J. Chem. Eng. Data **1996,** *41,* 669−677

Summary of Melting and Transition Temperatures of Pure Substances and Congruent and Incongruent Melting Temperatures of Molecular Addition Compounds

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Melting temperatures, along with transition temperatures when they occur, are summarized for 70 pure chemicals used as the components in the study of 112 binary (solid + liquid) phase diagrams reported by us over the past 35 years. The melting temperatures and compositions of 68 solid molecular addition compounds determined as a part of these studies are also reported, and the proposed molecular interactions leading to the formation of these addition compounds are reviewed and discussed. Temperatures were measured with strain-free platinum resistance thermometers (Leeds and Northrup or Rosemount) that were calibrated to conform with the ITS-48 or the IPTS-68 temperature scales. The temperature scale used is estimated to be accurate to ±0.02 K over the temperature range of the measurements. Equations are given to convert temperature from ITS-48 or IPTS-68 to the more recent ITS-90 scale, and used to convert the temperatures reported in the tables to ITS-90.

1. Introduction

Over the course of a 35 year time period as we have determined binary (solid + liquid) phase diagrams for 113 systems, we have reported the measurement of the melting temperatures of 71 pure substances and 68 molecular addition compounds. These measurements were made with high accuracy using ITS resistance thermometers and high-purity chemicals. The papers reporting these measurements focused on the melting temperatures of the binary mixtures, and often the melting temperatures of the pure substances became lost in the tables and have not been used as a source for melting temperatures nor compared with the measurements of other workers reported in the literature. We felt it would be useful to summarize the melting temperatures of all the substances we have studied, along with the melting temperatures of the molecular addition compounds that we reported, since all were obtained with high accuracy. In this paper we report these results. We have not attempted to compare these results with others reported in the literature. Such a comparison would require an extensive tabulation.

We have also reported transition temperatures that occurred in some of the substances. Often, solid state transitions occur more easily in a mixture in which the solid is in equilibrium with liquid than in a pure substance. In some instances, phase transitions were observed in the mixtures that are so sluggish that they can be detected in the pure substance only by using special annealing techniques, if at all.

2. Temperature Scale

The earlier measurements were made with Leeds and Northrup strain-free platinum resistance thermometers in conjunction with a Leeds and Northrup high-presision recording Mueller Bridge. Later measurements were made with a Rosemount platinum resistance thermometer coupled to a Solartron high-precision resistance meter. Output from the Solartron was fed into a computer for data analysis. Details of the temperature scales and the melting temperature apparatus are described in the literature (61-goa/ott, 87-ott/woo). All of the thermometers were calibrated to read temperatures on the International Practical Temperature Scale. The measurements before 1972 relied on the ITS-48 scale of fixed points, while those in 1972 and after were based on the IPTS-68 scale. We estimate our temperature scale to be accurate with reference to either ITS-48 or IPTS-68 to within ±0.02K over the temperature range of the measurements. Calibrations were checked periodically at the ice point and two secondary reference points that are easy to reproduce, the freezing point of mercury and the sodium sulfate decahydrate peritectic point. In this report, we have corrected the melting temperatures to the more recent ITS-90 scale. Preston-Thomas (90-pre) has tabulated ($T_{90} - T_{68}$), the correction that converts T_{68}, the IPTS-68 temperature, to T_{90}, the ITS-90 temperature, and made a similar tabulation for ($T_{68} - T_{48}$), the difference between T_{68} and T_{48}, the ITS-48 temperature (76-pre). The two tables can be combined to obtain ($T_{90} - T_{48}$), the correction to convert ITS-48 to ITS-90. Over the temperature range of our measurements ($150 \le T/\mathrm{K} \le 400$), the corrections are small. ($T_{90} - T_{48}$) has a maximum value of 0.045 K at $T = 200$ K and a minimum value of −0.027 K at $T = 360$ K. For ($T_{90} - T_{68}$) the maximum difference is 0.014 K at $T = 150$ K and a minimum difference of −0.032 K at $T = 400$ K.

