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VAPOR PRESSURE MEASUREMENTS FOR THE SYSTEM: URANIUM HEXAFLUORIDE-CHLORIDE TRIFLUORIDE

AUTHOR:

W. C. Kuykendall

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Oak Ridge Gaseous Diffusion Plant
Oak Ridge, Tennessee

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ABSTRACT

This report presents supplementary information related to the investigation of McGill and Barber on "Phase Equilibria of the Ternary System: Uranium Hexafluoride-Chlorine Trifluoride-Hydrogen Fluoride. Part IV. Liquid-Vapor Equilibria of the Binary System: Uranium Hexafluoride-Chlorine Trifluoride", (K-1102).

Vapor pressures for the system uranium hexafluoride-chlorine trifluoride at approximately 76°, 83°, and 92°C. over the entire composition range are reported. Curves showing vapor pressure versus gross composition indicate that the system is one exhibiting complete miscibility. At 75°C. vapor pressures of 128 and 32 psia. were observed at compositions of 0 and 1.0 mole fraction uranium hexafluoride, respectively. The smooth curve within these limits shows a maximum positive deviation from a Raoult's law relationship of approximately 13 pounds occurring at 0.4 mole fraction uranium hexafluoride.

VAPOR PRESSURE MEASUREMENTS FOR THE SYSTEM: URANIUM HEXAFLUORIDE-CHLORINE TRIFLUORIDE

Comparison of the liquid-vapor equilibria for the system uranium hexafluoride-chlorine trifluoride obtained by Ellis (1) using a static equilibrium technique at a constant temperature of 75°C., and those obtained by McGill and Barber (4) using a dynamic equilibrium technique at constant pressure and covering the pressure range from 1 to 3 atmospheres indicated that reconciliation of the two sets of data would require the existence of a miscibility gap having a lower consolute temperature between 50°C. and 75°C. Since the existence of a lower consolute temperature in a liquid-liquid system normally implies relatively strong bonding between the components, and since there are no a priori reasons to suspect any chemical bonding between uranium hexafluoride and chlorine trifluoride, further investigation of a possible miscibility gap existing over the gross composition range of 0.3 to 0.5 mole fraction uranium hexafluoride at 75°C. was undertaken.

Samples of uranium hexafluoride-chlorine trifluoride at compositions of approximately 0.4 mole fraction uranium hexafluoride were prepared and heated to a temperature of 75°C. in a clear Fluorothene* tube so that the separation into two liquid layers might be observed visually if a miscibility gap existed. No indication of immiscibility was observed by use of this technique.

Since this observation failed to support the data of Ellis (1), a more detailed study was conducted using vapor pressure as an indicator of the absence or presence of a miscibility gap. The results of this study are reported herein.

SUMMARY AND CONCLUSIONS

Vapor pressures for the system uranium hexafluoride-chlorine trifluoride were measured at approximately 76°, 83°, and 92°C. over the complete range of composition. The data employed to obtain a curve, vapor pressure versus gross composition at 75°C., indicated that the system is one exhibiting complete miscibility. This is in direct conflict with conclusions reported by Ellis (1) and is consistent with data presented by McGill and Barber (4). The smooth curve shows vapor pressures of 128 and 32 psia. at compositions of 0 and 1.0 mole fraction uranium hexafluoride, respectively, at 75°C. and has a maximum positive deviation from a straight line of approximately 13 pounds at 0.4 mole fraction uranium hexafluoride.

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*Plastic polymer of chlorotrifluoroethylene.

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EXPERIMENTAL

Apparatus

The pressure vessel (figure 1) was made of nickel and was equipped with a calibrated bronze-tube Duragauge having a scale range of 30 inches vacuum to 150 pounds pressure. A thermocouple well in the bottom of the pressure vessel permitted the necessary temperature measurements. The total volume of the pressure vessel was approximately 50 cc., with the base having a volume of 30 cc. and the bourdon tube in the gauge having a volume of about 20 cc. The transfer manifold shown in figure 1 was fabricated from 1/4-inch copper tubing and 1/4-inch Crane HGP valves. To permit heating during stabilization and uranium hexafluoride transfer operations, the manifold was wrapped with asbestos covered Nichrome wire.

Mercury-filled thermoregulators were used with an oven to maintain the pressure vessel and sample on which vapor pressures were to be measured within ± 0.2°C. of the desired temperature. The oven door contained a glass observation panel, and extending through the door was a rod for shaking the pressure vessel. A copper-constantan thermocouple inserted in the bottom of the pressure vessel led to a Rubicon potentiometer which was read to the nearest one-hundredth millivolt.

