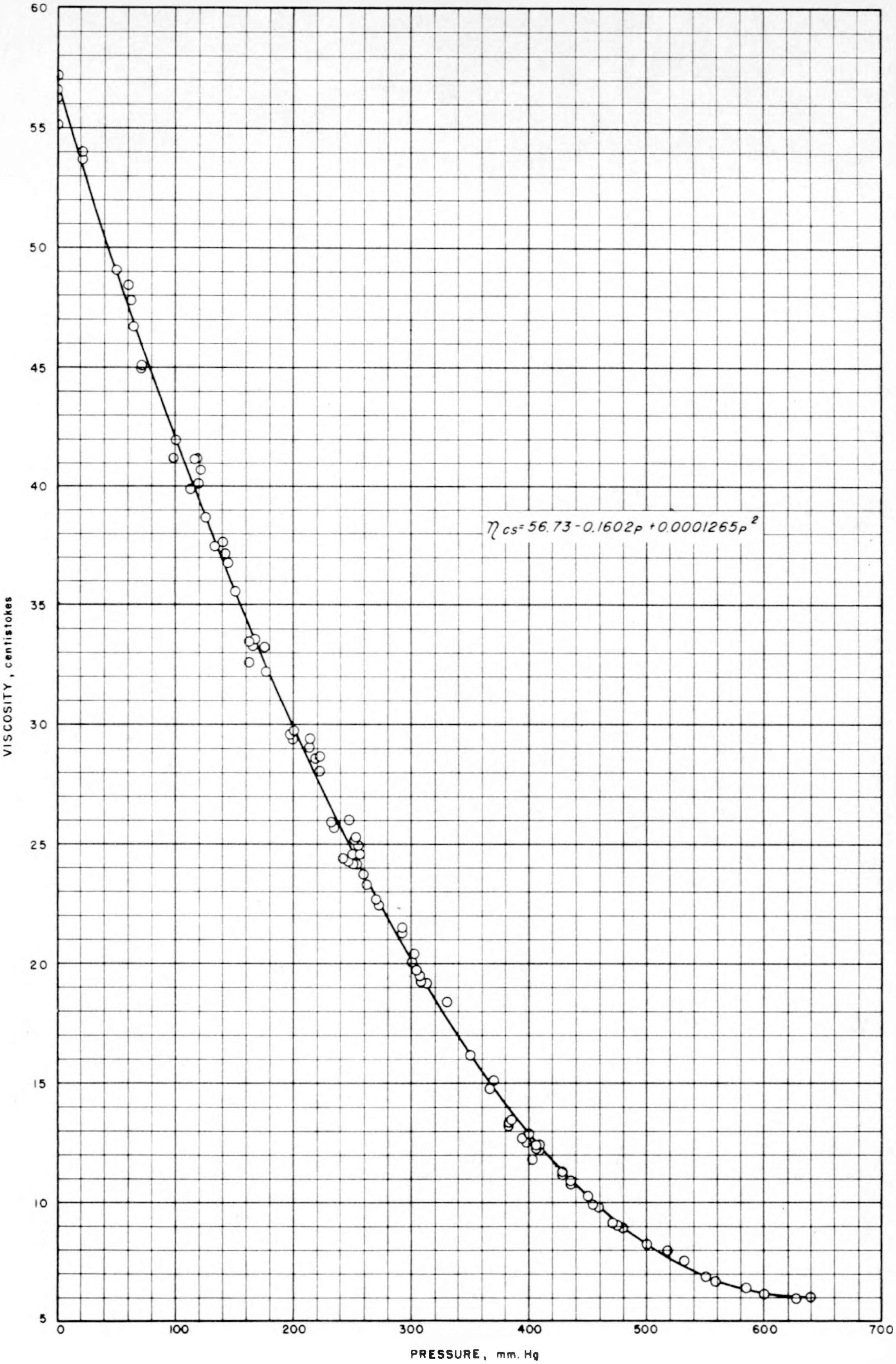

FIGURE 2

VISCOSITY OF CHLOROTRIFLUOROETHYLENE POLYMER AND URANIUM HEXAFLUORIDE SOLUTIONS AS A FUNCTION OF THE EQUILIBRIUM PRESSURE OF URANIUM HEXAFLUORIDE AT 60° C.

