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DECOMPOSITION OF THE
TRIBUTYL PHOSPHATE - NITRATE COMPLEXES

by

G. S. Nichols
Separations Engineering Division

November 1960

E. I. du Pont de Nemours & Co.
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Aiken, South Carolina

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Explosives Department - Atomic Energy Division
Technical Division - Savannah River Laboratory

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ABSTRACT

Rates of decomposition are reported for the tributyl phosphate complexes of uranyl nitrate and nitric acid under isothermal and adiabatic conditions. These data are used to estimate conditions at which the decomposition reaction becomes self-accelerating.

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DECOMPOSITION OF THE TRIBUTYL PHOSPHATE - NITRATE COMPLEXES

INTRODUCTION

In earlier work at the Savannah River Laboratory⁽¹⁾ the initiation temperatures for violent reactions in the systems of tributyl phosphate (TBP) with nitric acid and uranyl nitrate were determined by heating a mixture of phases in a sealed, heavy-walled reactor. The initiation temperature was taken as the temperature at which the rate of pressure rise exceeded that resulting from the vapor pressures of the components under test.

The present experimental work was undertaken to determine the rate of decomposition of only the TBP phase, which contains the TBP - nitrate complexes, and then to estimate the conditions under which the reaction becomes self-accelerating. The aqueous phase was not studied because it does not contain sufficient organic material to contribute to a thermal decomposition hazard. The degradation hazard of nitrate complexes of TBP was then evaluated in terms of the temperature at which the decomposition can become self-accelerating.

SUMMARY

The thermal decomposition of TBP solutions that contained dissolved nitric acid and uranyl nitrate was demonstrated to be a first-order reaction. The half life of these complexes was correlated by the Arrhenius equation,

$$t_{\frac{1}{2}} = \frac{0.693}{s} e^{E/RT}$$

The energy of activation (E) was found to be 26,800 cal/g-mol and was independent of whether the nitrate in the complex was formed from nitric acid or uranyl nitrate. The frequency factor, s, was 4.3×10^{10} sec⁻¹ when nitric acid was used to form the complex, but diminished as the amount of uranyl nitrate in the complex was increased (see Table I). Thus the nitric acid complex was more reactive than the uranyl nitrate complex.

Figure 3 shows the calculated temperature at which the reaction becomes self-accelerating, as a function of area, volume, concentration, and heat transfer coefficient. Figure 5 shows the same temperature for reaction in cylindrical vessels and illustrates that for these calculations and the indicated assumptions the degradation reaction can become self-accelerating at 120°C (248°F) if a tank 8 feet in diameter contains 0.25 foot (37 gallons) of 100% TBP with a concentration of nitric acid equivalent to equilibration with an aqueous phase of 10.7M HNO₃.

However, laboratory experiments that approximated an adiabatic condition of reaction demonstrated runaway reactions at temperatures of 130°C but not at 125°C.

DISCUSSION

GENERAL

The experimental work was divided into two sections: (a) the isothermal - constant volume experiments in which a small sample was sealed into a "Pyrex" capillary and quickly heated, and (b) an approach to adiabatic conditions in which a larger sample was quickly charged to a heated chamber. All samples were prepared by agitating one volume of TBP with five volumes of a specified aqueous phase. Since gas generation occurred only when the organic phase was heated, only the organic phase was studied.

ISOTHERMAL - CONSTANT VOLUME EXPERIMENTS

PROCEDURE

A small sample (0.1 to 0.2 g) was sealed into a heavy-walled "Pyrex" capillary that had an inside diameter of 2 mm and was about 100 mm long when sealed. The sealed capillaries were immersed in a constant-temperature oil bath and removed after different exposures. Root⁽²⁾ at the US Forest Products Laboratory used a similar procedure for studying the acid hydrolysis of wood sugars. The extent of reaction was determined by the amount of gas released when the capillary was broken. The isothermal design of the experiments was verified by actual measurement with a thermocouple in a capillary filled with TBP. A 95% approach to thermal equilibrium was attained in 35 seconds. This time is only 4% of the shortest exposure and indicates adequate approximation of isothermal conditions.

The capillaries were broken in a stainless steel cylinder that was held under oil. The gas released was collected in an inverted funnel and transferred to a gas burette for measurement. The gas volume was assumed to be proportional to the extent of reaction, and the samples of longest exposure were assumed to represent completion of the reaction. The fraction of each sample that was not decomposed (1 - fraction of total gas that was released) was then plotted as a function of the exposure time, as illustrated by Figure 1. The half life of the reaction was determined directly from the best straight line (semilog plot) through the experimental points.