We have fitted the differences between the temperature scales to the equation

$$(T_{90} - T_{mn})/K = \sum_{j=1}^{6} a_j[10^{-3}(T_{mn} - 273.150)]^j \qquad (1)$$

where T_{mn} (in Kelvins) is T_{48} for $mn = 48$ or T_{68} for $mn = 68$. The coefficients are

$$mn = 68{:}\ \ a_1 = -0.224,\ a_2 = -0.84,\ a_3 = 2.8,\ a_4 = 19,\ a_5 = 0,\ a_6 = 0$$

$$mn = 48{:}\ \ a_1 = -0.732,\ a_2 = 4.07,\ a_3 = 50.3,\ a_4 = -508,\ a_5 = -780,\ a_6 = 14600$$

The small correction terms, which can be calculated from eq 1 to an accuracy of ±0.002 K over the temperature range from 140 K to 400 K, were used to correct the results from IPTS-48 to ITS-90 for measurements made before 1972 and

S0021-9568(96)00106-9 CCC: $12.00

from IPTS-68 to ITS-90 for the measurements made in 1972 and after.

Melting and transition temperatures were obtained from time against temperature cooling and warming curves. The melting temperatures of the pure substances reported before 1983, along with some later measurements as indicated in Table 1, were corrected for impurity by extrapolating a graph of melting temperature against the reciprocal of the fraction melted. This procedure has been described in the literature (92-ott/goa, p 552). The chemicals used in the study were of high purity, and the impurity correction was small.

3. Chemicals

Some of the chemicals were purchased with a known high purity and were used directly. Others were purified by fractional distillation or crystallization, and the purity level was determined from gas chromatographic analysis or from the change of melting temperature with the fraction melted. This latter procedure has been reported in the literature (92-ott/goa, p 552). The purities of the chemicals used in the melting temperature determinations are reported in the tables that follow. Some of the hydrocarbons that were used without further purification were Phillips Research Grade Chemicals, a source that is no longer available, since the Special Products Division of Phillips Petroleum Company has discontinued the manufacture. High-purity hydrocarbons and related chemicals, prepared with the care of those obtained from Phillips, are continually needed, especially as reference materials.

Care was taken to ensure continued high purity of the chemicals. To exclude moisture, the hydrocarbons were stored over sodium ribbon, and many of the alkanols were stored over 0.3 nm molecular sieves. Some chemicals (such as chloroform and bromotrichloromethane) were freshly distilled before use to minimize decomposition. To avoid moisture contamination, the samples were handled in septum-capped bottles and injected into the melting temperature apparatus with hypodermic syringes.

4. Results

The melting temperatures of the pure substances are reported in Table 1. The chemical names used in the original papers, some of which are “common” names that date to a number of years ago before the IUPAC nomenclature system was in common usage, are used in the paper and given in the table. IUPAC names for some of the less common substances are given in the paper. The chemical formulas are also given in the tables, from which a better indication of the structure can usually be obtained. Multiple measurements were made of the melting temperatures of some of the substances that appeared as components in a number of different binary systems. Usually, the most reliable measurement is reported in Table 1, unless there is some special reason for doing otherwise. Melting temperatures are grouped by class in order to make them easier to find in the table.

Melting temperatures of the molecular addition compounds determined in the studies are reported in Table 2. Some are congruent melting temperatures, while others result from incongruent melting. Table 2 indicates which type of melting occurs. Values for the observed transition temperatures are summarized in Table 3. In general, transition temperatures are sluggish and difficult to obtain for a pure solid from time against temperature cooling and warming curves. Usually, the addition of a second component so that liquid is present at the transition temperature helps transitions to occur more readily, and time against temperature cooling and warming curves of the binary mixtures could be used to determine the transition temperature. Values obtained in the mixtures represent the transition temperature for the pure substance, unless solid solutions result when the mixtures are frozen. With only a few exceptions, solid solutions were not present in the systems we reported. This was verified by the presence of a eutectic halt in the cooling and warming curves of the mixtures that persisted to compositions near that of the pure substances. Transition temperatures were not reported when solid solution formation was suspected. Even with liquid present, transition temperatures are usually more difficult to obtain from time against temperature cooling and warming curves than are melting temperatures. This is reflected in the higher estimated errors for the transition temperature measurements as given in Table 3.

