HEAT CAPACITIES OF H2O + H2O2, AND H2O + N2H4, BINARY SOLUTIONS--ETC (U)

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Heat Capacities of $\text{H}_2\text{O} + \text{H}_2\text{O}_2$, and $\text{H}_2\text{O} + \text{N}_2\text{H}_4$, Binary Solutions;
Isolation of a Singular Component for $C_p$ of Supercooled Water
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Binary Solutions; Isolation of a Singular Component for $C_p$ of Supercooled Water

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In an effort to examine further the suggestion that anomalies in the properties of supercooled water reflect the approach to a thermodynamic singularity in the vicinity of $-45^\circ\text{C}$, an attempt has been made to separate the total heat capacity of water into "anomalous" and "normal" components. The basis for such a separation used here is extrapolation to zero solute content of $C_p$ of binary aqueous solutions from which the low temperature anomalies have disappeared. We have studied two closely related systems based on the second components (cont.)
The low temperature molar $C_p$-isotherms are very unusual. The extrapolations to zero solute of $C_p$ isotherms in the two systems yield similar but not identical "normal" components for pure water. The corresponding alternative sets of "anomalous" $C_p$ components vs temperature data, when best-fitted to the singular point equation $C_p(\text{anom}) = A (T/T_s - 1)^\gamma$, yield within one degree, the same $T_s$ value, 226 K, and exponents either side of the classical value of unity. When the value $\gamma = 1.0$ is assigned to the anomalous components of the dilute aqueous $H_2O_2$ solutions, the best fit $T_s$ values accurately mirror the behavior of the solution homogeneous nucleation temperatures.
TABLE OF CONTENTS

Abstract .................................................. 1
Introduction ............................................... 1
Experimental .............................................. 3
    Materials ............................................. 3
    Heat Capacity Measurements .......................... 3
Results .................................................. 6
Discussion ................................................ 8
Concluding Remarks ..................................... 11
Acknowledgements ....................................... 12
References .............................................. 13
Figure Captions .......................................... 14
Distribution List
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Abstract

In an effort to examine further the suggestion that anomalies in the properties of supercooled water reflect the approach to a thermodynamic singularity in the vicinity of $-45^\circ$C, an attempt has been made to separate the total heat capacity of water into "anomalous" and "normal" components. The basis for such a separation used here is extrapolation to zero solute content of $C_p$ of binary aqueous solutions from which the low temperature anomalies have disappeared. We have studied two closely related systems based on the second components $H_2O_2$ and $N_2H_4$. The low temperature molar $C_p$-isotherms are very unusual. The extrapolations to zero solute of $C_p$-isotherms in the two systems yield similar but not identical "normal" components for pure water. The corresponding alternative sets of "anomalous" $C_p$ components vs temperature data, when best-fitted to the singular point equation

$$C_p(\text{anom}) = A (T/T_s - 1)^\gamma,$$

yield within one degree, the same $T_s$ value, 226 K, and exponents either side of the classical value of unity. When the value $\gamma = 1.0$ is assigned to the anomalous components of the dilute aqueous $H_2O_2$ solutions, the best fit $T_s$ values accurately mirror the behavior of the solution homogeneous nucleation temperatures.
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Isolation of a Singular Component for $C_p$ of Supercooled Water

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Introduction

There has been considerable discussion recently of the anomalous temperature dependences of various thermodynamic and relaxational properties of water which become particularly pronounced under supercooled conditions. One interpretation advanced by this laboratory, and supported by others though by no means generally accepted, is that the behavior observed reflects approach to a singularity associated with either a liquid state mechanical instability or some internal network singularity. Impeding the proper assessment of this interpretation has been the difficulty of appropriate partitioning of the total observed thermodynamic quantity ($C_p$, $\alpha$, $\kappa T$) into normal and singular components, such that the 'critical exponents' can be determined and interpreted.