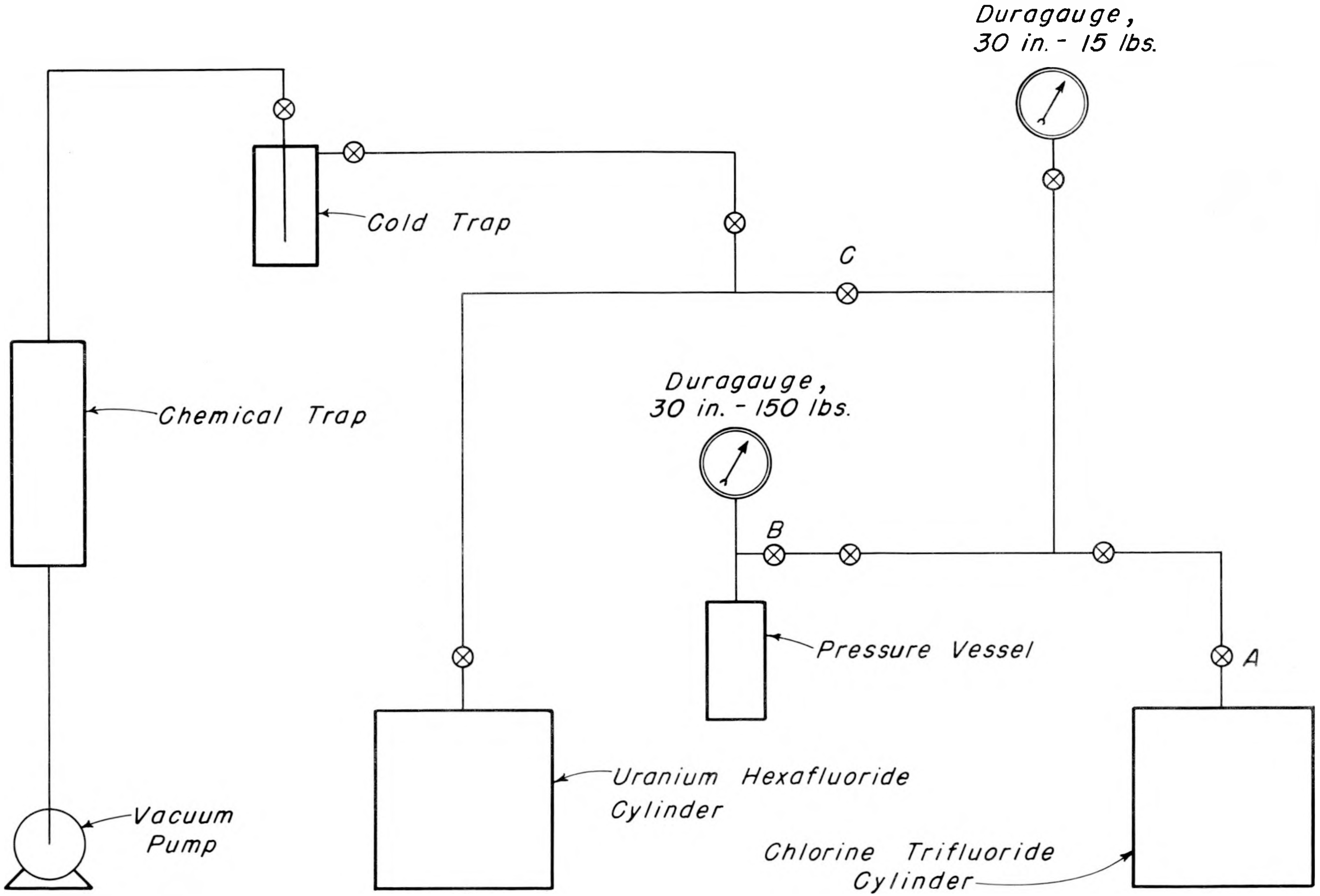
Phase Components

Since purity of components could affect the liquid-vapor equilibria and hence the vapor pressure of a system, the purest components available were used for the study. Infrared analysis of the chlorine trifluoride showed that it contained less than 0.4 mole per cent hydrogen fluoride. The uranium hexafluoride was obtained from a larger sample being used as a purity control standard and was better than 99.95 mole per cent uranium hexafluoride. To maintain a high state of purity, successive flashing as described by Wendolkowski and Barber (6) was carried out on the components before use each time.

Procedure

The pressure vessel was stabilized for 72 hours at 150°C. with excess chlorine trifluoride, evacuated, weighed, and attached to the transfer manifold which had been thoroughly conditioned with chlorine trifluoride. The connector between the pressure vessel and the manifold was conditioned with chlorine trifluoride after each exposure to air.