5. Discussion

In reporting the molecular addition compounds summarized in Table 2, we were able to correlate the results and draw upon X-ray, spectroscopic, and calorimetric studies of the compounds to draw conclusions about the nature of the bonding that holds them together. We also observed interesting phase behavior in the mixtures, such as metastable melting temperatures for the pure substances and for molecular addition compounds, and phase transitions that occur in the mixtures, but were difficult, if not impossible, to get to occur in the pure substances. The following discussion summarizes these findings. More detail can be obtained by referring back to the original papers.

(a) Molecular Addition Compounds. Charge Transfer. We have proposed (62-ott/goa) that the solid addition compounds formed between carbon tetrachloride and [benzene, toluene, *p*-xylene, pseudocumene, and anisole (the IUPAC names are as follows: methylbenzene for toluene; 1,4-dimethylbenzene for *p*-xylene; 1,2,4-trimethylbenzene for pseudocumene; methoxybenzene for anisole)] result from a charge-transfer process in which the chlorines in the carbon tetrachloride act as electron acceptors and the aromatic ring acts as an electron donor. The stability of solid molecular addition compounds can be compared through the enthalpy of formation reaction

$$m\mathrm{A(s)} + n\mathrm{B(s)} = \mathrm{A}_m\mathrm{B}_n\mathrm{(s)} \qquad (2)$$

where m moles of component A react with n moles of component B to form the molecular addition compound $\mathrm{A}_m\mathrm{B}_n$. This enthalpy change applied to the formation of $C_6H_6 \cdot CCl_4(s)$, $C_6H_5CH_3 \cdot CCl_4(s)$, and 1,4-$C_6H_4(CH_3)_2 \cdot CCl_4(s)$ has been calculated from (solid + liquid) phase equilibria studies (85-boe/goa). The values obtained were (−3.24, −4.01, and −9.43) $\mathrm{kJ \cdot mol^{-1}}$ for the three addition compounds, respectively. These numbers support the explanation that the stability is due to a charge-transfer process. The electron density on the aromatic ring increases in going from benzene to toluene to *p*-xylene, and the richer the electron density, the more easily the aromatic ring can donate charge to the charge-transfer process, and the more stable the addition compound becomes.

We have suggested that the electron pairs on the oxygen in *p*-dioxane (64-ott/goa), 1,2-dimethoxyethane (86-che/ott), cyclopentanone, and 4-butyrolactone (86-che/ott-1) and on the nitrogen in *N*,*N*-dimethylformamide (66-goa/ott), *N*,*N*-dimethylacetamide (66-ott/goa), and 1-methyl-2-pyrollidinone (86-che/ott-1) can also act as electron donors. In the systems studied, the chlorines in carbon tetrachloride and

Table 1. Melting Temperatures T/K for Pure Substances As Determined from Two-Phase (Solid + Liquid) Phase Equilibria Studies[a]