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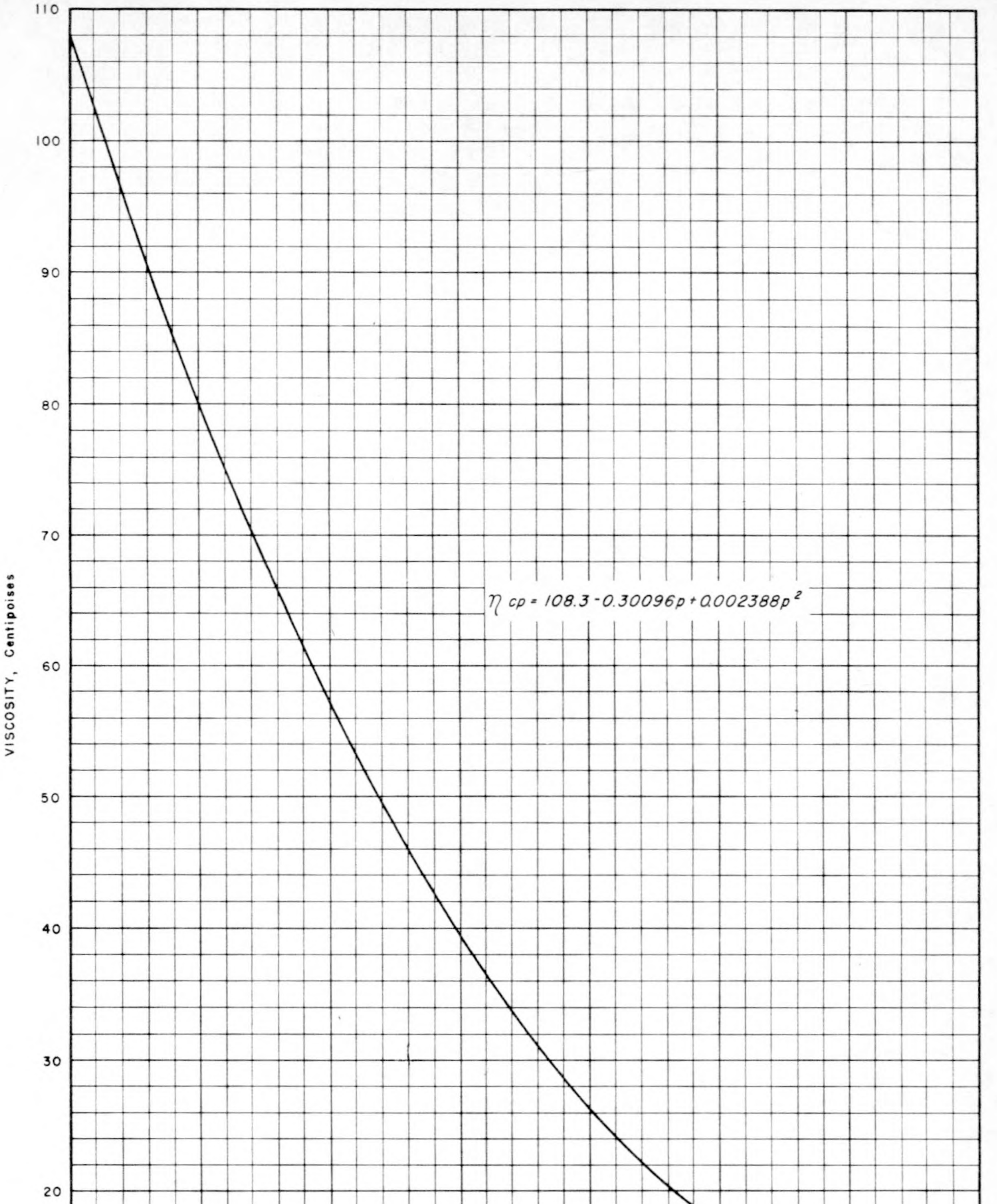

FIGURE 3

VISCOSITY OF CHLOROTRIFLUOROETHYLENE POLYMER AND URANIUM HEXAFLUORIDE SOLUTIONS AS A FUNCTION OF THE EQUILIBRIUM PRESSURE OF URANIUM HEXAFLUORIDE AT 60°C.

