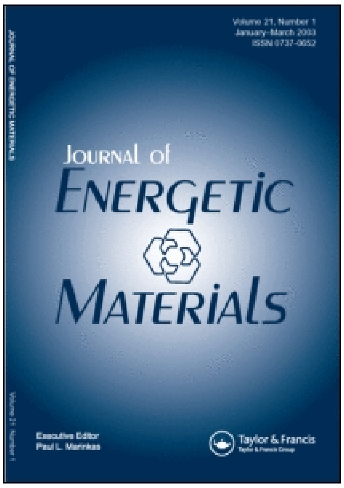

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Solid liquid phase equilibria in the hydroxylammonium nitrate water system

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SOLID + LIQUID PHASE EQUILIBRIA IN THE HYDROXYLAMMONIUM NITRATE + WATER SYSTEM

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ABSTRACT

The binary solid + liquid phase diagram has been measured for the water + hydroxylammonium nitrate (HAN) system. The phase diagram is a simple eutectic type with the eutectic at 231.5 K (41.7°C) and a mole fraction HAN of 0.281 (wt fraction HAN = 0.676).

The enthalpy of fusion of the HAN was determined from the solid + liquid results to be 11 ± 2 $kJ \cdot mol^{-1}$. The HAN was obtained from Southwestern Analytical Chemicals, Inc. as an approximately 2.8 molar solution. The water was removed by vacuum drying over a three month time period, but the sample still contained some impurity. The impurity level calculated from the change in melting temperature with fraction melted is 0.040 mole fraction. Chemical analysis indicates the sample contains 0.005 mole fraction HNO_3 and 0.007 mole fraction NH_4NO_3, with $N_2H_5NO_3$ absent. The remainder of the impurity could be water, but this is

not known for sure.

We obtained a melting temperature for the impure sample of HAN of 315.9 K (42.7°C). The melting point corrected to zero impurity is 317.7 ± 1 K (44.5°C).

INTRODUCTION

In this paper we report the binary solid + liquid phase equilibria for hydroxylammonium nitrate (HAN) with water. The system is of commercial interest since HAN has potential as a high energy propellant. The system is also of interest from a fundamental point of view. HAN is a very low melting ionic substance in which the cation NH_3OH^+ can hydrogen bond to other cations, to the NO_3^- anion, and to the water. Many other aqueous systems in which the second component contains the hydroxyl group form solid hydrates through hydrogen bond formation. Examples are systems in which the second component is an alcohol such as methanol, ethanol, 2-propanol or 2-methyl-2-propanol[1], or an acid such as sulfuric[2] or nitric[3]. It is of interest to see if HAN also forms solid hydrates.

EXPERIMENTAL

The HAN was obtained as an approximately 2.8 molar aqueous solution from Southwest Analytical Chemicals. The solution is certified to contain less than 10 ppm sulfate, 2 ppm calcium and magnesium, 10 ppm chloride, 0.2 ppm iron, and 10 ppm ash. The amounts of other nitrogen containing materials such as nitric acid, hydrazonium nitrate, and ammonium nitrate, are not known. We will see later that some of these substances are present in the sample as impurities.

The water was removed from the HAN by evacuation through a liquid nitrogen cold trap. Two different concentrated samples were prepared. Approximately one half of the water was removed from sample #1. It served as the stock solution for preparing the water rich mixtures. HAN sample #2 was prepared by pumping continuously on the aqueous solution over a time period of approximately three months. For much of the time, the sample was held at 50°C during the day to keep it liquid. The sample would solidify overnight and the melting procedure was repeated the next day. For approximately the last month, the sample was kept as a solid during evacuation. By this time very little vapor from the sample was being deposited in the liquid nitrogen trap. Often, this solid in the trap had a blue color which disappeared when it was melted. This suggested that oxides of nitrogen were being removed, presumably due to slow decomposition of the sample.

About 300 grams of dry HAN were obtained in sample #2. Water mixtures of known composition were prepared from this starting material by weighing. HAN is very hygroscopic and was never handled in contact with the air. It was transferred to sealed weighing bottles inside a glove bag filled with nitrogen. The composition of sample #1, which contained some water, was determined by obtaining freezing points of solutions of both sample #1 and sample #2 in an overlapping temperature range and adjusting the starting composition of sample #1 until the solid + liquid lines for the solutions of the two samples coincide.