The purpose of the present measurements has been to provide a plausible basis for performing an appropriate partitioning, for the case of the constant pressure heat capacity. $C_p$ has been chosen for study because it is a quantity which can be measured rapidly for both bulk and emulsion samples, and therefore may be obtained over the maximum possible temperature range.
The method of partitioning C into normal and anomalous parts which we explore in this paper is based on the extrapolation, to zero solute content, of heat capacity isotherms for binary solutions of water and some appropriate second component which does not exhibit the anomalies characteristic of water. As will be seen, the water anomalies are completely eliminated by addition of some 20% of the second component and, at higher second component-concentrations linear, or approximately linear, composition - C functions are found. The latter lend themselves to plausible extrapolations to zero solute content and, from a series of such isotherms, one can thereby obtain a set of C vs T points assignable to the "normal" component of the pure water heat capacity.

Some data are already available in the literature which indicate the form the latter curve may take, but these were obtained from electrolyte solutions which seem in principle less appropriate for the purpose than molecular solutions which preserve much of the liquid-range character of water itself. Our primary choice of system for this study is H₂O + H₂O₂ on the basis that each liquid is extensively hydrogen-bonded by oxygen-proton interactions and that the melting points and boiling points of each component are very similar (273.1, 271.5: 373.1, 431.0). The essential difference lies in the proton donor:proton acceptor site ratio, which is 1:1 for water but 1:2 for H₂O₂. For H₂O + N₂H₄ (m.p., 275.0; b.p., 386.7), an almost equally attractive system on which studies are also reported, this ratio is inverted, viz. 2:1. (We note that a 1:1 mixture of H₂O₂ and N₂H₄ would have the same ratio as water and in principle could form a saturated open network which would perhaps exhibit water-like anomalies. Unfortunately hydrazine is as strong a reducing agent as H₂O₂ is an oxidizing agent!) In each case there are composition ranges in which supercooling into the glassy state becomes possible.
Experimental

Materials

Stabilized 50 g% \( \text{H}_2\text{O}_2 \) reagent, which was commercially available from Fisher Chemical Co., was used for the preparation of each aqueous \( \text{H}_2\text{O}_2 \) solution without any purification. The actual concentration was analyzed using the reaction:

\[
\text{H}_2\text{O}_2 + 2 \text{Ce(IV)}^+ \rightarrow 2 \text{Ce(III)} + \text{O}_2 + 2\text{H}^+
\]

with \((\text{NH}_4)_2\text{Ce(NO}_3)_6\) as the standard reagent, and found to be 37.6 mol % \( \text{H}_2\text{O}_2 \). The fact that no appreciable eutectic phenomena at 217 K and 221 K were observed in the melting curve of the dihydrate, \( \text{H}_2\text{O}_2 \cdot 2\text{H}_2\text{O} \) sample which was prepared on the basis of the analyzed concentration provides a confirmation of the analysis.

\( \text{N}_2\text{H}_4 \) aqueous solutions were prepared using the \( \text{N}_2\text{H}_4 \) reagent from Eastman Kodak Co. without further purification. The presence of some water in the sample was implied by the presence of a small heat absorption at the known \( \text{N}_2\text{H}_4 + \text{N}_2\text{H}_4 \cdot \text{H}_2\text{O} \) eutectic temperature, 218 K. This could be used as a basis for quantitative \( \text{H}_2\text{O} \) determination by the simple (but uncommon) method of measuring the eutectic heat absorption as a function of known water additions and extrapolating the linear plot vs weight % \( \text{H}_2\text{O} \) back to zero heat absorption (at negative % added water). The negative addition gives the original water content, 0.6% in this case, with an estimated uncertainty of 0.1 %.

Heat Capacity Measurements

The heat capacities were measured on 5-20 mg samples hermetically sealed in metal pans using the Perkin Elmer DSC-2 instrument with the scanning auto zero accessory. The DSC measured the energy required to keep the temperatures
of sample and reference pans identical during continuous heating or cooling. The heat capacity difference between sample and reference is therefore considered to be proportional to the difference between energies supplied under isothermal conditions on the one hand, and during continuous heating or cooling on the other. This difference is registered as a pen displacement during the run from the 'isothermal hold' position at each temperature, the latter usually being determined from the pen position at beginning and end of each run. The heat capacity of a sample is then derived from the difference between the displacements in scans of empty pan and loaded pan, respectively.