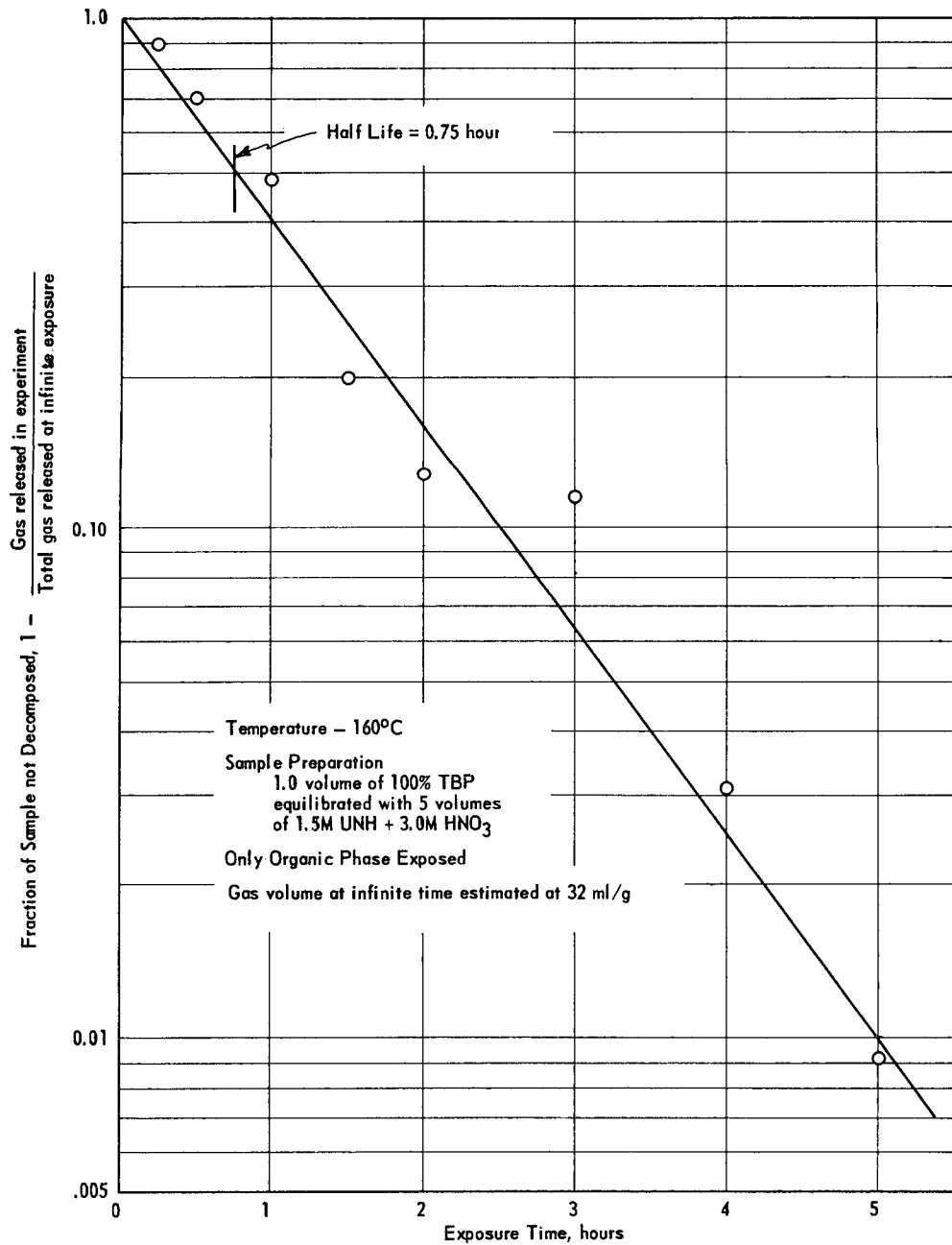


FIG. 1 DECOMPOSITION OF TRIBUTYL PHOSPHATE CONTAINING
 URANYL NITRATE AND NITRIC ACID

RESULTS

The decomposition of tributyl phosphate - nitrate complexes, as studied by the constant volume - isothermal process, was found to be a first-order reaction. The half lives of the reaction, which are proportional to the rate constants, were correlated by the Arrhenius equation and the coefficients of the Arrhenius equation are tabulated in the following table. The energy of activation was found to be independent of the source of nitrate molecule constituting the complex, but the frequency factor was decreased as the nitric acid content of the complex was replaced with uranyl nitrate. The larger uranyl nitrate molecule presumably is responsible for the increased stability.

TABLE I

Coefficients of the Arrhenius Equation

$$t_{\frac{1}{2}} = \frac{0.693}{s} e^{E/RT}$$

$t_{\frac{1}{2}}$ = half life of reaction

R = gas constant, cal/(g-mol)(°K)

T = temperature, °K

s = frequency factor, sec⁻¹

E = activation energy, cal/(g-mol)(°K)

| | | | |
|--|--------|--------|--------|
| Uranyl nitrate in aqueous phase, M | 0 | 0.8 | 1.5 |
| Nitric acid in aqueous phase, M | 6-11 | 8.9 | 3.0 |
| Energy of activation, cal/(g-mol)(°K) | 26,800 | 26,800 | 26,800 |
| Frequency factor x 10 ⁹ , sec ⁻¹ | 43 | 24 | 7.6 |

A summary of half lives observed and the concentrations of the aqueous solutions used for equilibrating the pure TBP phase are presented on Table II and plotted on Figure 2. The straight lines drawn on Figure 2 represent the Arrhenius equation with the coefficients tabulated in Table I.

TABLE II

Half Life of Thermal Decomposition Reaction, Isothermal Data

(Hours)

| <u>Aqueous Phase Analysis</u> ^(a) | <u>Symbol</u> (Fig. 2) | <u>Temperature of Decomposition, °C</u> | | | | | |
|--|---------------------------|---|------------|------------|------------|------------|------------|
| | | <u>115</u> | <u>120</u> | <u>130</u> | <u>140</u> | <u>150</u> | <u>160</u> |
| <u>Nitric Acid Alone</u> | | | | | | | |
| 10.7M HNO ₃ (50.5% HNO ₃) | ■ | | 3.3 | 1.3 | 0.60 | 0.30 | 0.12 |
| 9.2M HNO ₃ (45% HNO ₃) | □ | 3.9 | 2.43 | 1.54 | 0.47 | 0.23 | |
| 8.5M HNO ₃ (42.5% HNO ₃) | x | | 3.7 | 1.15 | 0.45 | 0.27 | 0.16 |
| 6.3M HNO ₃ (33.6% HNO ₃) | ● | | 5.2 | 1.8 | 0.9 | 0.32 | 0.16 |
| <u>Catalytic Effects</u> | | | | | | | |
| 10.7M HNO ₃ + 1% Urea | ◆ | | | | 0.42 | | |
| 10.7M HNO ₃ + 1% Fe(NO ₃) ₃ | ◇ | | | | 0.32 | | |
| <u>Neutral Salt Effect</u> | | | | | | | |
| 9.2M HNO ₃ saturated with NaNO ₃ at 25°C | ○ | | 2.6 | 1.25 | 0.73 | 0.22 | |
| <u>Uranyl Nitrate Effect</u> | | | | | | | |
| 1.5M UNH + 3M HNO ₃ | △ | | 18.7 | - | 4.3 | 1.6 | 0.75 |
| 0.8M UNH + 8.9M HNO ₃ | ▲ | | 5.8 | 2.4 | 1.3 | 0.6 | |

(a) The nitrate salt was extracted into the pure TBP phase at equilibrium conditions where the volume of the aqueous phase was five times the volume of the pure TBP used.