The apparatus has been described in a previous paper.[4] Temperatures were measured with a Rosemount strain free resistance thermometer (IPTS-68) in combination with a computerized data collection system.[5] At the beginning of the measurements, we checked the calibration of the thermometer at the ice point and found it to agree within 0.01 K. We estimate our temperature scale to be accurate to ±0.05 K. Melting temperatures were obtained from time against temperature warming curves. In previous papers[5-6], we have shown that melting points accurate to 0.1 K can be obtained by this procedure. However, the HAN + water system was hard to hold in solid + liquid equilibrium. Different melting point determinations on the same sample gave values differing by as much as 0.5 K. Because of this, we estimate the uncertainty of our measurements to be as large as ±1 K.

RESULTS AND DISCUSSION

The solid + liquid results for xHAN + (1-x)H_2O are given in Table 1 and shown in Figure 1. In this paper, we define mole fraction x as moles HAN/(moles HAN + moles H_2O) and do not consider the ionic dissociations in calculating the composition. A simple eutectic phase diagram is obtained with the eutectic at x

TABLE 1

Solid + Liquid Phase Equilibria for the HAN + H_2O System. x is Mole Fraction HAN, f is Weight Fraction HAN and δT is the Deviation of the Experimental Temperature Results from Equations (2) and (3). The Molecular Weights of HAN and H_2O Were Taken as 96.04 g·mol^{-1} and 18.015 g·mol^{-1} Respectively.

x	f	T/K	δT/K	x	f	T/K	δT/K
0	0	273.2	0	0.404	0.783	255.6[c]	0.6
0.013	0.066	272.1	0.6	0.414	0.790	255.4	-1.4
0.030	0.142	269.5	0.2	0.426	0.798	258.7	-0.1
0.054	0.233	266.1	-0.1	0.436	0.805	261.0[c]	0.5
0.102	0.377	260.1	0.1	0.442	0.809	261.6	0.1
0.129	0.441	256.1	-0.3	0.458	0.818	264.3	0.2
0.152	0.489	252.8	-0.4	0.471	0.826	267.4	1.3
0.170	0.522	250.4	-0.2	0.498	0.841	270.0[c]	-0.2
0.193	0.560	247.2	0.0	0.555	0.869	278.4[c]	0.3
0.229	0.613	242.0	0.7	0.605	0.891	284.2[c]	-0.1
0.251	0.641	236.9	-0.4	0.659	0.912	289.4[c]	-0.8
0.281[a]	0.676[a]	231.5[a]	-0.1,1.0[b]	0.724	0.933	297.7[c]	1.1
0.292	0.687	233.5	0.6	0.777	0.949	301.2[c]	0.1
0.314	0.709	236.9	-0.7	0.852	0.968	306.9[c]	0.1
0.319	0.714	238.0	-0.7	0.916	0.983	310.0[c]	1.0
0.335	0.729	241.6	-0.3	0.938	0.988	312.0[c]	-0.3
0.355	0.746	245.8	0.1	0.950	0.990	312.7[c]	-0.4
0.380	0.766	250.2	-0.5	0.976	0.995	314.2[c]	-0.4
0.398	0.779	252.6	-1.3	1	1	315.9[c]	0

[a] Eutectic composition and temperature.

[b] The first deviation at the eutectic composition is from equation (2) and the second is from equation (3).

[c] Melting temperatures obtained from solutions prepared from sample #2. All other melting temperatures were obtained by diluting sample #1 with water.

= 0.281 and T = 231.5 K. The eutectic halt in the time against temperature cooling curve was obtained over the entire composition region except for the mixture most concentrated in water (x = 0.013), and in that sample, the lack of a eutectic halt may be due to limited sensitivity or supercooling. We have concluded that solid phase solubility is very limited in this system and that essentially pure HAN or pure H_2O freezes from solution. We found no evidence for solid hydrate formation in this system, although we cannot completely rule it out since supercooling effects may make it very difficult to form the hydrate. An analogous example is the water + ethylene glycol system[7] in which a stable 1:1 hydrate forms, but only when some very specific cooling and warming procedures are followed which initiate the crystallization of the hydrate.