substance	formula	T/K	δT	mole fraction purity	ref
Alkanes					
hexane	$CH_3(CH_2)_4CH_3$	177.80	(a)	0.9999	79-goa/ott
octane	$CH_3(CH_2)_6CH_3$	216.33	(a)	0.9991	83-ott/goa
undecane	$CH_3(CH_2)_9CH_3$	247.55	(c)	0.9979	83-ott/goa
dodecane	$CH_3(CH_2)_{10}CH_3$	263.49	(c)	0.9967	83-ott/goa
tetradecane	$CH_3(CH_2)_{12}CH_3$	278.97^{b}	(a)	0.9990	86-sno/ott
hexadecane	$CH_3(CH_2)_{14}CH_3$	291.27^{b}	(a)	0.9999	86-sno/ott
Cycloalkanes and Cycloalkenes					
cyclohexane	c-C_6H_{12}	279.74^{b}	(a)	0.9999	86-sno/ott
cycloheptane	c-C_7H_{14}	264.69	(b)	0.9988	83-ott/goa
cyclooctane	c-C_8H_{16}	287.74	(b)	0.9997	83-ott/goa
cyclohexene	c-C_6H_{10}	169.65	(b)	0.9998	74-ott/goa
1,5-cyclooctadiene	1,5-c-C_8H_{12}	203.81	(b)	0.9991	74-ott/goa
Aromatic Hydrocarbons					
benzene	C_6H_6	278.64^{b}	(a)	0.9997	86-sno/ott
toluene	$C_6H_5CH_3$	178.20	(a)	0.9996	64-goa/ott
p-xylene	1,4-$C_6H_4(CH_3)_2$	286.39	(a)	0.9991	76-goa/ott
mesitylene	1,3,5-$C_6H_3(CH_3)_3$	228.43^{c}	(b)	0.9969	76-goa/ott
mesitylene	1,3,5-$C_6H_3(CH_3)_3$	223.34^{d}	(b)	0.9969	76-goa/ott
mesitylene	1,3,5-$C_6H_3(CH_3)_3$	221.42^{e}	(b)	0.9969	76-goa/ott
pseudocumene	1,2,4-$C_6H_3(CH_3)_3$	229.38	(b)	0.998	64-goa/ott
Halogen-Substituted Benzenes					
fluorobenzene	C_6H_5F	230.97	(a)	0.9994	76-goa/ott
chlorobenzene	C_6H_5Cl	227.84	(a)	0.9987	76-goa/ott
bromobenzene	C_6H_5Br	242.43	(a)	0.9999	76-goa/ott
-difluorobenzene	1,4-$C_6H_4F_2$	249.60	(b)	0.9964	76-goa/ott
-dichlorobenzene	1,4-$C_6H_4Cl_2$	326.24	(a)	0.9994	76-goa/ott
- dibromobenzene	1,4-$C_6H_4Br_2$	360.58	(a)	0.9996	76-moe/ott
hexafluorobenzene	C_6F_6	278.18	(a)	0.9998	74-goa/ott
Halogen-Substituted Toluenes					
,α,α-trifluorotoluene	$C_6H_5CF_3$	244.20	(a)	0.9998	66-ott/goa
,α,α-trichlorotoluene	$C_6H_5CCl_3$	268.73	(a)	0.9991	66-ott/goa
Other Substituted Benzenes					
anisole	$C_6H_5OCH_3$	236.02	(a)	0.9999	64-goa/ott
phenetole	$C_6H_5OCH_2CH_3$	243.72	(a)	0.9991	64-goa/ott
diphenyl ether	$(C_6H_5)_2O$	299.96	(a)	0.9981	64-goa/ott
N,*N*-dimethylaniline	$C_6H_5N(CH_3)_2$	275.57	(a)	0.9984	64-man/goa
Heterocyclic Aromatics					
furan	C_4H_4O	187.57	(b)	0.9994	73-goa/ott
thiophene	C_4H_4S	234.94	(a)	0.9989	73-goa/ott
pyridine	C_5H_5N	231.45	(a)	0.9994	73-goa/ott
N-methylpyrrole	$C_4H_4NCH_3$	216.83	(a)	0.9998	86-che/ott-2
Halogen Compounds					
carbon tetrachloride	CCl_4	250.42	(a)	0.9999	85-boe/goa
silicon tetrachloride	$SiCl_4$	204.41	(a)	0.9993	74-shi/goa
germanium tetrachloride	$GeCl_4$	221.65	(a)	0.9999	74-shi/goa
tin tetrachloride	$SnCl_4$	239.08	(a)	0.9996	74-shi/goa
silicon tetrabromide	$SiBr_4$	278.54	(a)	0.9999	64-goa/ott-1
titanium tetrachloride	$TiCl_4$	249.03	(a)	0.9999	64-goa/ott
trichlorofluoromethane	$CFCl_3$	162.70	(a)	0.9998	66-ott/goa
trichlorobromomethane	$CBrCl_3$	267.50	(c)	>0.995	66-goa/ott
phosphorus oxychloride	$POCl_3$	274.33	(a)	0.9995	74-shi/goa
chloroform	$CHCl_3$	209.74	(a)	0.9997	87-ott/woo
methylene chloride	CH_2Cl_2	178.21	(b)	0.9999	63-goa/ott
isopropyl chloride	$CH(CH_3)_2Cl$	156.03	(b)	0.9999	63-goa/ott
1,1,1-trichloroethane	CH_3CCl_3	242.96	(a)	0.9990	66-ott/goa
pentachloroethane	$CHCl_2CCl_3$	244.37	(b)	0.9994	72-goa/ott
1,1,1-trichlorotrifluoroethane	CCl_3CF_3	287.52^{b}	(a)	0.9998	87-ott/woo
Alkanols					
tertiary butyl alcohol	$C(CH_3)_3OH$	298.84	(a)	0.9994	79-ott/goa
ethylene glycol	$(CH_2OH)_2$	260.46	(a)	0.9999	72-ott/goa
2,3-dimethyl-2,3-butanediol	$\{C(CH_3)_2OH\}_2$	316.47	(b)	0.9988	83-pri/woo
2,2-dimethyl-1,3-propanediol	$C(CH_3)_2(CH_2OH)_2$	402.28	(b)	0.9980	82-ott/goa
2,5-dimethylhexane-2,5-diol	$\{C(CH_3)_2OHCH_2\}_2$	361.65	(b)	0.9980	82-ott/goa
Ethers					
tetrahydrofuran	c-C_4H_8O	164.71	(b)	0.9999	74-goa/ott
p-dioxane	1,4-$C_4H_8O_2$	285.00	(a)	0.9994	74-goa/ott
1,2-dimethoxyethane	$(CH_3OCH_2)_2$	203.95	(a)	0.9990	86-che/ott