Uranium hexafluoride was transferred to the pressure vessel by heating the uranium hexafluoride cylinder (figure 1) and cooling the pressure vessel with liquid nitrogen. After determining the weight of uranium hexafluoride transferred in this manner, the amount of chlorine trifluoride required to give a total sample volume of approximately 30 cc. of uranium hexafluoride and chlorine trifluoride at 75°C. was then transferred to the pressure vessel cooled in liquid nitrogen. By calibrating a portion of the manifold (between ABC, figure 1) so that it could be used as a gas pipette, fairly accurate estimation of the incremental amounts of chlorine trifluoride transferred was possible.



URANIUM HEXAFLUORIDE - CHLORINE TRIFLUORIDE TRANSFER MANIFOLD
FIGURE I

From appropriate weighings, the gross composition of the final sample was determined.

The pressure vessel containing the sample was placed in the thermostatically controlled oven and heated to the desired temperature. When this temperature was reached, the vessel was alternately shaken and allowed to stand until no further change in pressure occurred over a 30-minute interval. Vapor pressure readings were obtained in this manner at three different temperatures for each sample over a complete range of compositions.

RESULTS AND DISCUSSION

The vapor pressure data obtained on the binary system uranium hexafluoride-chlorine trifluoride are given in table I.

For direct comparison with the results obtained by Ellis (1), these data were extrapolated to obtain the vapor pressures of the various compositions at 75°C. Curves representing the two sets of data are shown in figure 2. The curve from Ellis' data indicates that at 75°C. and 110 psia. the system uranium hexafluoride-chlorine trifluoride is one exhibiting partial miscibility with the compositions of the limiting saturated solutions being approximately 0.3 and 0.5 mole fraction uranium hexafluoride, respectively. Data extrapolated to 75°C. from those shown in table I produce a smooth curve which is indicative of the absence of a miscibility gap.

The volume of the liquid sample was sufficiently large in relation to the total volume of the pressure vessel that the variation between the gross composition and the liquid composition due to difference between the vapor phase and liquid phase compositions was negligible. The maximum correction, 0.0003 mole fraction uranium hexafluoride, would have occurred in the sample having a gross composition of 0.1970 mole fraction uranium hexafluoride. This concentration adjustment is well within the limits of experimental error.

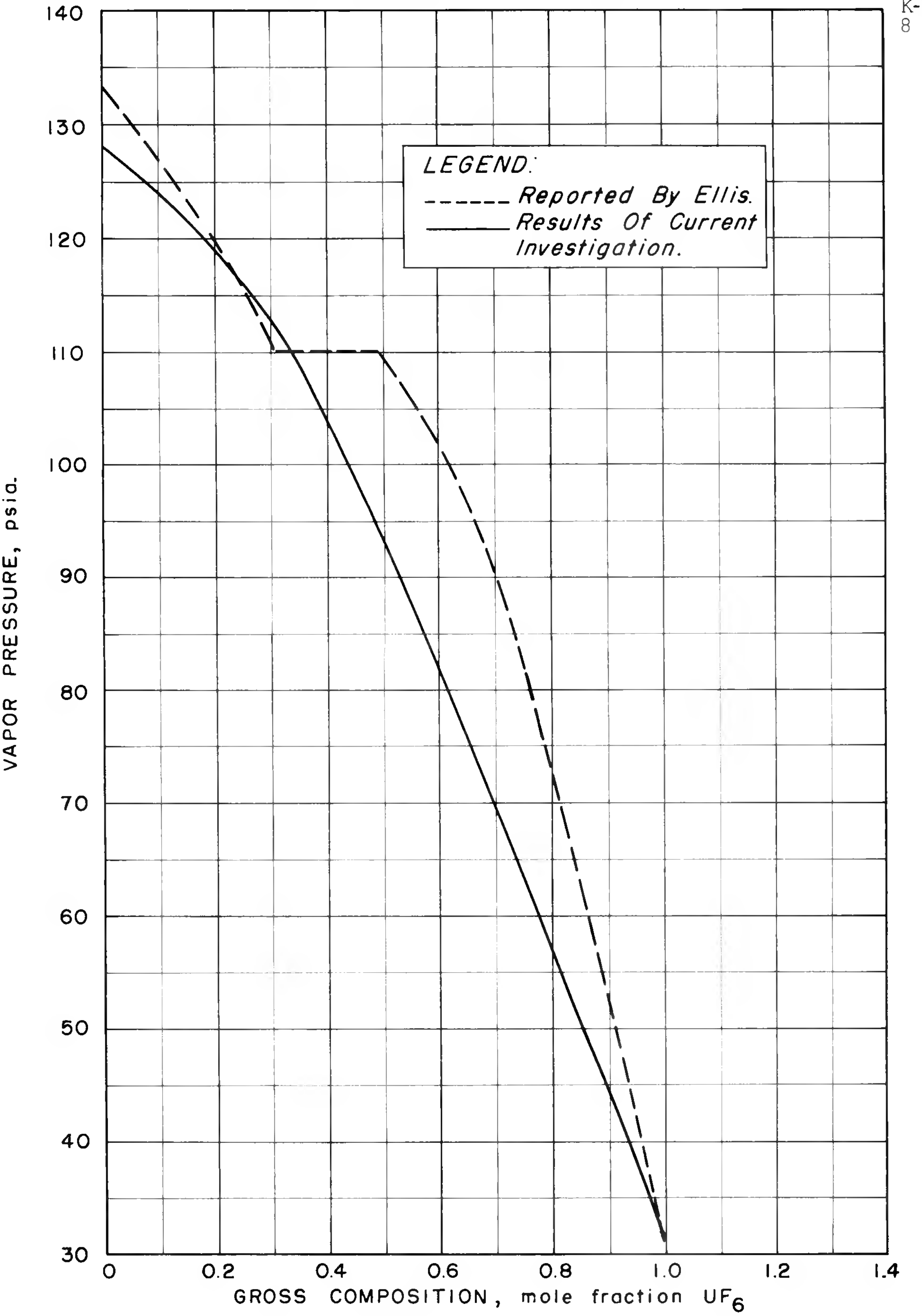
At 75°C. the vapor pressure of chlorine trifluoride was observed to be 128 psia. Grisard, Oliver and Bernhardt (2) reported an equation which gives a value of 123 psia. Workers at Argonne National Laboratory (5) have reported another equation which also gives 123 psia. as the vapor pressure of chlorine trifluoride at 75°C. The value of 133 psia. reported by Ellis is somewhat higher than the pressure from any of these other data.