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Viscosity and Composition

The ideal viscosities of solutions of uranium hexafluoride and chlorotrifluoroethylene liquid polymer are predicted by the Bingham equation,

$$\frac{1}{\eta} = X \frac{1}{\eta_1} + X_2 \frac{1}{\eta_2} \qquad (3)$$

where X_1 and X_2 = the mole fraction of components one and two, respectively,
and η, η_1, and η_2 = the viscosities of the mixture and components one and two, respectively.

The ideal values were much less than the experimental values obtained for these solutions for concentrations of uranium hexafluoride up to 60 mole percent. The hypothetical viscosity of uranium hexafluoride at 60°C. was obtained by extrapolating from 65°C.

An attempt was made to relate the viscosity of the solution with their densities and composition by use of the equation[6].

$$\eta^{1/8}\left[\frac{M_1X_1 + M_2X_2}{D}\right] = \left[\eta_1^{1/8}\frac{M_1X_1}{D_1} + \eta_2^{1/8}\frac{M_2X_2}{D_2}\right]\left[\frac{D}{D_1X_2 + D_2X_2}\right]^M \qquad (4)$$

where X_1 and X_2 = the mole fraction of components one and two, respectively,
M_1 and M_2 = the molecular weight of components one and two, respectively.
D, D_1, and D_2 = the densities of the mixture and components one and two, respectively,
M = an empirical constant.

However, this equation for non-ideal mixtures was found to be inadequate.

Density and Pressure

The densities and vapor pressures were related by means of an empirical equation:

$$D = 1.909 - 9.25 \times 10^{-5}p + 9.929 \times 10^{-7}p^2 \qquad (5)$$

where D = density of the solution
p = the vapor pressure of the solution.

This function, plotted in figure 4, was fitted to the data by a method of least squares with the limitation of a fixed intercept. The intercept or density of the liquid polymer was known to be 1.9087 (95% confidence interval is ± 0.0004) at 60°C. The maximum range of the observed data from calculated function is 1.5%, while 90% of the data has a range of less than 1%. A tabulation of these data is shown in table II.

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[6] Chacravarti, A. S., Current Sci. (India), 16 22-3 (1947).

