Greek Letters

ρ = density g cm^{-3}
σ = standard error of estimate defined by Equation 6
τ = vibration period, sec

Subscripts

0 = reference liquid (pure component or mixture)
1 = ketone component in mixture
2 = nonpolar component in mixture (benzene or carbon tetrachloride)

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Solubility Product of Thallium(I) Thiocyanate in Water at 10–40°C

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With an ion-selective electrode the thiocyanate activities in saturated aqueous solutions of thallium(I) thiocyanate were measured at seven temperatures in the range 10–40°C, and the solubility products were calculated. The logarithm of the solubility product is a linear function of the reciprocal of the absolute temperature, and the heat of solution of the compound is 66.25 kJ mol^{-1}.

The solubility product (*K*) of TlSCN was determined potentiometrically by Suzuki (*6*), who reported a value of 1.7 × 10^{-4} at 25°C, whereas a subsequent similar study by Golub and Skorobogatko (*2*) gave 1.35 × 10^{-4} at 20°C and 7.91 × 10^{-4} at 40°C. From polarographic measurements, Sundaram et al. (*5*) obtained a value of 2.31 × 10^{-4} at 30°C. The above results appear to lack consistency since a plot of log *K* against the reciprocal of the absolute temperature does not yield the expected straight line.

The recent development of the thiocyanate ion-selective electrode presents a new and relatively simple method of measuring ionic activity directly, and from it the activity solubility product. One possible source of error thereby avoided is the effect of incomplete dissociation of thallium(I) thiocyanate. In addition to the ion-pair TlSCN, ionic complexes of the type $Tl(SCN)_n^{(1-n)}$ are known to form at higher concentrations of the thiocyanate ion. However, several studies indicate that such complexing is weak (*1, 2, 4*), and no allowance for it has been made in the present work.

Experimental

Thallium(I) thiocyanate was prepared by precipitation from equimolar solutions of thallium(I) sulfate and sodium thiocyanate. After filtration the product was washed and recrystallized several times from hot water.

Saturated solutions of thallium(I) thiocyanate were prepared by adding a slight excess of the salt to a convenient

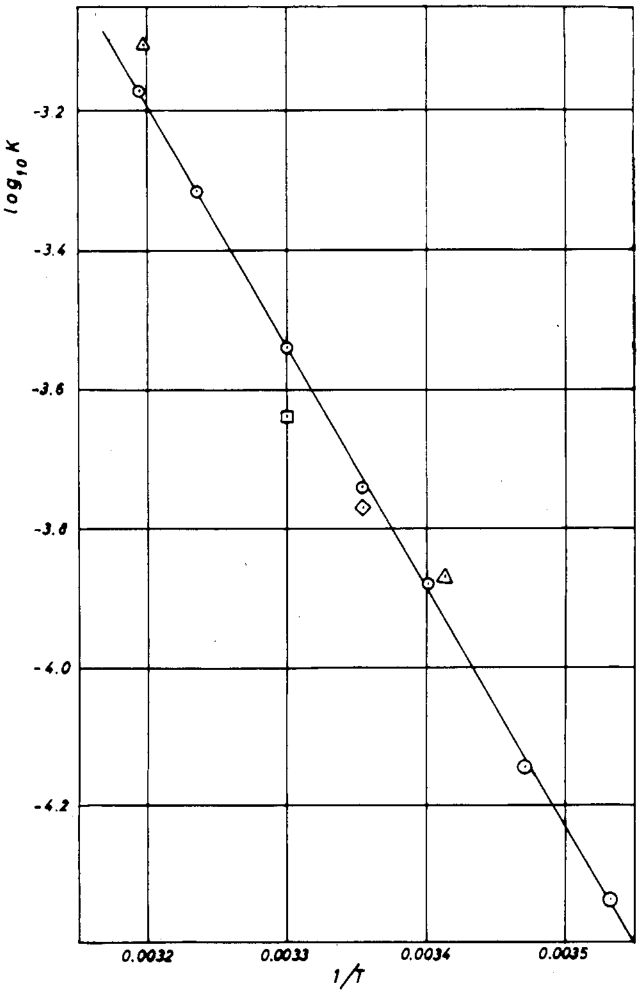

Figure 1. Least-squares plot of logarithm of solubility product (*K*) of thallium(I) thiocyanate against reciprocal of absolute temperature (*T*). Experimental points: ⊙, present work; △, Golub and Skorobogatko (*2*); ⊡, Sundaram and coworkers (*5*); ◇, Suzuki (*6*)