At 75°C. the vapor pressure of uranium hexafluoride was found to be 32 psia. which compares favorably with the 31 psia. value reported by Grisard and Oliver (3).

TABLE I

VAPOR PRESSURE DATA FOR THE SYSTEM URANIUM HEXAFLUORIDE-CHLORINE TRIFLUORIDE

Total Pressure, psia.	Temperature, °C.	Gross Composition, mole fraction UF_6
35	77.0	1.0000
44	84.0	1.0000
54	92.6	1.0000
91	76.5	0.5749
107	83.2	0.5749
130	92.0	0.5749
98	76.5	0.4681
115	83.2	0.4681
143	92.0	0.4681
108	76.5	0.3791
127	83.2	0.3791
154	92.0	0.3791
117	76.5	0.3456
137	83.2	0.3456
164	92.0	0.3456
124	76.5	0.2394
137	80.0	0.2394
146	83.2	0.2394
122	76.5	0.1970
141	83.2	0.1970
167	90.6	0.1970
105	67.8	0.0000
129	75.0	0.0000
134	76.5	0.0000
96	65.0	0.0000
111	70.0	0.0000
127	75.0	0.0000



VAPOR PRESSURE FOR THE SYSTEM URANIUM HEXAFLUORIDE – CHLORINE TRIFLUORIDE
FIGURE 2

BIBLIOGRAPHY

1. Ellis, J. F., Liquid-Vapor Equilibria in the System Uranium Hexafluoride-Chlorine Trifluoride, Isotopes Development Laboratory, Division of Atomic Energy (Production), June 25, 1953, (Risley-5197).

2. Grisard, J. W., Oliver, G. D., and Bernhardt, H. A., The Vapor Pressure and Heat of Vaporization of Chlorine Trifluoride, Union Carbide Nuclear Company, Oak Ridge Gaseous Diffusion Plant, June 23, 1950, (K-613).

3. Grisard, J. W. and Oliver, G. D., The Vapor Pressure and Heat of Vaporization of Uranium Hexafluoride, Union Carbide Nuclear Company, Oak Ridge Gaseous Diffusion Plant, February 28, 1951. (K-722).

4. McGill, R. M. and Barber, E. J., Phase Equilibria of the Ternary System: Uranium Hexafluoride-Chlorine Trifluoride-Hydrogen Fluoride. Part IV. Liquid-Vapor Equilibria of the Binary System: Uranium Hexafluoride-Chlorine Trifluoride, Union Carbide Nuclear Company, Oak Ridge Gaseous Diffusion Plant, February 26, 1954, (K-1102).

5. Summary Report - October, November, December 1949, Argonne National Laboratory, Chemistry Division, Section C-1, February 13, 1950, (ANL-4411, p. 28-29).

6. Wendolkowski, W. S. and Barber, E. J., Phase Equilibria of the Ternary System: Uranium Hexafluoride-Chlorine Trifluoride-Hydrogen Fluoride. Part I. Solid-Liquid Equilibrium of the Binary System: Uranium Hexafluoride-Chlorine Trifluoride, Union Carbide Nuclear Company, Oak Ridge Gaseous Diffusion Plant, December 28, 1951, (K-846).

NOTEBOOK REFERENCE

Kuykendall, W. C., ORGDP Notebook Number 2933, p. 73-92.

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