Burger's analysis⁽³⁾ of older literature data on the rate of hydrolysis of TBP resulted in lower activation energy than reported here. His temperatures only went to 100°C. The data of this report extrapolate to the middle of the data available to Burger and therefore substantiate the value of energy of activation and frequency factor.

Gowenlock⁽⁴⁾ reports that normal unimolecular reactions should have frequency factors between $10^{11.5}$ and $10^{14.5}$ sec⁻¹. Table III shows that the frequency factors reported here are closer to the "normal" value than the analysis of Burger.

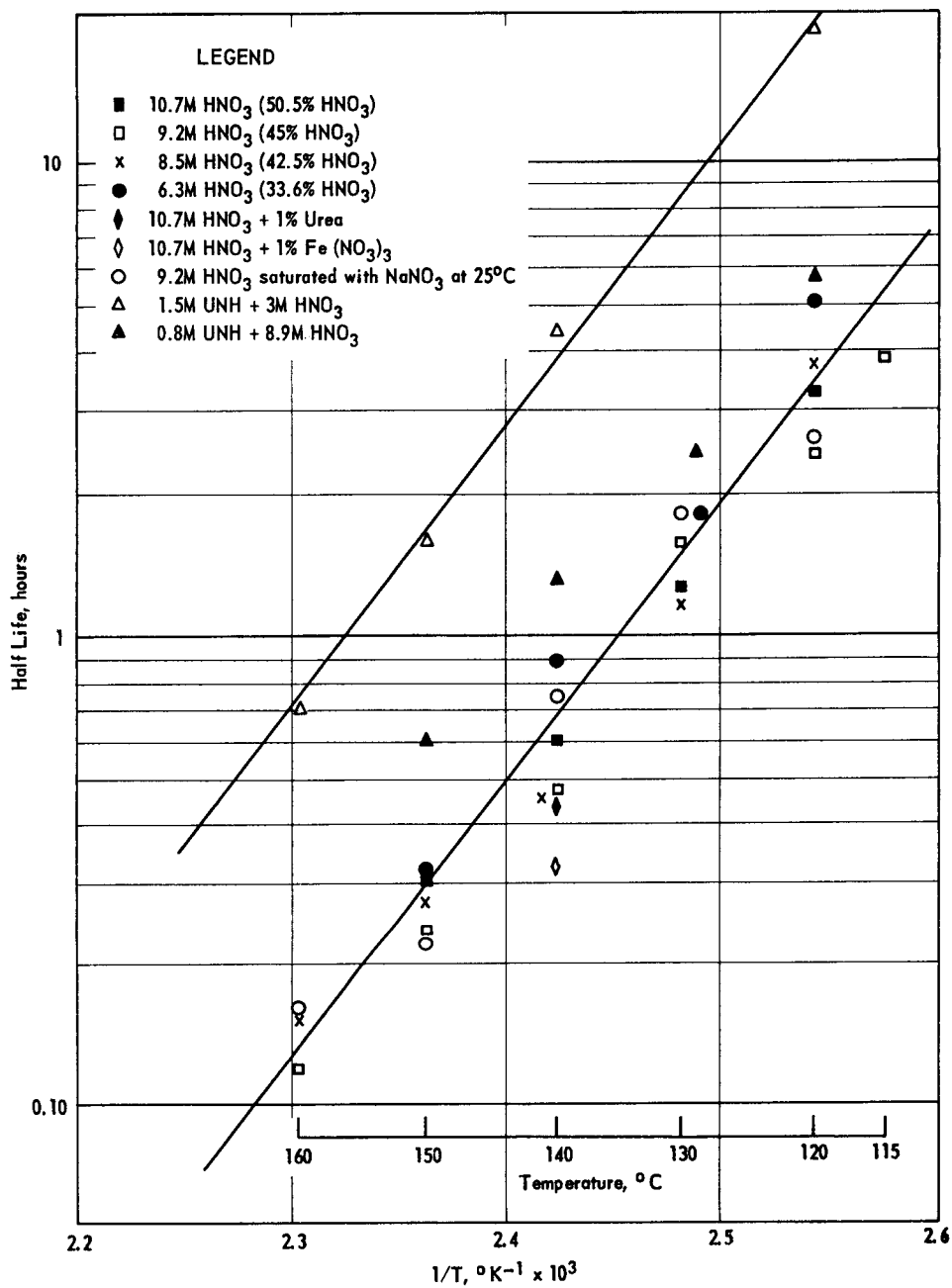


FIG. 2 ARRHENIUS PLOT OF HALF LIFE OF THE REACTION

TABLE III

Summary of Frequency Factors

| | Sec ⁻¹ |
|---|--|
| Accepted range ⁽⁴⁾ | 10 ^{11.5} to 10 ^{14.5} |
| Computed from Burger's analysis ⁽³⁾ for 20% TBP | 10 ⁰ |
| for 100% TBP | 10 ^{6.7} |
| Data of this report for 100% TBP | 10 ^{10.6} |

The half life of the reaction was found to be independent of the nitric acid concentration and of the presence of salts such as sodium nitrate and suspected catalysts such as urea and ferric nitrate. These data can be explained by the existence of a molecular complex that decomposes completely into gaseous products. A higher concentration of nitric acid in the aqueous phase provides more complex but does not alter the half life of the complex.

Saturation of nitric acid with sodium nitrate dilutes the concentration of nitric acid in the aqueous phase. The rate of reaction of the equilibrated organic phase was unchanged and the final gas volume was reduced. It was concluded that sodium nitrate addition resulted in a reduction of the quantity of the TBP - nitric acid complex in the starting TBP phase; its effect was similar to that of dilution of the aqueous phase with water.

The final value of gas release was a function of temperature as well as the starting concentration of nitric acid, as shown by Table IV. The higher temperatures shifted the reaction toward the gaseous products by increasing the rate of the CO₂-producing reaction as shown by Table IV. The higher starting concentration of nitric acid produced more gaseous products, but only in proportion to the higher concentration of reactant.

