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THE HEATS OF FUSION OF TRINITROTOLUENE, TETRYL AND PICRIC ACID[1]

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Introduction

Several articles[4] have been published in which the binary systems trinitrotoluene-tetryl, trinitrotoluene-picric acid and tetryl-picric acid are discussed and the data collected in the course of these investigations can be utilized for the purpose of calculating the heats of fusion of these compounds.

Method

Generalizations concerning the lowering of the freezing point of a pure solvent by the addition of a solute, and the relation of this phenomenon to the heat of fusion of the solvent, have been worked out on the basis of dilute solutions, whereas these binary systems are solutions of comparatively high concentrations. It was endeavored to apply the known relations to this problem in order to obtain a result within the limit of reasonable error in each case.

Starting with the known relations[5] $M_1 = Em/t$ and $E = RT_0^2/100w$, we can derive the following: $L_f = M_2R.T_0^2/100\ M_1S$ where L_f is the latent heat of fusion of the solvent at T_0 in calories per gram molecule, M_1 is the molecular weight of the solute, M_2 is the molecular weight of the pure solvent, T_0 is the absolute freezing point of the solvent, R is the gas constant (1.9869), m is the number of grams of solute per 100 g. of solvent, t is the depression of the freezing point of the solvent for m, w is the latent heat of fusion of the solvent at T_0 in calories per gram, E is the molecular depression of the freezing point, S is the slope of the curve obtained by plotting percentage of solute against the depression of the freezing point, t.

In this derivation it should be remembered that although the percentage of solute present in any given mixture is $100\ m/(100 + m)$, when the value of m approaches zero in extremely dilute solutions, this value becomes practically identical with m, and as equal molecular fractions cause equal lowering of the freezing point, it is unnecessary to consider the formation or molecular weight of any molecular complex present.

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[1] Published by permission of the Director, U. S. Bureau of Mines.

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[4] Taylor and Rinkenbach, *Ind. Eng. Chem.*, **15,** 73, 795, 1070 (1923).

[5] Nernst, "Theoretical Chemistry," MacMillan Co., 5th edition, **1923,** p. 302.

Accordingly, we have available all the factors in the above equation except the values of S and L_f; by deriving the equation of each side of the curve for each binary mixture when percentage composition (percentage of solute) and temperature of equilibrium are plotted against each other and taking the value of S when x (percentage of solute) equals zero, we can easily calculate the value of L_f in each case.

The System, Trinitrotoluene-Picric Acid

After plotting the actual concentration-temperature data for the system, trinitrotoluene-picric acid, in the form of a large curve, intermediate values were taken from this curve so that those used for the calculation of heats of fusion would cover smaller and more uniform concentration ranges.

The trinitrotoluene side of the curve proved to be a straight line of equation $y = 0.59x - 0.03$, so that $L_f = 4163$ and $w = 18.3$.

The picric acid side of the curve, from the data,

TNT, %............	5.0	10.0	15.0
Equil. temp..........	118.4	114.6	110.7
t..................	3.5	7.3	11.2

gives the equation $y = -0.2 + 0.73x + 0.002x^2$, so that when $x = 0$, $L_f = 4282$ and $w = 18.7$.

Guia[6] also studied the system trinitrotoluene-picric acid. However, as shown by Bell and Herty[7] in their duplication of his work on the nitrotoluenes, Guia misinterpreted his cooling curves, with the result that his values for equilibrium temperatures were always too low. This has been found to be true also for his results on the system, trinitrotoluene-picric acid, so that values derived from his data are erroneous.

The System, Tetryl-Picric Acid

From the temperature-concentration data

% Tetryl	Equilibrium temperature °C.	t	% Picric acid	Equilibrium temperature °C.	t
10.0	115.2	6.7	5.0	125.3	3.42
20.0	108.2	13.7	10.0	121.6	7.12
40.0	90.0	31.9	15.0	117.5	11.22

$y = 1.1 + 0.49x + 0.007x^2$; $y = 0.12 + 0.62x + 0.008x^2$, and when we derive values for S when x is zero, we find L_f of picric acid $= 5041$; L_f of tetryl $= 6482$; w of picric acid $= 22.1$; w of tetryl $= 22.6$.

The System, Trinitrotoluene-Tetryl

Inspection showed the trinitrotoluene side of the temperature-concentration curve of this system to be a straight line, the slope of which is 0.39. From this, $L_f = 5025$ and $w = 22.1$.

[6] Guia, *Gazz. chim. ital.*, **46**, 2 (1916).

[7] Bell and Herty, *J. Ind. Eng. Chem.*, **11**, 1124 (1919).

The tetryl side of the curve, with data

TNT, %	10.0	20.0	40.0
Equil. temp., °C	120.8	112.2	90.8
t	7.92	16.52	37.92

gave the equation $y = 0.72 + 0.65x + 0.007x^2$. From this, taking the value of S when x is zero, L_f of tetryl = 6237 and $w = 21.7$.

Guia[8] has published an incomplete freezing-point-solubility curve for this system, showing the formation of a molecular compound but not identifying it. The same criticism applied to his study of the system, trinitrotoluene-picric acid was found to apply here, his equilibrium temperatures being too low, as shown by Taylor and Rinkenbach.[4] For this reason, his data cannot be used for the calculation of heats of fusion.

Summary

A summary of the values obtained for the heats of fusion of trinitrotoluene, picric acid and tetryl is as follows.

	Heat of fusion in gram-calories per gram of substance			Heat of fusion in gram-calories per gram molecule of substance		
	TNT	Picric acid	Tetryl	TNT	Picric acid	Tetryl
TNT-Picric	18.3	18.7	..	4163	4282	..
Tetryl-picric	..	22.1	22.6	..	5041	6482
TNT-Tetryl	22.1	..	21.7	5025	..	6237
Av.	20.2	20.4	22.2	4594	4662	6360

The results are of the same order, as is to be expected because of the similarity of the compounds and the average results are in the same general ratio as their molecular weights.

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A NEW ABSORBENT FOR OXYGEN IN GAS ANALYSIS

BY LOUIS F. FIESER

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On dissolving in dilute alkali a mixture of sodium anthraquinone-β-sulfonate and sodium hyposulfite in large molar excess, a deep red solution is obtained which absorbs oxygen with great rapidity. This paper reports a brief investigation of the suitability of this reagent as an absorbent for oxygen in gas analysis.

Since sodium hyposulfite has itself been recommended for this purpose,[1]

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[8] Guia, *Z. ges. Schiess. und Sprengstoffw.*, **10,** 111 (1915).

[1] (a) Franzen, *Ber.*, **39,** 2069 (1906). (b) Durig, *Biochem. Z.*, **4,** 65 (1907). See also (c) Tobiesen, *Skand. Arch. Physiol.*, **6,** 278 (1895). Pettersson and Högland, *Ber.*, **22,** 3324 (1889). Descamps, *J. Chem. Soc.*, **112,** ii, 216 (1917).