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Table I. Solubility Products of Thallium(I) Thiocyanate at Various Temperatures

°C	40.0	36.0	30.0	25.0	21.0	15.0	10.0
$K \times 10^4$	6.76	4.84	2.89	1.82	1.32	0.72	0.46

volume of doubly distilled water in a hard glass cell (12 cm long, 3.5 cm in diameter), with continuous agitation by means of a glass-covered magnetic stirrer. To prevent condensation on the walls, the entire inner space of the closed cell was below the water level in the thermostat, whose temperature was controlled to ±0.1°C. Saturation was generally achieved within 24 hr, this being checked by continuing the analyses over longer periods.

Thiocyanate activities were measured by means of a thiocyanate specific-ion electrode (Orion Research Inc., Model 94-58) and a double-junction reference electrode (Model 90-02), connected to an Orion Model 407 specific-ion meter. Before use, the electrodes were first brought to the thermostat temperature while immersed in distilled water and in the outer-chamber filling solution, respectively; they were then quickly blotted dry and inserted in the test solution. A steady meter response was usually obtained within 5 min, and the thiocyanate activity could be measured to within $\pm 1 \times 10^{-4} M$.

The thiocyanate solutions used for calibrating the specific-ion meter were prepared from reagent-grade sodium thiocyanate and standardized by titration against silver nitrate with fluorescein as indicator (*7*). The mean ionic activities of these standard solutions were calculated at each temperature by use of the Güntelberg form (*3*) of the Debye-Hückel equation.

Results and Discussion

The solubility products $[K = (a_{Tl^+})(a_{SCN^-})]$ were calculated by assuming that the activity of the thallium ion (a_{Tl^+}) is equal to that of the thiocyanate (a_{SCN^-}). The results at various temperatures are presented in Table I.

A plot of log K against the reciprocal of the absolute temperature (T) was rectilinear, giving a correlation coefficient of 0.98, and the four points obtained from data of previous workers were scattered on either side (Figure 1). A least-squares analysis of the present results gives the expression:

$$\log_{10} K = (-3460/T) + 7.879$$

from which the heat of solution of TlSCN is 66.25 ± 0.34 kJ mol^{-1}.

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Enthalpies to 100 bar for Nitrogen–Methane Mixtures in Range 247.5–366.7K

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The enthalpy-pressure behavior up to 100 bar for three nitrogen–methane gaseous mixtures with 90, 50, and 25 mol % methane content is determined from measurements of the Joule-Thomson effect along five isotherms at 247.50, 273.15, 298.15, 333.25, and 366.70K. Data for pure nitrogen at 247.50K are also reported. The Joule-Thomson effect, when expansion takes place to atmospheric pressure, and derived enthalpies are represented as functions of pressure. The precision of the enthalpies is believed to be 5 J mol^{-1}. Values of the heat of mixing for these mixtures over the range of conditions are calculated and compared with the results of other workers.

Enthalpy values of a fluid or fluid mixture as a function of temperature and pressure are needed in determining energy and heat transfer effects in much process equipment, as well as for the testing of fluid theories.

Because of the inadequacies of existing predictive methods based on equations of state and mixing rules, it is preferable if enthalpies can be experimentally determined over the range of conditions involved.

There have been very few direct measurements of the high-pressure enthalpies of industrially important mixtures because most of the calorimeters are complicated, slow to reach a thermal steady state, and use large quantities of materials, which can be very costly. Some heat of mixing data have been published, but to be really useful, these require an accurate knowledge of the pure component enthalpies, which are not always available. The method of Joule-Thomson throttling (an isenthalpic process) can be used to determine high-pressure enthalpies.

The Joule-Thomson effect is the overall temperature change in a fluid undergoing an isenthalpic expansion between fixed pressures. It is a measure of the nonideality of the fluid and can be used to obtain its thermodynamic quantities at high pressure. The virtues of determining enthalpies of gases above atmospheric pressure using an adiabatic Joule-Thomson expansion method are that, in theory, only the intensive variables, temperature and pressure, need be measured and that mixture enthalpies can be obtained as readily

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