The theoretical volume of nitrogen gases (N₂ + N₂O) from the reaction was calculated from the concentration of nitric acid complexed in the TBP, which was estimated from equilibrium data of Alcock, et al.⁽⁵⁾ These calculations are reported in Table IV and show that it was reasonable to assume that the gas released from the long exposure samples (infinite time) represented complete decomposition of the nitric acid in the organic phase. The measured gas volume at infinite time was, in every case but one, greater than the theoretical nitrogen gases; the balance of gas was calculated as CO₂. The amount of CO₂ increased with an increase in temperature, but at any temperature level the variation in the percentage of CO₂ was random. The average values of CO₂ reported in Table IV were used to calculate the heat of reaction for the composite reaction. The details of this calculation are shown in the Appendix and in Table A-I.

TABLE IV

Calculations to Show Production of CO₂ Increases
with Increase in Temperature

| | | | | | |
|--|------------------|---------------|------------|--------------|----------------------------------|
| Composition of aqueous phase used in equilibration, HNO ₃ , M | | 6.3 | 8.5 | 10.7 | |
| Calculation of organic phase molarity using data of Ref. 3, HNO ₃ , M | | 2.75 | 3.13 | 3.60 | |
| Theoretical volume of N ₂ + N ₂ O at 25°C, ml/g | | 32.6 | 36.9 | 42.2 | |
| | <u>Temp., °C</u> | | | | <u>Ave. % CO₂</u> |
| Total gas volume at infinite time; calculated % CO ₂ (a) tabulated in parenthesis | 120 | 31 (0) (b) | 44 (16) | 54 (22) | (19) |
| | 130 | 40 (19) | 45 (18) | 59 (29) | (22) |
| | 140 | 45 (27) | 47 (21) | 64 (34) | (27) |
| | 150 | 47 (31) | 51 (28) | 71 (41) | (33) |
| | 160 | 49 (33) | 61 (39) | 73.5 (42) | (38) |

(a) CO₂ was assumed to be the difference between total gas found and theoretical volume of N₂ + N₂O.

(b) Not included in average

Gas samples were scrubbed with sodium hydroxide and the volume loss was reported as carbon dioxide. The presence of NO or NO₂ was ruled out by the lack of color either before or after the addition of a small amount of air. Several samples that had been scrubbed with sodium hydroxide were composited and submitted as a single sample for mass spectrometer analysis. The analysis of the composite is shown in Table V.

TABLE V

Composition of Gaseous Reaction Products

160°C Decomposition Temperature

| | |
|---------------------|--------------|
| | <u>Mol %</u> |
| CO ₂ (a) | 40 |
| N ₂ | 48 |
| O ₂ | 3 |
| N ₂ O | 7.8 |
| Butyl groups (b) | <u>1.2</u> |
| | 100.0 |

(a) CO₂ was determined by adsorption in NaOH. The other components were determined by mass spectrometer analysis of the CO₂-free mixture.

(b) The butyl groups are an estimate. No calibration of the mass spectrometer with specific butyl compounds was attempted, but the results indicated a behavior similar to that of butyl esters.

The heat of reaction was calculated by assuming that nitric acid supplied the oxygen and that butyl alcohol was oxidized either to butric acid or completely to CO₂ as calculated from the material balance between the nitrogen component and the CO₂ component found in the product gas. The details of the material and heat balance are presented in the Appendix. The heat of reaction of the complex prepared by contacting TBP with 10.7M HNO₃ was computed to be 177 cal/1000 grams at 120°C and 258 cal/1000 grams at 160°C. A complete range of heats of reaction is tabulated in Table A-I.

CALCULATION OF INITIATION TEMPERATURE

The temperature at which the reaction becomes self-accelerating was defined and calculated as the temperature at which the heat release of the chemical reaction is equal to the heat loss from the walls of the reaction vessel. This definition was also used by Bowden and Yoffe⁽⁶⁾ in evaluation of hazardous storage conditions. A knowledge of the rate of reaction and the heat of reaction are sufficient for calculating the rate of heat release, and a knowledge of over-all heat transfer coefficient and area is sufficient for calculating the heat loss. Engineering units are used in this section, whereas cgs units were used in sections involving experimental results. The heat balance is given by equation 1.

$$UA(T - t) = HCV\rho s e^{-E/RT} \quad (1)$$

where

U = heat transfer coefficients; Btu/(hr)(ft²)(°F)

A = effective area for heat loss, ft²

T = temperature of organic phase, °R

t = ambient temperature, 540°R

H = heat of reaction, Btu/lb, Table A-1

C = relative concentration of the nitrate complex. C = 1.0 where 10.7M HNO₃ was used for equilibrating the TBP, Figure 4.

ρ = density, 62 lb/ft³

s = Arrhenius frequency factor, hr⁻¹

E = energy of activation, Btu/lb-mol

R = gas constant Btu/(lb-mol)(°R)

V = volume of reactants in cylindrical vessel, ft³

After the variables of geometry are separated from those of temperature the equation becomes:

$$\frac{UA}{VCp} = \frac{Hse^{-E/RT}}{T - t} \quad (2)$$

The solution of equation 2 is given on Figures 3 and 4.

