course of their undergraduate thesis work (1934–1935) at this College.

Conclusions

Vapor–liquid equilibrium data have been obtained for methylcyclohexane–toluene mixtures at normal barometric pressures, as well as data for the analysis of liquid mixtures of these two hydrocarbons by density, refractive index and boiling point. This binary hydrocarbon mixture has proved to be entirely practical for testing fractional distillation equipment.

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[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF RHODE ISLAND STATE COLLEGE]

The Vapor Pressure and Dissociation of Tungsten Hexachloride in the Gas Phase[1]

BY ARTHUR A. VERNON

In the course of an investigation dealing with incandescent lamps, the vapor pressure of tungsten hexachloride was determined. A study of its dissociation in the gaseous state yielded preliminary values for the equilibrium constant of the reaction

$$\mathrm{WCl_6(g)} \rightleftharpoons \mathrm{W(s)} + 3\mathrm{Cl_2(g)} \qquad (1)$$

The tungsten hexachloride was prepared by passing purified chlorine gas over C. P. tungsten heated to redness in an oxygen-free atmosphere.

Vapor Pressure Measurements

A current of hydrogen was passed over tungsten hexachloride in a glass container inside a small heating furnace. A coil immersed in liquid air was connected to the outlet of the furnace to condense the tungsten hexachloride carried over by the hydrogen. A known amount of gas was passed through the apparatus and the vapor pressure of tungsten hexachloride calculated from the increase in weight of the coil. The results are given in Table I.

TABLE I

VAPOR PRESSURE OF TUNGSTEN HEXACHLORIDE

Temp., °C.	Vapor pressure, mm.
25	5×10^{-3}
50	2.6×10^{-2}
100	1.01×10^{-1}
150	25.1

The results conform to a log p *vs.* $1/T$ plot with a maximum deviation of measured point from the straight line of 5%. The heat of vaporization calculated from the slope of the line is 23,800 cal. per mole and the equation for the line is $\log p = 3.1 - 1198/T$.

Dissociation Measurements

In preliminary experiments dissociation data were obtained by the use of tungsten filaments of known diameter mounted in glass bulbs which were evacuated and baked. The filaments were sintered while the bulbs were on the vacuum system and solid tungsten hexachloride introduced before being sealed off. Four filaments of the same diameter were burned at different current ratings and the changes in cold resistance noted at intervals. The tungsten hexachloride vapor was decomposed by the hot filaments and tungsten deposited on the wire. When equilibrium was reached, the resistance of the wires became constant. From the change in resistance of the filaments, the amount of tungsten deposited was calculated and from this the chlorine present at equilibrium could be found. The final temperatures of the filaments were determined by the method of Forsythe and Worthing.[2]

More accurate data presented here were obtained by a modification of this method in which the filaments were burned at a constant temperature determined by comparison with an optical pyrometer. To determine the vapor pressure of tungsten hexachloride more accurately and to have a check on the chlorine pressures as calculated from resistance changes, a quartz fiber manometer was attached to the stem of the bulb. The time for the amplitude of vibration of the fiber to drop from a value I to i was determined and the damping coefficient calculated by means of the expression $d = (1/t) \log (I/i)$. Haber and Kerschbaum[3] found that for a mixture of gases $\alpha = a + b\,[P_\mathrm{A}\sqrt{M_\mathrm{A}} + P_\mathrm{B}\sqrt{M_\mathrm{B}}]$ where a is the value of α in a vacuum and P and M are pres-

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[1] The data upon which this paper is based were obtained while the author was employed by the General Electric Company.

[2] Forsythe and Worthing, *Astrophys. J.*, **61**, 146–85 (1925).

[3] Haber and Kerschbaum, *Z. Elektrochem.*, **20**, 296 (1914).

TABLE II

DISSOCIATION OF TUNGSTEN HEXACHLORIDE

Filament temp., °C.	Pressure, at. WCl$_6$-fiber	Cl$_2$-fiber	Cl$_2$-resistance	$\frac{(P_{Cl_2})^3}{P_{WCl_6}}$ Resistance
1087	2.32×10^{-6}	3.75×10^{-5}	3.68×10^{-5}	2.3×10^{-8}
1227	2.32×10^{-6}	6.7×10^{-4}	1.67×10^{-4}	2.1×10^{-6}
1327	2.32×10^{-6}	6.9×10^{-5}	4.08×10^{-4}	2.6×10^{-5}
1727	2.32×10^{-6}		1.64×10^{-3}	6.2×10^{-3}

sures and molecular weights, respectively. For a given value of α for air and for a mixture of WCl$_6$ and Cl$_2$, the relation would be

$$a + b\,P_{\text{air}}\sqrt{M_{\text{air}}} = a + b\,[P_{WCl_6}\sqrt{M_{WCl_6}} + P_{Cl_2}\sqrt{M_{Cl_2}}]$$

or

$$P_{Cl_2} = \frac{P_{\text{air}}\sqrt{M_{\text{air}}} - P_{WCl_6}\sqrt{M_{WCl_6}}}{\sqrt{M_{Cl_2}}}$$

if the factor b is the same in each case. In the same way a relation can be obtained involving only air and tungsten hexachloride which can be used for the calculation of the vapor pressure of tungsten hexachloride. The results of these measurements are shown in Table II.

The agreement between the chlorine pressure as determined by the fiber and from resistance measurements is very good at the temperature of 1087°. At higher temperatures the chlorine pressures developed are above the range at which the fiber manometer can be used accurately since the pressures were not linearly proportional to the damping coefficients above 1×10^{-4} atmospheres. Therefore the equilibrium constants were calculated using the tungsten hexachloride pressures determined by the fiber and the chlorine pressures calculated from the deposition of tungsten on the filaments which were maintained at constant temperature.

The logarithms of the equilibrium constants are plotted against the reciprocal of the absolute temperature in Fig. 1. The slope of the best line through these points is near 2000 corresponding to a value of 9000 cal. for the heat of dissociation of tungsten hexachloride in this temperature range.

Thanks are due Dr. G. R. Fonda for his helpful criticisms and suggestions during the progress of the work.

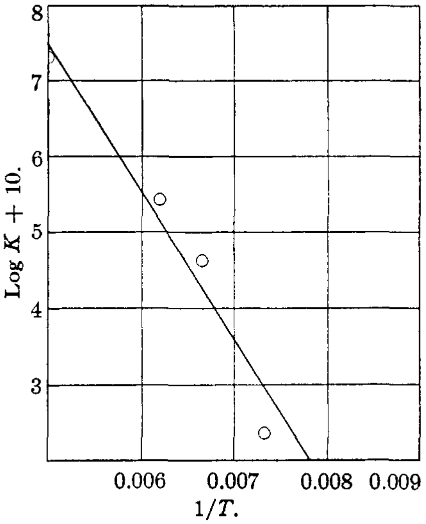

Fig. 1.—Variation of equilibrium constant with absolute temperature.

Summary

1. The vapor pressure of tungsten hexachloride has been determined from 25 to 150°. The heat of vaporization is 1198 cal. per mole and the change of vapor pressure with temperature is given by the equation $\log p = 3.1 - (1198/T)$.

2. An experimental method for the determination of the equilibrium constants of the dissociation of tungsten hexachloride is described.

3. The equilibrium constants have been determined at 1087, 1227, 1327 and 1727° and the heat of dissociation found to be approximately 9000 cal.

KINGSTON, R. I.

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