The thermal conditions in the actual measurements on the empty and sample loaded pans, unfortunately, differ slightly depending on time of measurement, different positioning of the pans, environmental conditions and other instrumental factors. These differences have undesirable effects on the display in two ways causing an error in heat capacity determination:

(i) the change of magnitude in displacement $\Delta l$, of the pen in the run from the isothermal hold position, and

(ii) the change of isothermal hold pen position without any change of the displacement $\Delta l$. Though the former problem is difficult to overcome except by repeating the measurements on the same concentration of samples, the latter may be solved by measuring the isothermal hold position at various temperatures in the range scanned, before and/or after the heating or cooling run. In conventional procedure, one measures the isothermal hold position only at the starting and ending temperatures in a run and assumes those lines at intermediate temperatures to behave in the same manner for the runs of empty and sample-loaded pans. The heat capacity values derived might involve an error of up
to 5% in $C_p$ of 10 mg bulk sample if the factors referred to above are unfavorable. Of course, the smaller the temperature range scanned in one run, the smaller the uncertainty becomes. We therefore measured the isothermal hold displacement at 10 K intervals, scanned the sample over a range of 100 K or so, and introduced the observed 'hold' positions into the data processing.

Both bulk and emulsion samples were used, according to the temperature range studied. Our emulsification procedure followed the method described by Rasmussen and MacKenzie (10) using methyl cyclohexane (MCH) or mixture of MCH and methyl cyclopentane (MCP) as a non-crystallizing carrier.

In the case of emulsions, we measured the heat capacity of the aqueous solution with the same amount of carrier placed in the reference pan as was contained in the sample, i.e. we "offset" the heat capacity due to the carrier. There are some difficulties, in the transfer by microsyringe of emulsion samples, in ensuring that the volume % of water remains identical with the "made up" percentage on which the offset carrier mass is chosen. In three cases, (0.9, 1.67 and 4.15% H$_2$O$_2$) the heat capacity of the solution found for the emulsion sample differed from that of the bulk sample of the same nominal composition by as much as 5%—more than the normal uncertainty of the measurement. In these cases the difference was assigned to an offset mismatch, and a constant correction factor applied to the emulsion data. For pure water, new and improved data obtained using both "offset" and "frozen sample comparison" techniques, are being reported elsewhere (11) (where they are compared with the behavior of superheated water near the spinodal temperature).
The overall uncertainty in the heat capacities measured for bulk samples is estimated at less than ± 2% while, for emulsion samples including the corrections described above, we estimate ± 4%.

For emulsion samples the runs were terminated by a sudden crystallization presumed to represent approximately the "homogeneous" nucleation temperature for ice I. Bulk samples crystallized at much higher temperatures but these heterogeneous nucleation temperatures also showed systematic composition dependences.

Results

Data in the form \( C_p \) vs temperature obtained direct from the experiment are plotted in Fig. 1 for the case of \( H_2O + H_2O_2 \) solutions of composition \( 0 - 37\% H_2O_2 \). The rapid depression of the anomalously increasing low temperature \( C_p \) on addition of \( H_2O_2 \) is immediately apparent.

From these data, and from similar data for \( H_2O + N_2H_4 \) solutions, isotherms for the molar heat capacity of the solutions were constructed. These are shown in Figs. 2 and 3. The 240 K (-33°C) isotherms must be counted extraordinary by any standard.

The only comparisons which can be made with previous work are with some average heat capacity values between 0 and 26.9°C obtained by Giguère et al(12) over the whole composition range. These were performed with a Bunsen calorimeter and although an accuracy estimate was not given, comparison with the literature data for pure water indicates the surprisingly high accuracy of 0.1%. Their solution data lie consistent 2% above ours.

Figures 2 and 3 show extensive binary solution regions above 20% \( H_2O_2 \) (or \( N_2H_4 \)) in which the composition dependence of \( C_p \) is simple, and it is reasonable to suggest that in these regions the molecular species are mixing in a manner appropriate to simple mixtures. Extrapolation of the linear regions to pure
H₂O₂ or pure N₂H₄ heat capacities respectively show the presence of moderate deviations from ideality in each case but not more than expected for simple binary mixtures, i.e. in the "simple" regions the mixtures behave like dispersions of molecules of two liquids which, individually, are similar in character with intermolecular interactions of comparable magnitude. Extrapolations to 0° H₂O₂ or N₂H₄ might therefore be expected to give a heat capacity for H₂O close to that of H₂O molecules interacting in a "normal" liquid state fashion like those of N₂H₄ or H₂O₂ in their pure liquid states. Figures 2 and 3 show, of course, that when H₂O molecules are present in sufficient concentration (> 80%) to permit extensive H₂O - H₂O interactions, a new and anomalous element enters the heat capacity causing sharp departures from the extrapolated binary C_p isotherm; it is this anomalous element which we wish to separate out.