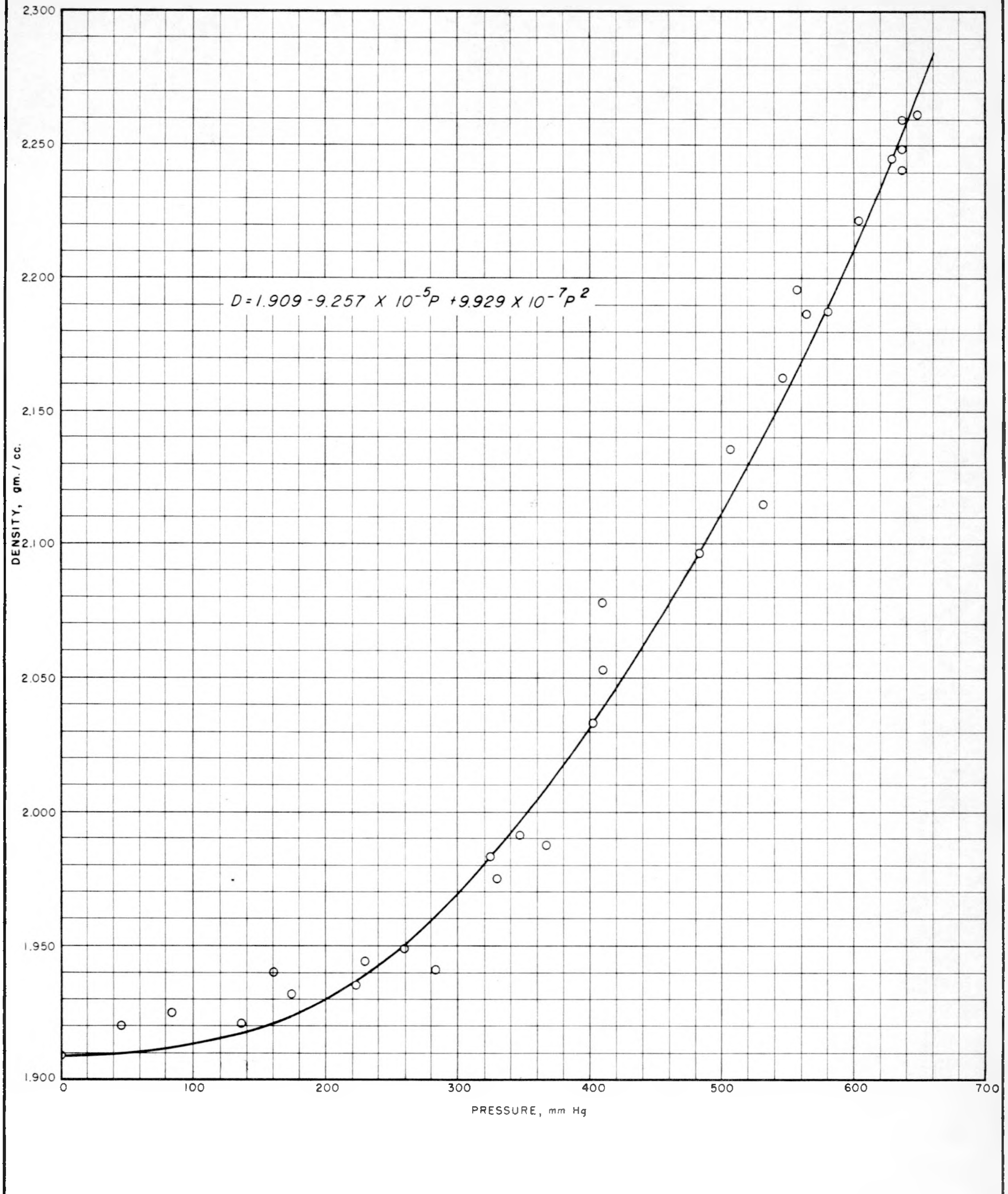

FIGURE 4

DENSITY OF CHLOROTRIFLUOROETHYLENE POLYMER AND URANIUM HEXAFLUORIDE SOLUTIONS AS A FUNCTION OF EQUILIBRIUM PRESSURE OF URANIUM HEXAFLUORIDE AT 60°C

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Composition and Pressure

The composition and vapor pressure of the solutions were related by means of the Margules equation:

$$\ln p = \ln p_o + \ln N_1 + 6.922N_2^2 - 10.458N_2^2 + 6.536N_2^4 \qquad (6)$$

where N_1 and N_2 = the mole fraction of uranium hexafluoride and liquid polymer, respectively.

p and p_o = the vapor pressure of the solution and uranium hexafluoride, respectively.

Since the partial pressure of the liquid polymer is never greater than 10.4μ mercury, its contribution to the total pressure is neglected. The maximum range of the data from the curve is two mole percent of uranium hexafluoride, while 85% of the data has a range of less than one mole percent. These data are listed in table II and a plot is shown in figure 5.

Mixtures of uranium hexafluoride and chlorotrifluoroethylene polymers have a negative deviation from Raoult's law at concentrations of uranium hexafluoride of less than 40 mole percent and a positive deviation at concentrations greater than 40 mole percent. These deviations are the resultant of the positive and negative factors adding in such a manner to produce a change in the deviation from positive to negative. To add in such a manner to give a net effect of a negative and positive deviation, the negative deviation would have to be largest at high concentrations of polymer and the positive deviation would have to be largest at high concentration of uranium hexafluoride. The most probable factor which would cause a positive deviation is the difference in internal pressures of the two components. The internal pressures are approximately 51.4 cal./cm.^{3} for uranium hexafluoride and 29.2 cal./cm.^{3} for the chlorotrifluoroethylene polymer. There may be positive deviation due to association of the polymer but not of the uranium hexafluoride, since it has been shown to behave as a normal liquid . The only probable factor causing negative deviation is the difference in the size of the molecules of the two components. This conclusion is consistent with the deviations of the viscosities from the ideal.