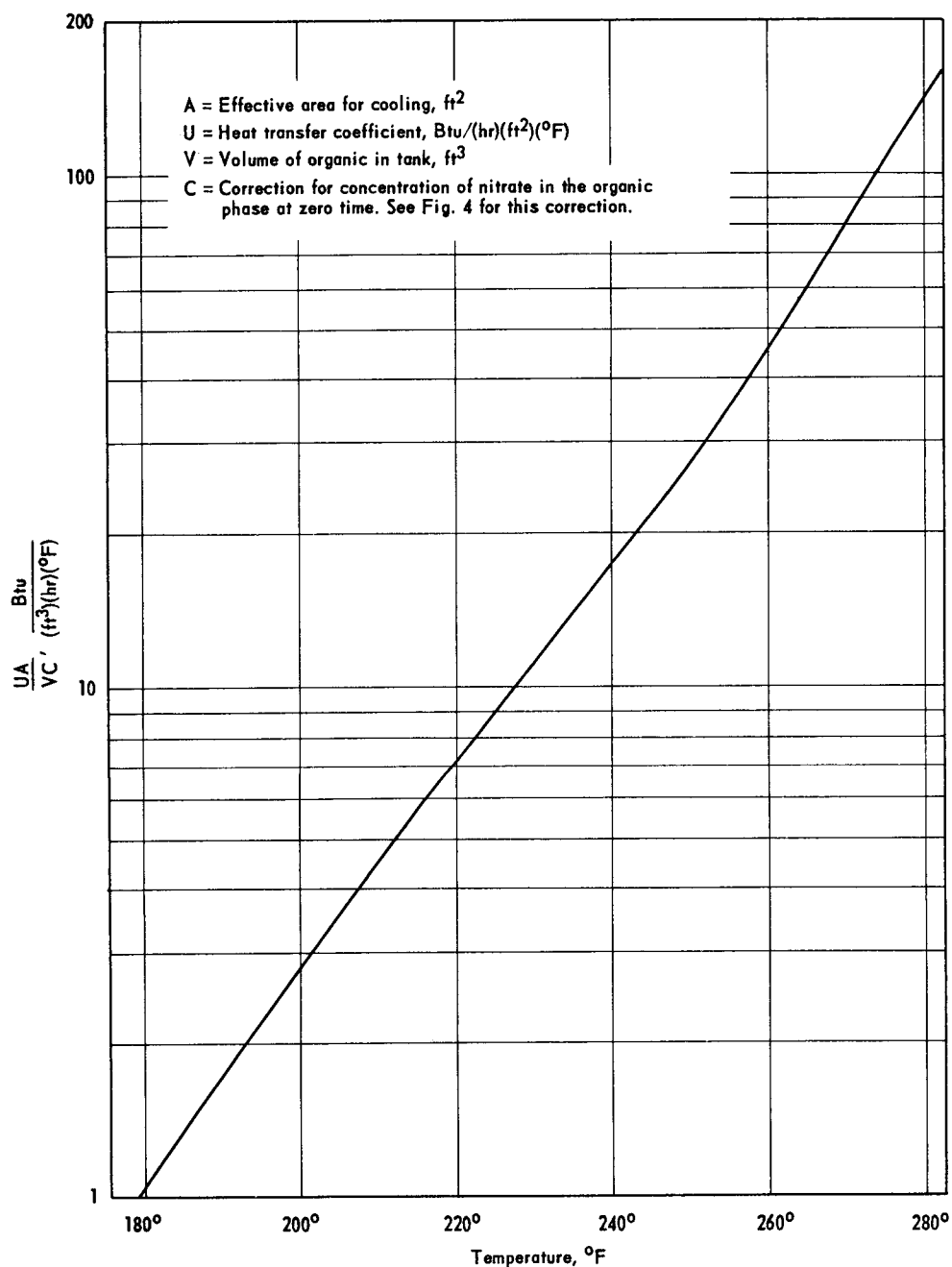


FIG. 3 TEMPERATURE AT WHICH REACTION BECOMES SELF-ACCELERATING

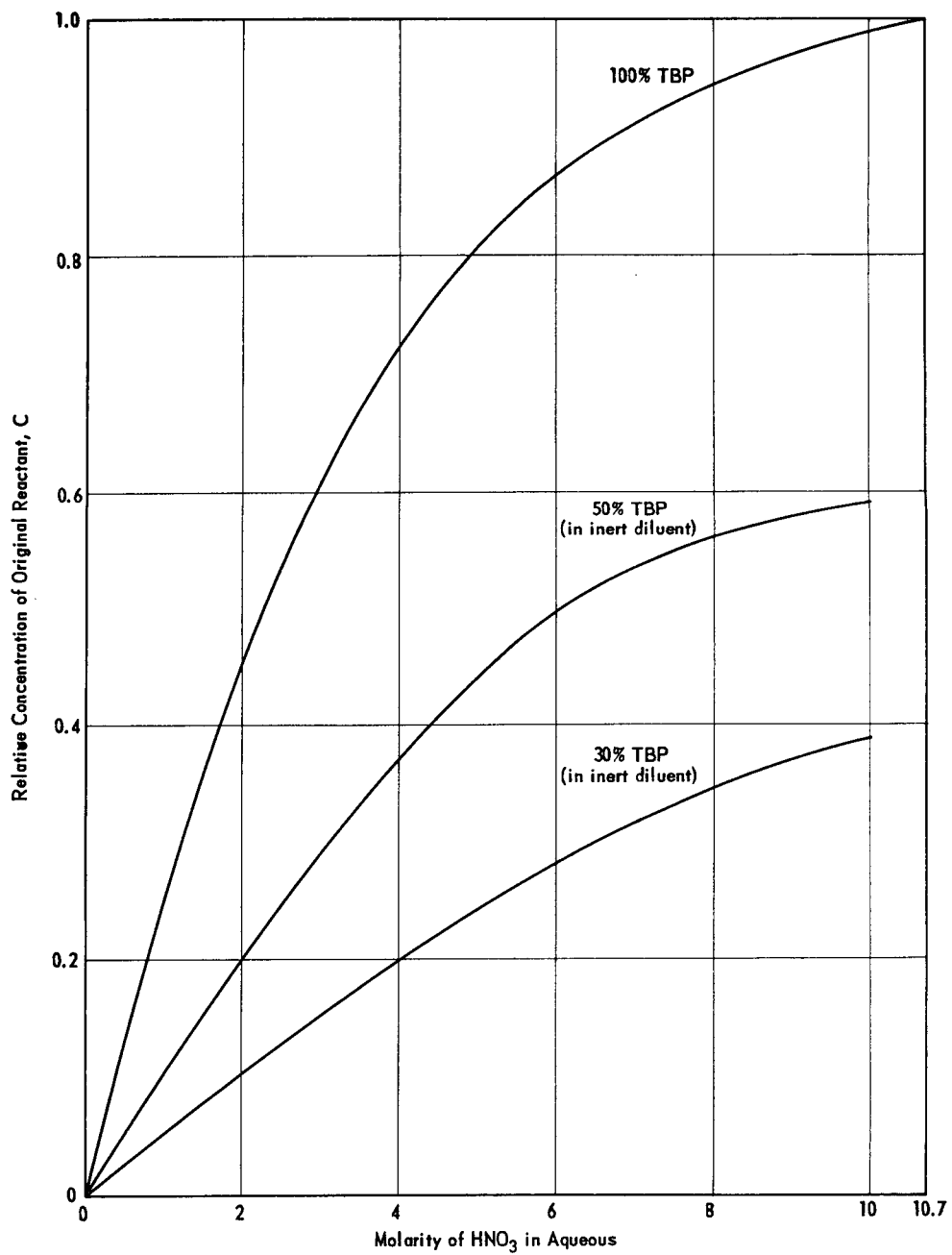


FIG. 4 CORRECTION FOR CONCENTRATION OF NITRATE
IN THE ORGANIC PHASE AT ZERO TIME
(100% TBP and 10.7 M HNO₃ taken as unity)

Figure 5 is a calculated example for vertical cylindrical vessel with a heat transfer coefficient of 5 Btu/(hr)(ft²)(°F) at the surface of the vessel. These calculations indicate, for example, that a tank 8 feet in diameter should not be exposed to direct heat that would raise the temperature of the pure TBP-HNO₃ complex to above 203°F.

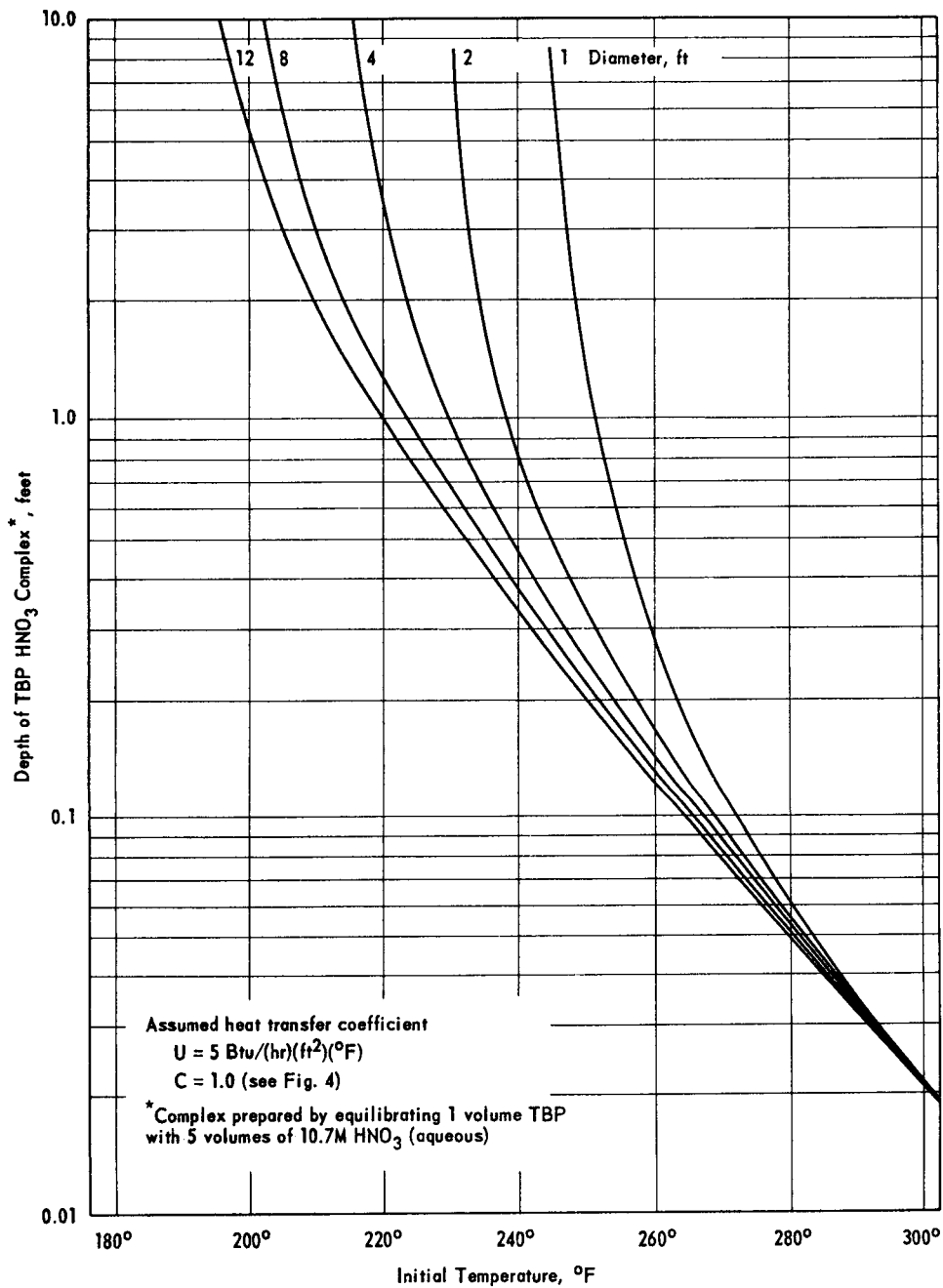


FIG. 5 TEMPERATURE FOR SELF-ACCELERATING REACTION TO OCCUR

Fortunately, the sensible heat required to raise the reaction temperature from this limiting condition to a level of hazardous proportions is greater than can be supplied by the fuel present. The temperatures calculated from Figure 5 thus define a safe operating condition whereas the initiation temperature determined by the adiabatic experiments described in the following section are definitely beyond the threshold of uncontrolled chemical reactions.

ADIABATIC EXPERIMENTS

PROCEDURE

The initiation temperature described in the previous section depends upon how closely the reactor or storage vessel approximates adiabatic conditions. Under perfectly adiabatic conditions, the temperature would rise in a manner that would depend upon the amount of heat that is generated and the sensible heat of the reactants and the products. An explosion would develop if the reaction started at a high enough temperature and with enough fuel that the reaction products could not be readily dispersed to the atmosphere. A detonation would be a special case in which the rate of reaction would proceed faster than the shock wave could vent the reaction products. This section describes four experiments in which larger samples were tested near adiabatic conditions.