Table 1 (Continued)

substance	formula	T/K	δT	mole fraction purity	ref
Ketones and Sulfoxides					
cyclopentanone	C_5H_8O	221.25[b]	(b)	0.9972	86-che/ott-1
4-butyrolactone	$C_4H_6O_2$	229.54[b]	(b)	0.9956	86-che/ott-1
1-methyl-2-pyrollidinone	C_5H_9NO	250.06[b]	(b)	0.9978	86-che/ott-1
dimethyl sulfoxide	$(CH_3)_2SO$	291.04	(b)	0.9993	72-goa/ott
Nitrogen Compounds					
acetonitrile	CH_3CN	229.33	(a)	0.9980	61-goa/ott
N,*N*-dimethylformamide	$HCON(CH_3)_2$	212.75	(a)	0.9990	66-goa/ott
N,*N*-dimethylacetamide	$CH_3CON(CH_3)_2$	254.56[f]	(a)	0.9990	66-ott/goa
N,*N*-dimethylacetamide	$CH_3CON(CH_3)_2$	251.19[g]	(a)	0.9990	66-ott/goa
N-methylpiperidine	c-$C_5H_{10}NCH_3$	170.5[h]	(d)	0.9977	74-ott/goa-1
N-methylpiperidine	c-$C_5H_{10}NCH_3$	168.2[i]	(d)	0.9977	74-ott/goa-1
N-methylpiperidine	c-$C_5H_{10}NCH_3$	167.3[j]	(d)	0.9977	74-ott/goa-1
N,*N*′-dimethylpiperazine	1,4-c-$C_4H_8(NCH_3)_2$	272.56[b]	(a)	0.9996	74-ott/goa-1
N-methylmorpholine	1,4-c-$C_4H_8ONCH_3$	208.75	(a)	0.9988	74-ott/goa-1
Alkali Metals					
sodium	Na	371.02	(a)	0.9999	69-ott/goa
potassium	K	336.83	(a)	0.9999	69-ott/goa
rubidium	Rb	312.43	(a)	0.9992	70-goa/ott
cesium	Cs	301.57	(c)	0.9990	71-ott/goa

The results before 1983 were corrected to zero impurity while those in 1983 and after were not, except as noted. Temperatures were corrected to ITS-90 using eq 1. Temperature uncertainties δT are (a) ±0.05 K, (b) ±0.10 K, (c) ±0.20 K, (d) ±0.50 K, and (e) ±1.0 K. Corrected to zero impurity. [c] Stable melting temperature of mesitylene. [d] First metastable melting temperature of mesitylene. [e] Second metastable melting temperature of mesitylene. [f] Stable melting temperature of *N*,*N*-dimethylacetamide. [g] Metastable melting temperature *N*-dimethylacetamide. [h] Stable melting temperature for *N*-methylpiperidine (not corrected to 0% impurity). [i] First metastable melting temperature of *N*-methylpiperidine (not corrected to 0% impurity). [j] Second metastable melting temperature of *N*-methylpiperidine (not corrected to 0% impurity).

in various related substances such as trichlorofluoromethane, trichlorobromomethane, and α,α,α-trichlorotoluene act as electron acceptors to form molecular addition compounds with these donors.