The overlap region between solutions formed from sample #1 and from sample #2 is in the mole fraction range from x = 0.4 to x = 0.5. The overlap was not perfect in that the slopes of the solid + liquid lines for each sample were not quite the same in the overlap region. We attribute this effect to different amounts of impurity in sample #1 and sample #2.

Table 1 also gives the weight fraction f of HAN and Figure 2 shows the phase diagram plotted in terms of centigrade temperature and weight fraction rather than mole fraction. The rapid change of the melting temperature of the HAN with weight fraction is apparent. Thus, an 85 wt per cent HAN solution has a melting temperature near 0°C.

We have used a fitting equation described in an earlier paper[8] to represent the temperature vs. mole fraction results. The equation has the form

$$T = T^*[1 + \sum_{j=1}^{n} a_j(x-x^*)^j] \tag{1}$$

where T is the melting temperature in Kelvin at mole fraction x, T^* is the melting temperature of the pure substance in Kelvin, x^* is the value of x at the composition where T^* is taken (0 or 1, for a simple eutectic system), and the a_j's are fitting coefficients. For a simple eutectic such as $x\mathrm{HAN} + (1-x)\mathrm{H_2O}$, it takes two equations to completely describe the system, one for each side of the eutectic. They are

$$T = 273.2[1 - 0.4838x + 0.2920x^2 - 1.7831x^3] \tag{2}$$

for x equal to or less than 0.281 (the eutectic composition) and

$$T = 315.9[1 + 0.1741(x-1) - 0.1040(x-1)^2 + 0.2460(x-1)^3] \tag{3}$$

for x equal to or greater than 0.281. The standard deviations of the experimental results from equation (2) and (3) are 0.33 K and 0.65 K, respectively. Deviations of the individual data points from the fitting equations are given in Table 1.

For convenience, we have also related the centigrade temperature t to f, the weight fraction of HAN. The relationships are

$$t = -24.8\left(\frac{f}{1-0.8124f}\right) + 2.81\left(\frac{f}{1-0.8124f}\right)^2 - 3.2\left(\frac{f}{1-0.8124f}\right)^3 \tag{4}$$

for f equal to or less than 0.676 (the eutectic composition) and

$$t = 42.7 - 55.0\left(\frac{1-f}{1-0.8124f}\right) - 32.9\left(\frac{1-f}{1-0.8124f}\right)^2 - 77.7\left(\frac{1-f}{1-0.8124f}\right)^3 \tag{5}$$

for f equal to or greater than 0.676. The functional dependence on f in equations (4) and (5) was deduced by substituting into equation (1) the relationship between weight fraction and mole fraction as given by equation (6)

$$x = \frac{\alpha f}{1+f(\alpha-1)} \qquad (6)$$

where $\alpha = 0.1876$ is the ratio of the molecular weights of water to HAN. As a result the standard deviations from equations (4) and (5) are the same as from equations (2) and (3).

It was very difficult to make solid + liquid phase equilibria measurements on the HAN + water system. Even with vigorous stirring, the HAN supercooled very badly, often as much as 25 to 30°C. In some cases, the only way to obtain solid HAN was to cool the sample below the melting temperature and add a small crystal of HAN. Often, adding a small amount of an inert solid helped start crystallization, but sometimes this was not effective.

We have already mentioned that it was difficult to maintain solid + liquid equilibrium when both phases were present. To compound the problem, in the mole fraction range from $x = 0.2$ to $x = 0.6$, the liquid became very viscous when cooled and formed upon stirring, what appeared to us to be an emulsion, or at least a very finely divided dispersion, of air in the liquid HAN. This emulsion or dispersion separated only very slowly upon standing and made the sample opaque so that it was impossible to make any visual observations of the melting point. In some of the samples near the eutectic composition, this mixture took on the appearance of a very soft white solid when cooled to temperatures near the eutectic temperature. It was difficult to tell if the sample contained solid instead of a very thick creamy emulsion or dispersion. If a solid did form, it must have had a small enthalpy of fusion since its formation was not detected in the time against temperature cooling or warming curve; and it must be metastable, since the conversion to the solid form for which we measured the melting temperature was spontaneous (although often after extreme supercooling) and gave an obvious break in the time against temperature cooling or warming curve.