Fifty-milliliter samples of the TBP-HNO₃ complex were quickly exposed to a steam-heating coil and the time-temperature data were recorded. Thirty seconds were required to charge the sample to the preheated reaction chamber. The sample container was surrounded by an electrically heated jacket that was maintained by manual control to give near-adiabatic conditions in the reactor chamber. Temperature readings were considered reliable to within $\pm 3^{\circ}\text{C}$. The TBP-HNO₃ complex was prepared by equilibrating one part of TBP with five parts of 10.7M HNO₃ at room temperature.

RESULTS

Rapid reaction of the mixtures was observed when the initial temperature of the reaction chamber was 130°C, but not when it was 125°C. The temperature curve for initiation at 130°C is shown in Figure 6, and a summary of four runs is shown in Table VI. Preheating at a reduced temperature (125°C) prevented a rapid decomposition when the temperature was later raised to 130°C (see Run 2). It was assumed that the preheat step at 125°C resulted in controlled decomposition of the complex, and when the reaction chamber was raised to 130°C there was insufficient fuel present to cause any rapid degradation. The results of the adiabatic experiments are in agreement with earlier bomb experiments⁽¹⁾. The initiation temperature and therefore the temperature limitations on process conditions still remain at 130°C (266°F).

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TABLE VI

Adiabatic Decomposition of the TBP-HNO₃ Complex

| Run | Steam-Heating Coil | | Liquid Temperature | | % Loss ^(b) |
|-----|----------------------------|---------------------------|--------------------|----------------------|-----------------------|
| | Steam Pressure, psig | Steam Temperature, (a) °C | Maximum, °C | Maximum Rate, °C/min | |
| 1 | 14 | 123 | (c) | 0 | 3 |
| 2 | 18 (1st hr) 20 (2nd hr) | 125 130 | (c) | 0 | 10 |
| 3 | 20 | 130 | 186 | 100 | 25 |
| 4 | 40 | 155 | 208 | 123 | 32 |

(a) The recorded steam temperatures indicate that the electrical heaters used for tracing the steam lines were actually superheating the steam.

(b) Volume % of material charged to reaction chamber.

(c) Where no rapid reaction occurred, the temperature of the mixture was approaching the steam temperature when the experiment was terminated.

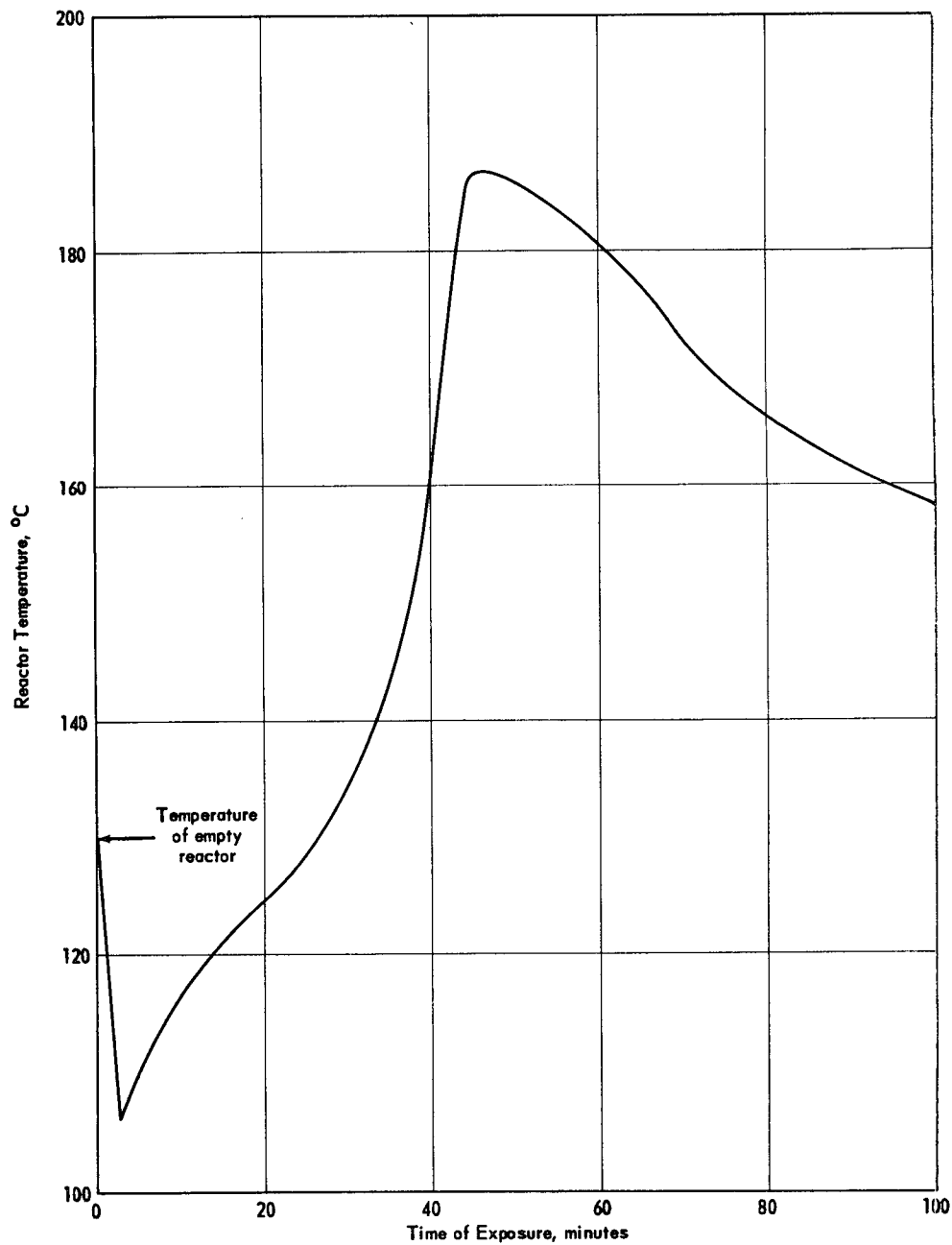


FIG. 6 ADIABATIC DECOMPOSITION OF TRIBUTYL PHOSPHATE - NITRIC ACID COMPLEX TEMPERATURE RECORD

APPENDIX

CALCULATION OF HEAT AND MATERIAL BALANCE

Basis is 1000 grams of the TBP - nitric acid complex. This example was chosen for organic that had been contacted with 10.7M HNO₃ and was estimated to have a molar concentration of 3.60M HNO₃. Exposure temperature was 120°C (Table IV).