Hydrogen Bonding. The hydrogens in chloroform, methylene chloride, and pentachloroethane have a positive charge due to the attraction of the electronegative chlorines in the molecule to the electrons in the carbon−hydrogen bond. This positive charge is large because of the enhanced attraction of the multiple chlorines, and the hydrogen is capable of hydrogen bonding, but forms only weak bonds with the chlorines present in these molecules, since individual chlorine atoms form only weak hydrogen bonds. When a second molecule containing smaller and more electronegative fluorine, oxygen, or nitrogen atoms is introduced, strong hydrogen bonds can form. It was proposed that these hydrogen bonds cause the solid molecular addition compounds to form when *p*-dioxane (63-goa/ott), 1,2-dimethoxyethane (86-che/ott), or dimethyl sulfoxide (72-goa/ott) are mixed with chloroform, methylene chloride, or pentachloroethane.

Alcohol Hydrates. We have measured binary (solid + liquid) phase diagrams for mixtures of water with ethylene glycol (72-ott/goa); (methyl, ethyl, isopropyl, and tertiary butyl) alcohol (79- ott/goa), 2,5-dimethylhexane-2,5-diol (82-goa/ott), 2,2-dimethyl-1,3-propanediol (82-ott/goa), and 2,3-dimethyl-2,3-butanediol (the common name pinacol is often used for 2,3-dimethyl-2,3-butanediol) (83-pri/woo). Hydrates are present in each system, although the composition of the hydrate changes with the system. These studies were the first to discover a solid hydrate in the (water + ethylene glycol) system, in spite of its importance as an antifreeze agent. The hydrate supercools badly and was difficult to obtain, even when the mixtures were cooled with stirring to temperatures well below the melting temperature of the hydrate. Metastable ice or solid ethylene glycol was obtained instead. The hydrate was obtained only by cooling the mixture well below the melting temperature without stirring. A viscous glassy solution resulted that crystallized as the hydrate when the mixture was finally stirred.

Hydrates in the (ethyl alcohol + water) and the (isopropyl alcohol + water) systems are also difficult to obtain (79-ott/goa). Extensive supercooling occurred in these systems, and it was often difficult to obtain complete conversion to the hydrate. These supercooling effects caused uncertainty in obtaining the stoichiometry of the incongruently melting (ethyl or isopropyl) alcohol hydrates, and the compositions of these hydrates are not reliably known. The hydrates $\{C(CH_3)_2(OH)_2{\cdot}H_2O\}$ and a $\{C(CH_3)_2(OH)_2{\cdot}6H_2O\}$ form in the (2,3-dimethyl-2,3-butanediol + water) system (83-pri/woo). Kim and Jeffrey (70-kim/jef) have used X-ray diffraction to determine the structure of this hydrate. They report an arrangement in which the methyl and methylene groups of the 2,3-dimethyl-2,3-butanediol molecule are in a cage within a hydrogen-bonded framework of water molecules. Calorimetric studies (83-pri/woo) have shown that the enthalpy of formation (reaction 2) for this hydrate is $-12.5\ \mathrm{kJ{\cdot}mol^{-1}}$. In a similar study, the enthalpy of formation of $\{C(CH_3)_2OHCH_2\}_2{\cdot}4H_2O(s)$ was determined to be $-8\ \mathrm{kJ{\cdot}mol^{-1}}$ (82-goa/ott). These large negative enthalpies of formation attest to the stability of the hydrates. It is reasonable to expect that the other hydrates result from similar hydrogen-bonded structures, although the enthalpies of formation may not be as large as for the hydrates of the symmetrical alkanols as described above.

It is interesting to note that a hydrate forms in every (water + alkanol) system that we studied. There may, of course, be (alkanol + water) systems where hydrates do not form, but hydrate formation is common in these kinds of mixtures, although often difficult to initiate because of supercooling effects.