R.A. Fifer[9] has used infra-red spectral measurements to detect the presence of a metastable form of solid HAN which crystallizes from an aqueous HAN solution when it is cooled to low temperatures (-30°C). The conditions under which he obtained this metastable form, which he calls β-HAN to distinguish it from the stable α-HAN, are similar to the conditions under which we obtained the soft creamy material described earlier. It is possible we may have been observing the metastable β-HAN. Our solid + liquid equilibrium measurements were made with the stable α-HAN since in all instances conversion to the stable form was observed before the melting temperature was determined.

In earlier papers[10-12], we have described a technique for calculating the enthalpy of fusion of a solid from solid + liquid phase equilibria measurements. The only necessary assumption is that solid solutions do not form. The process calculates $\Delta_{fus}H$ at

$x = 1$ and does not require the assumption of ideal solution behavior, which is required for most methods that calculate $\Delta_{fus}H$ from solid + liquid data.

We have applied this process to HAN and obtained an enthalpy of fusion of 11 ± 2 $kJ \cdot mol^{-1}$. We have already shown that solid solutions do not form in the HAN + water system and hence, the procedure for calculating $\Delta_{fus}H$ is valid. The large uncertainty in $\Delta_{fus}H$ is due to the presence of impurities in the HAN which we will describe later. L.J. Decker and R.A. Fifer[13] have recently made d.s.c. measurements on a HAN sample prepared by a method very similar to the procedure we followed in obtaining our sample #2. They obtained an enthalpy of fusion of 10.8 $kJ \cdot mol^{-1}$, in excellent agreement with our value.

The time against temperature cooling curve for the supposedly pure HAN in sample #2 was not flat, indicating either the presence of water that was not removed during the drying process or of impurities. It does not appear that water can completely account for the problem. The eutectic temperature, especially for samples near the eutectic composition, was not invariant, but changed during solidification over a 2 to 3 degree temperature range. This change in temperature of the eutectic requires the presence in the liquid of additional substances as impurities. Also, no halt or break in the cooling curve for sample #2 was obtained at a temperature corresponding to the HAN + water eutectic, but this may be due to a lack of sensitivity in detecting the halt and does not completely rule out the presence of some water.

The amount of liquid soluble + solid insoluble impurity in a liquid can be estimated from the change in melting temperature with fraction melted. By assuming the impurity forms an ideal solution with the liquid, the solution is dilute, and pure solid crystallizes from the liquid, the following equation can be derived[14-15]:

$$T = T^* - \frac{RT^{*2}}{\Delta_{fus}H}\left(\frac{y}{z}\right) \qquad (7)$$

where T is the melting temperature when z is the mole fraction of the substance in liquid form, T^* is the melting temperature of the pure substance, $\Delta_{fus}H$ is the enthalpy of fusion, R is the gas constant, and y is the mole fraction of impurity in the liquid sample. When this equation applies, a graph of T vs 1/z should be a straight line with intercept T^* and slope equal to $-RT^{*2}y/\Delta_{fus}H$, from which y can be calculated when $\Delta_{fus}H$ is known.

Figure 3 shows a graph of T vs. 1/z for sample #2 and obviously a straight line relationship is not obtained. We fitted the results to an extended form of equation (7) which allows for higher concentrations of impurity and for non ideal behavior. This extended equation has the form

$$T = T^* - \frac{RT^{*2}}{\Delta_{fus}H}\left[\left(\frac{y}{z}\right) + k_1\left(\frac{y}{z}\right)^2 + k_2\left(\frac{y}{z}\right)^3 + \cdots\right] \qquad (8)$$

where k_1, k_2, etc., are fitting coefficients. The line through the data in Figure 3 is the best fit of equation (8) with k_2, k_3, etc., set equal to zero. In this best fit, k_1 has a value of -4.36. T^*, the extrapolated melting temperature of the pure HAN, is 317.7 K;

and y, the mole fraction of impurity, is 0.040 when $\Delta_{fus}H$ of HAN is taken as 11 kJ·mol^{-1}. We estimate the uncertainty limits on T^* to be ±1 K and on y to be ±0.01 mole fraction. The only other value for the melting temperature of HAN that we could find in the literature was reported by Berthelot and Andre[16] in 1890. They give a value of 321 K (48°C).