CONCLUSION

1. The viscosity and density of chlorotrifluoroethylene polymer and uranium hexafluoride solutions may be represented as parabolic functions of the vapor pressure of the solution. The addition of uranium hexafluoride decreases the viscosity and increases the density of the solution. The rate of decrease of the viscosity diminishes with increasing concentration of uranium hexafluoride while the rate of increase of the density increases.

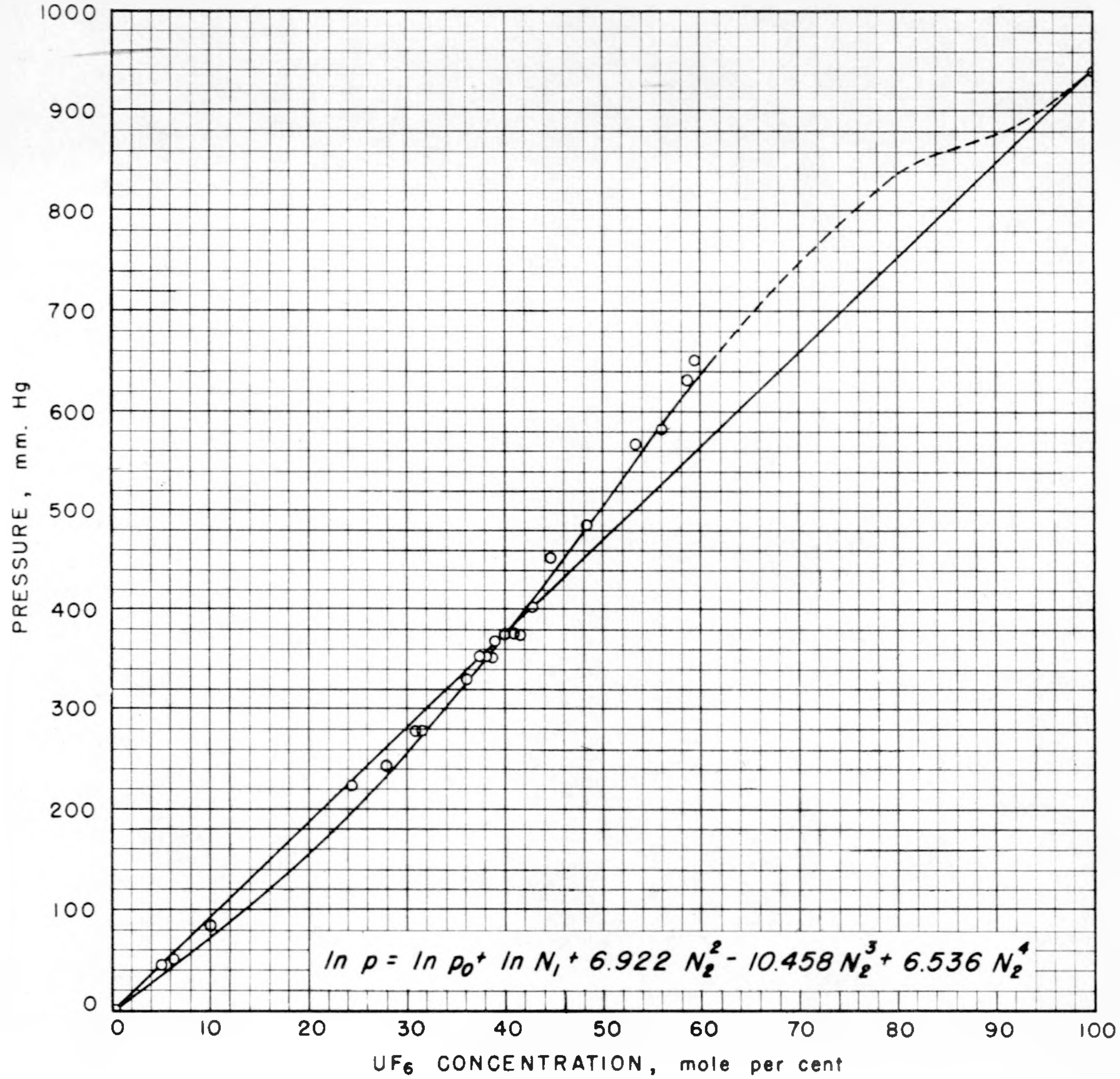

FIGURE 5

COMPOSITION OF CHLOROTRIFLUOROETHYLENE POLYMER AND URANIUM HEXAFLUORIDE SOLUTIONS AS A FUNCTION OF THE EQUILIBRIUM PRESSURE OF URANIUM HEXAFLUORIDE AT 60 °C.

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2. No ideal or general equation was found which would accurately relate the composition with the viscosity of the mixture.

3. The solution is non-ideal and deviates from Raoult's law. The Margules equation was found to fit the vapor pressure and composition data.

Table I

Viscosity of Chlorotrifluoroethylene Liquid Polymer and Uranium Hexafluoride as a Function of the Vapor Pressure of the Solution at 60°C.

Number of measurements	Vapor pressure, mm. Hg	Viscosity, cs.
5	0	56.7
3	21	53.8
3	60	48.5
4	62	47.9
1	64	46.7
2	71	45.0
4	98	41.2
1	112	39.9
2	119	40.7
1	121	40.7
1	125	38.7
3	140	37.6
1	142	37.2
1	144	36.8
3	162	33.2