Lewis Acid−Base Interactions. Infra-red studies (64-goa/ott) and X-ray studies (65-jen) support the conclusion (64-goa/ott) that the solid molecular addition compounds that form between titanium tetrachloride and anisole or phenetole (anisole is methoxybenzene, and phenetole is ethoxybenzene) result from a Lewis acid−base interaction between the oxygen of the aromatic ether and the titanium of the $TiCl_4$, rather than through a charge-transfer process similar to that in the (carbon tetrachloride + aromatics) systems. Further support for this conclusion is obtained

Table 2. Melting Temperatures *T*/K of Solid Molecular Addition Compounds Obtained from Two-Phase (Solid + Liquid) Phase Equilibria Studies[a]

system	formula	*T*/K	δT	type of melting	ref
Charge-Transfer Compounds					
benzene + carbon tetrachloride	$C_6H_6\cdot CCl_4$	239.15	(b)	incongruent	62-ott/goa
benzene + carbon tetrachloride	$C_6H_6\cdot 2CCl_4$	232.16	(b)	incongruent	62-ott/goa
benzene + carbon tetrachloride	$C_6H_6\cdot 2CCl_4$	232.88[b]	(b)	congruent	62-ott/goa
toluene + carbon tetrachloride	$C_6H_5CH_3\cdot CCl_4$	206.01	(b)	congruent	62-ott/goa
p-xylene + carbon tetrachloride	$1,4\text{-}C_6H_4(CH_3)_2\cdot CCl_4$	269.28	(b)	congruent	85-boe/goa
pseudocumene + carbon tetrachloride	$1,2,4\text{-}C_6H_3(CH_3)_3\cdot CCl_4$	229.88	(b)	congruent	62-ott/goa
anisole + carbon tetrachloride	$C_6H_5OCH_3\cdot 2CCl_4$	215.88	(b)	congruent	62-ott/goa
pyridine + carbon tetrachloride	$C_5H_5N\cdot 1.73CCl_4$[c]	231.13	(b)	congruent	86-che/ott2
N-methylpyrrole + carbon tetrachloride	$C_4H_4NCH_3\cdot CCl_4$	207.64	(b)	congruent	86-che/ott2
N-methylpyrrole + carbon tetrachloride	$2C_4H_4NCH_3\cdot CCl_4$	203.72	(b)	incongruent	86-che/ott2
1,2-dimethoxyethane + carbon tetrachloride	$(CH_3OCH_2)_2\cdot 2CCl_4$	205.81	(b)	incongruent	86-che/ott
1,2-dimethoxyethane + trichlorofluoromethane	$(CH_3OCH_2)_2\cdot 2CFCl_3$	176.92	(b)	congruent	86-che/ott
1,2-dimethoxyethane + trichlorofluoromethane	$(CH_3OCH_2)_2\cdot 4CFCl_3$[d]	169.03	(b)	incongruent	86-che/ott
p-dioxane + carbon tetrachloride	$1,4\text{-}C_4H_8O_2\cdot 2CCl_4$[e]	255.72	(b)	congruent	64-ott/goa
p-dioxane + trichlorofluoromethane	$1,4\text{-}C_4H_8O_2\cdot 2CFCl_3$	167.5	(e)	incongruent	64-ott/goa
p-dioxane + trichlorobromomethane	$(1,4\text{-}C_4H_8O_2)\cdot 3.41CBrCl_3$[f]	270.6	(e)	congruent	64-ott/goa
cyclopentanone + carbon tetrachloride	$C_5H_8O\cdot CCl_4$	233.6	(c)	congruent	86-che/ott-1
4-butyrolactone + carbon tetrachloride	$2C_4H_6O_2\cdot CCl_4$	232.3	(d)	congruent	86-che/ott-1
1-methyl-2-pyrrolidinone + carbon tetrachloride	$C_5H_9NO\cdot CCl_4$	282.2	(c)	congruent	86-che/ott-1
1-methyl-2-pyrrolidinone + carbon tetrachloride	$2C_5H_9NO\cdot CCl_4$	259.2	(c)	incongruent	86-che/ott-1