Using the above-described extrapolations taken to zero H₂O₂ or N₂H₄ contents respectively, we obtain a plot vs temperature of the "normal" component of the H₂O heat capacity. This component, not surprisingly, has a temperature dependence which is similar to those of the > 20% component 2 binary solutions in each system, some of which may be followed down into the supercooled state to the point of glass formation. Comparisons of these 'normal' components with the actual C_p of pure water on the one hand, and with the 37% binary solutions on the other, are shown in Fig. 4.

Unfortunately for simplicity of interpretation, the 'normal' component for H₂O is not independent of the binary system used to extract it. That obtained from the N₂H₄ + H₂O system is some 10% lower and corresponds closely with that derived from a recently reported study of heat capacities in binary salt + water solutions. A similar plot ~ 2% higher is obtained if the appropriate binary solution behavior in the "simple mixture" region for N₂H₄ + H₂O solutions is taken to be curved as the data suggest rather than linear. It is not clear which, if either, of the H₂O₂ - H₂O based and N₂H₄ - H₂O based
"normal" components is to be preferred. Indeed, it could be argued that because
the lone pair/proton ratios in $H_2O_2$ and $N_2H_4$ are inverted, and both different
from that of water, neither system extrapolation is appropriate and that a
mean value should be chosen. We will use both in the following analysis.
It has not escaped our attention that hydoxylamine $NH_2OH$ (m.p., 306.2; b.p., 329.7)
has the same lone pair/proton ratio as water.

The glass transition phenomena seen at 140 K (the same temperature observed
for vapor deposited vitreous water by McMillan and Los by DTA measurements at
comparable scan rates(13)) will be examined in more detail in a separate
publication.

Discussion

We can now proceed to the main objectives of this work. In Fig. 5 we
show the anomalous components of the heat capacity of water obtained as the
difference of the total $C_p$ and the 'normal' component based on the $H_2O + H_2O_2$
solution data extrapolation. Also shown are plots of the anomalous part of the
heat capacities of several binary $H_2O + H_2O_2$ solutions based on a "normal"
components taken from the extrapolated $C_p$ vs $%H_2O_2$ lines of Fig. 2 at the
appropriate compositions. Except for the case of pure $H_2O$ the lines through
the points are sight-guides for clarity only. For pure water the solid line
is the plot of the singular point equation(2)

$$C_p(\text{anomalous}) = A \left(\frac{T}{T_s} - 1\right)^{-\gamma}$$  \hspace{1cm} (1)

with parameters $T_s = 226.9$, $\gamma = 1.34$, $A = 0.922$, these being the values which give
the best fit to the data points. A log-log plot of these data with slope $\gamma = 1.34$
is shown in Fig. 6a. We will return to the remaining plots in Fig. 6 in a moro...
In Fig. 7 we show a similar log-log plot for the "anomalous" component of $C_p(H_2O)$ based on the subtraction, from the total $C_p$, of a $H_2O$ and solution "normal" component obtained from the curvilinearly extrapolated $H_2O + N_2H_4$ iso- 

erms of Fig. 3. For this estimate of the "normal" component for pure water, the 

cut parameters to Eq. (1) are $T_S = 226.4$ K, $\gamma = 0.933$ and $A = 2.309$. The 

fit is very good as indicated by a $R$ value of 0.9996. If the "normal" component 

based on the linear extrapolation of binary solution data is used, Fig. 3, dashed 

line, an even better fit of the anomalous or excess $C_p$ to eq. (1) is obtained, 

$R = 0.9998$, with $T_S = 225.2$ and $\gamma$ unchanged at 0.933. We note that this latter 

value is almost identical with the best fit value for $H_2O + H_2O_2$ - based 

excess $C_p$ data, but that $\gamma$ is now a little less than unity. A value of unity 

is anticipated from a mean field theory for the anomalous fluctuations near a 

singular point when $T$ is near $T_S$, or when higher order terms are weakly contrib- 

uting. (14) Fig. 7(b) shows that the fit of the data to Eq. (1) with $\gamma = 1.0$ 

is also excellent.