MATERIAL BALANCE

The volume of N₂ + N₂O was calculated as follows:

$$\frac{(3.60)(0.5)(22.4)(298)}{(1.045)(273)} = 42.2 \text{ liters at } 25^{\circ}\text{C}$$

1.045 = density kg/liter

0.5 = $\frac{1}{2}$ mol gas per mol HNO₃ present.

The volume of CO₂ was calculated from average gas analysis shown in Table V.

$$\frac{(42.2)(20)}{80} = 10.4 \text{ liters}$$

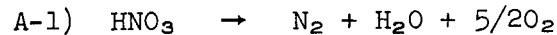
Total gas 52.6 liters

Using the N₂:N₂O:O₂ ratio of Table V, the following composite gas volume was obtained. (The gas can be assumed to be void of water vapor because of the high pressures in the sealed capsules.)

| | <u>Volume, liters</u> |
|------------------|-----------------------|
| N ₂ | 36.3 |
| N ₂ O | 5.9 |
| O ₂ | 2.3 |
| CO ₂ | 8.1 |

From reactions A-1 and A-2, listed below, the amount of O₂ that must have been derived from the decomposition of the available nitric acid can be computed.

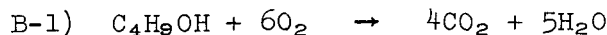
Decomposition of nitric acid



| | |
|---|--------------------|
| O ₂ from reaction forming N ₂ | 90.7 liters |
| O ₂ from reaction forming N ₂ O | <u>11.8</u> liters |
| Total | 102.5 liters |
| O ₂ left as O ₂ | <u>2.3</u> liters |
| O ₂ available for oxidation | 100.2 liters |

The amount of O₂ consumed by oxidization of butyl alcohol can be calculated from the CO₂ formed and the balance of the O₂ can be assumed to form butric acid. See reactions B-1 and B-2 below.

Oxidation of butyl alcohol



Mols C₄H₉OH going to CO₂

$$\frac{(8.1)(273)}{(22.4)(298)} \left(\frac{1}{4}\right) = 0.0829 \text{ g-mol}$$

Liters O₂ left for formation of C₃H₇COOH

$$100.2 - (8.1) \left(\frac{6}{4}\right) = 88.1 \text{ liters}$$

Mols C₃H₇COOH formed

$$\frac{(88.1)(273)}{(22.4)(298)} = 3.61 \text{ g-mols}$$

Mols C₄H₉OH consumed $3.61 + 0.0829 = 3.69 \text{ g-mols}$

Water is derived both from decomposition of the nitric acid and oxidization of butyl alcohol by either route.

H₂O from HNO₃

$$\frac{3.60}{(1.045)(2)} = 1.73 \text{ mols/1000 g}$$

H₂O from formation of CO₂

$$(0.0829)(5) = 0.41 \text{ mols/1000 g}$$

H₂O from formation of C₃H₇COOH

$$(3.61)(1) = \underline{3.61} \text{ mols/1000 g}$$

Total H₂O formed 5.75 mols/1000 g

HEAT BALANCE

Only those components that change in the chemical reaction are considered in the heat balance. The heat capacity of the reactants and products was neglected. The heat of formation of water vapor at the reaction temperature was used for water.

Heat of formation of the reactants (H_R)

$$\text{a) } \text{HNO}_3 = \frac{(-41.4)(3.60)}{1.045} = -142 \text{ cal/1000 g sol'n}$$

$$\text{b) } \text{C}_4\text{H}_9\text{OH} = (110.82)(3.69) = +409 \text{ cal/1000 g sol'n}$$

Heat of formation of the products (H_P)

$$\text{a) } \text{N}_2\text{O} = \frac{(5.9)(273)(19.49)}{(22.4)(298)} = +4.7 \text{ cal/1000 g sol'n}$$

$$\text{b) } \text{CO}_2 = (0.0829)(4)(-94.38) = -31.3 \text{ cal/1000 g sol'n}$$

$$\text{c) } \text{C}_3\text{H}_7\text{COOH} = (3.61)(126.5) = 456 \text{ cal/1000 g sol'n}$$

$$\text{d) } \text{H}_2\text{O} = (5.75)(-56.93) = -327 \text{ cal/1000 g sol'n}$$

Net heat of reactions (1000 g of TBP + HNO₃)

$$\Sigma H_P - \Sigma H_R = 179 \text{ cal/1000 g sol'n}$$

TABLE A-I

Heat of Reaction

Basis of 1000 g of organic phase prepared by contacting one part of 100% TBP with five parts of 10.7M HNO₃.

| Temperature, °C | 120 | 130 | 140 | 150 | 160 |
|---|------|------|------|------|------|
| Total mols C ₄ H ₉ OH consumed | 3.69 | 3.62 | 3.43 | 3.16 | 2.87 |
| Consumed by complete oxidation to CO ₂ and H ₂ O, % | 2.3 | 2.7 | 4.0 | 6.0 | 8.2 |
| Over-all heat of decomposition | | | | | |
| Cal/1000 g solution | 179 | 184 | 204 | 232 | 258 |
| Mols TBP present/1000 g | 2.95 | 2.95 | 2.95 | 2.95 | 2.95 |
| Heat of reaction, cal/g-mol (at the reaction temperature) | 60 | 62 | 69 | 79 | 87 |
| Heat of reaction, Btu/lb | 319 | 331 | 367 | 418 | 464 |

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