3	165	33.2
1	166	33.5
4	176	32.1
4	197	29.5
2	199	29.4
2	214	29.2
1	218	28.6
2	221	28.4
6	232	25.8
3	234	25.7
1	237	24.7
1	242	24.4
2	246	24.4
1	247	26.0
3	249	24.2
2	251	24.8
1	252	25.2
4	255	24.7
1	257	23.9
1	259	23.7
2	262	23.3
3	270	22.7
3	272	22.5
5	292	21.4
1	302	20.4

Table I (continued)

Number of measurements	Vapor pressure, mm. Hg	Viscosity, cs.
1	304	19.7
1	306	19.5
1	308	19.3
2	312	19.2
5	330	18.4
5	370	15.1
1	383	13.4
1	385	13.5
3	393	13.1
1	394	12.7
1	397	12.6
1	399	12.5
1	401	12.5
6	403	12.8
6	406	12.3
6	409	12.2
2	410	12.4
4	428	11.2
8	435	10.8
4	454	9.9
3	459	9.8
3	471	9.2
4	475	9.1
4	479	8.9
5	500	8.3
7	518	8.0
4	532	7.5
7	558	6.7
7	585	6.4
8	627	6.0

Table II

Vapor Pressure, Composition, and Density of Chlorotrifluoroethylene Liquid Polymer and Uranium Hexafluoride Solutions at 60°C.

Vapor pressure, mm. Hg	Composition, mole % UF_6	Density, gm./cc.
46	4.9	1.920
52	6.3	
84	9.9	1.925
136		1.921
160		1.940
174		1.932
223	24.2	1.935
225		1.944
244	27.8	
260		1.949
278	31.4	
278	31.1	
283		1.941
325		1.983
330	36.3	1.975
347		1.991
351	38.7	
351	38.0	
351	37.9	
351	37.4	
367	38.9	1.987
375	39.8	
375	40.7	
375	41.0	
375	41.5	
402	42.9	2.033
410		2.053
410		2.078
452	44.6	
484	49.2	2.097
507		2.136
532		2.130
547		2.163
558		2.196
565	53.2	2.187
581	55.9	2.188
605		2.222
630		2.246
638		2.249
638		2.241
638		2.260
649		2.262