It can be seen from the above that an intermediate "normal" component, 

possibility to be obtained from study of $H_2O + NH_2OH$ solutions, would yield 

anomalous $C_p$ values conforming well to mean field theory expectations, with 

a singular temperature slightly below the value of 228 K (~45°C) thought 

previously to be the best value. (2) This suggests the relevance of a Landau-

type theory such as described recently by Alexander and McTague for crystalliza-

tion of simple fluids with weakly first order fluid-crystal transitions. (15)

Although our primary aim in this work was to establish the feasibility of a 

mean-field description of the anomalous thermodynamic behavior of supercooled 

water, we are also interested in possible parallels between the manner in which 

this behavior is affected by small amounts of 2nd components and the way it is 

affected by pressure. The latter effect was reported recently for the case of 

isothermal compressibility (16) but without the benefit of any separation of 

anomalous from normal components.
The anomalous components of the heat capacities of the dilute $H_2O + H_2O_2$ solutions are subjected to best fit log-log plots in Fig. 6a. They do not show a very coherent pattern of behavior. On the other hand, if we assign $\gamma$ in Eq. (1) the value of unity suggested by mean field theory for singular point heat capacities, we obtain, as constrained best fits, the plots in Fig. 6b. In this case, although the individual fits are poor, the pattern of parameters is more intelligible since $A$ varies systematically with $\% H_2O_2$, and $T_s$ closely follows the line of homogeneous nucleation temperatures for the binary solutions. The latter relation is shown in Fig. 8 which summarizes equilibrium and non-equilibrium phase relation data for this system. $T_s'$ is the best fit value, and rapidly approaches zero.

There is a clear parallel between these findings and those of the earlier observation, from compressibility measurements, of the effect of pressure on $T_s'(16)$. The latter was found to follow $T_H$ in its pressure dependence when $\gamma$ was held constant at the appropriate value for the low pressure data. In those measurements, however, there was no satisfactory basis for separating anomalous from normal components of the property (compressibility) under study. From the present measurements it now seems that, when the water structure is severely disrupted by intrusion of molecules of a second component, the system does not conform well to Eq. (1), though the parallel of $T_s$ and $T_H$ when the constraint $\gamma = 1.0$ is introduced in the fitting procedure suggests it has some memory of it. Evidently the correlations involved in the cooperative phenomenon can grow in but only to a limited extent, thus eliminating the singular behavior at lower temperatures. The same may well be the case for high pressure behavior studied over the maximum temperature range.
It is significant that the parameter $A$ of Eq. (1), obtained from Fig. 6(b) (see inset) tends linearly to zero at about 12% $H_2O_2$ (Fig. 6, inset) where little anomalous character remains in the total $C_p$. The value of $A$ should reflect the fraction of water molecules in the system taking part in the cooperative behavior. In the high pressure study, $A$ for $\kappa_T$ remained almost constant while $T_s$ decreased parallel with $T_H$. The different behavior seen in the present case no doubt reflects the fact that water molecules are becoming increasingly "tied down" in non-cooperative structures with increasing $H_2O_2$ content. Concomitantly the character of the cooperative water molecule associations must change from one of a three-dimensionally connected gel-like structure$^{(17-19)}$ to one of small unconnected clusters ('sol' structure). The increasingly poor fits to Eq. (1) at higher concentrations may reflect the loss of gel-like character, where the "gel" is to be interpreted in the special sense of gelation of four bonded, hence open-structured, water molecules as described recently by Stanley.$^{(19)}$

Concluding Remarks

The attitude one takes to the present findings is largely a matter of taste and prejudice. On the one hand, one could conclude immediately from the fact that attempts to isolate a unique anomalous component of $C_p$ are less than completely successful, (Fig. 4) that attempts to interpret the behavior of water in these terms are futile. On the other hand, one could argue that a unique separation by the binary solution method could not be expected, and that the fact that a background term intermediate between the two values extrapolated gives mean field behavior for the anomalous component, makes the analysis of water properties in these terms highly plausible.