We have made an attempt to identify the nature of the impurity in the HAN. The impurity must be volatile and hence nonmetallic since the ash content of the HAN is less than 10 ppm. The best possibilities are nitrogen compounds in other oxidation states such as H^+ (from HNO_3), $N_2H_5^+$ (from $N_2H_5NO_3$) and NH_4^+ (from NH_4NO_3). The supplier which provided us with the HAN titrated two portions of our sample #2 with hydroxide ion. Separate endpoints were obtained for the three reactions.

$$H^+ + OH^- = H_2O$$

$$NH_3OH^+ + OH^- = NH_2OH + H_2O$$

$$NH_4^+ + OH^- = NH_3 + H_2O$$

from which the amount of HNO_3 was determined to be 0.005 mole fraction and the NH_4NO_3 was 0.007 mole fraction. $N_2H_5NO_3$ cannot be analyzed by this process in the presence of NH_4^+ and NH_3OH^+ since the endpoint for the reaction

$$N_2H_5^+ + OH^- = N_2H_4 + H_2O$$

is at a pH between the endpoints of the NH_4^+ and NH_3OH^+ titration and cannot be separately detected. Thus, any $N_2H_5^+$ would appear either as part of the NH_4^+ or of the NH_3OH^+.

We have tested for $N_2H_5^+$ ion by ion chromatography and by a colorimetric test involving the reaction of p-dimethylaminobenzaldehyde with hydrazine to form the colored p-dimethylaminobenzalazine.[17] In both instances, $N_2H_5^+$ was not detected, indicating that it is not present as an impurity in the HAN. We did find NH_4^+ in the ion chromatography test at a concentration in reasonable agreement with the value obtained in the titration.

The total impurity we have detected as HNO_3 and NH_4NO_3 is 0.012 mole fraction. This is still short of the 0.04 mole fraction we obtained from the phase equilibria measurements and the difference is larger than the combined experimental error limits of the two methods. It is possible that the difference may be due to water, but it is also possible that some other form of impurity is present in the HAN. It is interesting to note that the 0.028 mole fraction impurity unaccounted for amounts to 0.5 wt per cent if we assume it is due to water. A small amount of water has a large effect on a mole basis.

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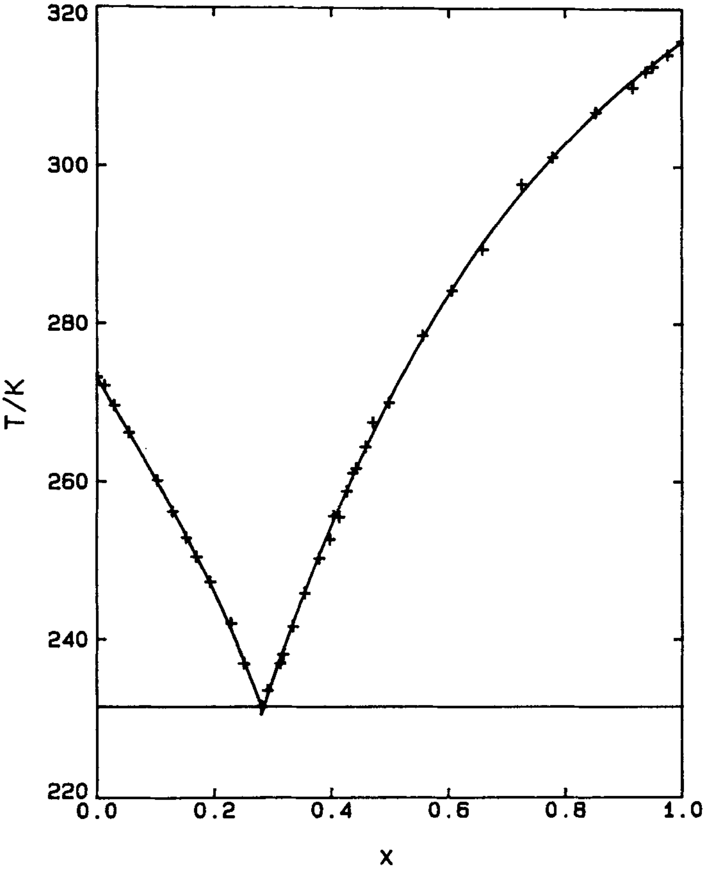

FIGURE 1

Solid + liquid phase diagram for xHAN + (1-x)H_2O. +, experimental results. The lines through the data points were generated from equations (2) and (3).

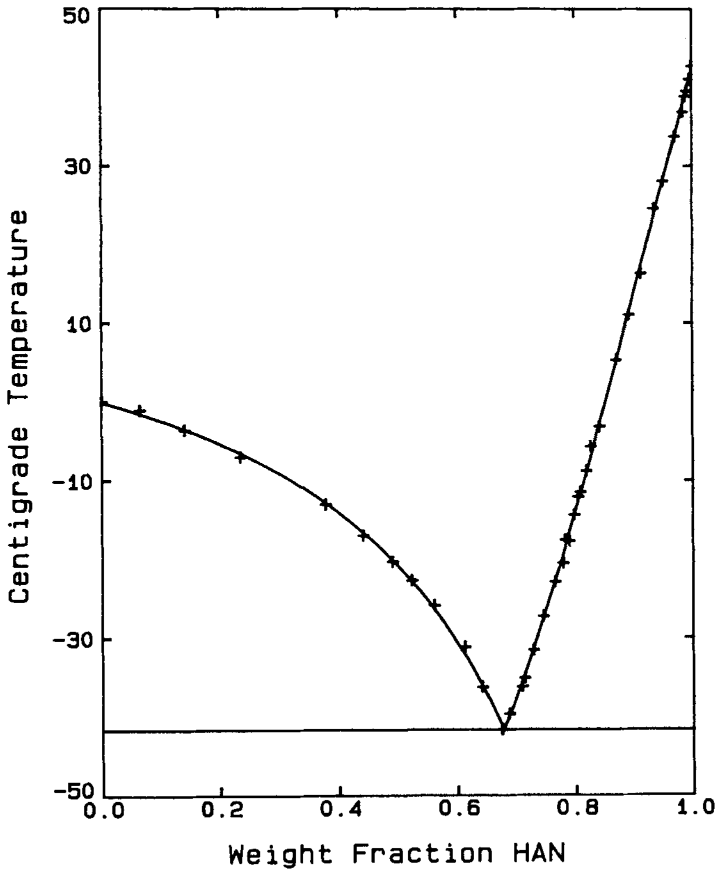

FIGURE 2

Solid + liquid phase diagram for HAN + water expressed in terms of Centigrade temperature and weight fraction of HAN. +, experimental results. The lines through the data points were generated from equations (4) and (5).

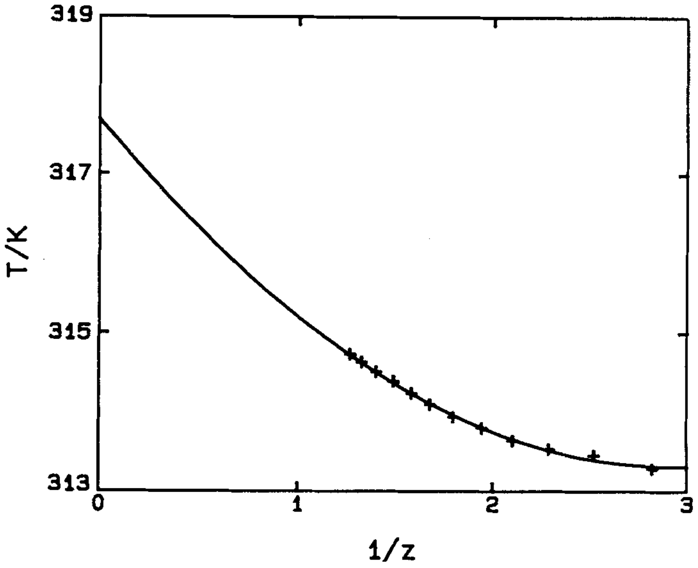

FIGURE 3

Graph of melting temperature against the reciprocal of the fraction melted for sample #2. +, experimental results. The line is the best fit of the data to equation (8). The intercept gives the melting temperature of pure HAN as 317.7 ± 1 K and the slope gives the purity as 0.96 ± 0.01 mole fraction.

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