Our view is that this sort of judgement is to be deferred pending results of similar solution studies currently being performed for the properties, compressibility and expansivity.
Acknowledgements

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References

14. H. E. Stanley (private communication).
Figure Captions

Figure 1 Heat capacities of water and H$_2$O + D$_2$O solutions as functions of temperature. Lower portion gives detail on low H$_2$O$_2$ content behavior. Open symbols represent bulk sample data; closed symbols represent emulsion sample data.

Figure 2 Heat capacity isotherms for H$_2$O + H$_2$O$_2$ solutions obtained from data plots displayed in Fig. 1.

Figure 3 Heat capacity isotherms for H$_2$O + N$_2$H$_4$ solutions obtained as for Fig. 2. (No emulsion samples studied in this system.)

Figure 4 "Normal" component of the heat capacity of water assessed by extrapolation to zero solute content of data of Figs. 2 and 3. Also shown for comparison are plots of the total C$_p$ of pure water and the 37% solutions. The latter are glass-forming. Low temperature data in these cases were obtained during reheating runs and exhibit the normal relaxational 'overshoot' of the glass transition phenomenon.

Figure 5 Anomalous components of the heat capacity of H$_2$O and H$_2$O$_2$-H$_2$O solutions obtained by subtraction of Fig. 4 background from Fig. 1 total C$_p$ data. The curve passing through the points for pure water is the best fit of Eq. (4) to the data.

Figure 6 Log-log plots for anomalous components of C$_p$ of H$_2$O and H$_2$O + H$_2$O$_2$ solutions, based on Eq. (4). Upper portion; best fit representations. Lower portion; best fits of data subject to constraint of constant exponent value, viz. $\gamma = 1.0$. Inset: composition dependence of A parameter of Eq. (4) for constrained best fits.
Figure 7 Log-log plot for anomalous component of H$_2$O obtained using 'normal' component derived from N$_2$H$_4$ – H$_2$O solution data, see Figs. 3 and 4.

Figure 8 Phase diagram for H$_2$O + H$_2$O$_2$ system showing heterogeneous and homogeneous nucleation temperatures, and T$_s$ values based on both constrained ($T_s$) and unconstrained ($T'_s$) fits to the anomalous contributions to solution C's. Glass transition temperatures, where measurable, are also shown.
Fig. 1

\[(H_2O)_x(H_2O)_{1-x}\]

\[\pm 2\%Cp\]

\[X=0.017\]
\[X=0.036\]
\[X=0.369\]
\[X=0.319\]
\[X=0.278\]
\[X=0.219\]
\[X=0.060\]
\[X=0.073\]
\[X=0.091\]
\[X=0.130\]
\[X=0.186\]
Fig. 2
Fig. 3

\[ (N_2H_4)_x(H_2O)_{1-x} \]

\[ I \pm 1\% \text{ of } Cp \]

\[ T = 290 K \]
\[ T = 260 K \]
\[ T = 240 K \]
\[ T = 220 K \]
\[ T = 200 K \]
\[ T = 150 K \]

\[ I \pm 1\% \text{ of } Cp \]

\[ X_{N_2H_4} \]
$X=0.0$

$I \pm 2\%$ of $C_p$

$I \pm 5\%$ of $C_p$

$I \pm 10\%$ of $C_p$

$X(H_2O_2)=0.0$

($\text{"normal component"}$)

$X(N_2H_4)=0.0$

($\text{"normal component"}$)

$X(H_2O_2)=0.369$

$X(N_2H_4)=0.369$

Fig. 4
\[ \Delta C_p = 0.639 \left( \frac{T}{224.9} - 1 \right)^{1.35} \]

\[ x = 0.0 \]

\[ (H_2C_2)_x (H_2O)_{1-x} \]

$\pm 1\%$ of $C_p$
Solid points: emulsion sample data
Open points: bulk sample data
BEST FITS

Linear extrapolation

\[ T_s = 225.2 \]
\[ \gamma = 0.933 \]

Curvilinear extrapolation

\[ T_s = 226.4 \]
\[ \gamma = 0.933 \]

Solid points: emulsion data
Open points: bulk sample data

CONSTRAINED FITS

\[ \gamma = 1.0 \]

Linear extrapolation

\[ T_s = 223.3 \]
\[ T_s = 224.6 \]

Curvilinear extrapolation

Fig. 7
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