N-dimethylformamide + carbon tetrachloride	$HCON(CH_3)_2\cdot CCl_4$	236.50	(b)	congruent	66-goa/ott
N-dimethylformamide + carbon tetrachloride	$2HCON(CH_3)_2\cdot CCl_4$	210.4	(d)	incongruent	66-goa/ott
N-dimethylformamide + trichlorofluoromethane	$HCON(CH_3)_2\cdot CFCl_3$	187.83	(b)	congruent	66-goa/ott
N-dimethylformamide + trichlorobromomethane	$HCON(CH_3)_2\cdot CBrCl_3$	258.5	(c)	congruent	66-goa/ott
N-dimethylformamide + trichlorobromomethane	$2HCON(CH_3)_2\cdot CBrCl_3$	224.31	(c)	incongruent	66-goa/ott
N-dimethylformamide + α,α,α-trichlorotoluene	$HCON(CH_3)_2\cdot C_6H_5CCl_3$	232.86	(b)	incongruent	66-goa/ott
N-dimethylacetamide + carbon tetrachloride	$CH_3CON(CH_3)_2\cdot CCl_4$	291.05	(b)	congruent	87-goa/boe
N-dimethylacetamide + trichlorofluoromethane	$CH_3CON(CH_3)_2\cdot CFCl_3$	218.98	(b)	incongruent	66-ott/goa
N-dimethylacetamide + trichlorobromomethane	$CH_3CON(CH_3)_2\cdot CBrCl_3$	299.0	(c)	congruent	66-ott/goa
N-dimethylacetamide + α,α,α-trichlorotoluene	$CH_3CON(CH_3)_2\cdot C_6H_5CCl_3$	232.08	(b)	incongruent	66-ott/goa
Hydrogen-Bonded Compounds					
1,2-dimethoxyethane + chloroform	$(CH_3OCH_2)_2\cdot CHCl_3$	190.59	(b)	congruent	86-che/ott
1,2-dimethoxyethane + chloroform	$(CH_3OCH_2)_2\cdot 2CHCl_3$	194.87[g]	(b)	congruent	86-che/ott
1,2-dimethoxyethane + chloroform	$(CH_3OCH_2)_2\cdot 2CHCl_3$	194.12[h]	(b)	congruent	86-che/ott
-dioxane + chloroform	$1,4\text{-}C_4H_8O_2\cdot 2CHCl_3$	215.69	(b)	congruent	63-goa/ott
-dioxane + methylene chloride	$1,4\text{-}C_4H_8O_2\cdot 2CH_2Cl_2$	205.64	(b)	incongruent	63-goa/ott
dimethyl sulfoxide + chloroform	$(CH_3)_2SO\cdot 2CHCl_3$	201.48[i]	(b)	congruent	72-goa/ott
dimethyl sulfoxide + chloroform	$(CH_3)_2SO\cdot 2CHCl_3$	189.13[j]	(b)	congruent	72-goa/ott
dimethyl sulfoxide + pentachloroethane	$(CH_3)_2SO\cdot CHCl_2CCl_3$	240.80	(b)	incongruent	72-goa/ott
Alkanol Hydrate Compounds					
methyl alcohol + water	$CH_3OH\cdot H_2O$	170.8	(d)	incongruent	79-ott/goa
ethyl alcohol + water	$CH_3CH_2OH\cdot 2H_2O$[k]	200.6	(d)	incongruent	79-ott/goa
isopropyl alcohol + water	$2\{(CH_3)_2CHOH\}\cdot 3H_2O$[l]	219.8	(d)	incongruent	79-ott/goa
tertiary butyl alcohol + water	$C(CH_3)_3OH\cdot 2H_2O$	273.53	(b)	congruent	79-ott/goa
tertiary butyl alcohol + water	$C(CH_3)_3OH\cdot 6H_2O$	266.42	(b)	incongruent	79-ott/goa
ethylene glycol + water	$(CH_2OH)_2\cdot H_2O$	230.56	(b)	congruent	72-ott/goa
2,3-dimethyl-2,3-butanediol + water	$\{C(CH_3)_2OH\}_2\cdot H_2O$	315.17	(b)	congruent	83-pri/woo
2,3-dimethyl-2,3-butanediol + water	$\{C(CH_3)_2OH\}_2\cdot 6H_2O$	318.77	(b)	congruent	83-pri/woo
2,2-dimethyl-1,3-propanediol + water	$C(CH_3)_2(CH_2OH)_2\cdot 6H_2O$	274.44	(b)	congruent	82-ott-goa
2,5-dimethylhexane-2,5-diol + water	$\{C(CH_3)_2OHCH_2\}_2\cdot 4H_2O$	311.55	(b)	incongruent	82-goa/ott
Lewis Acid−Base Compounds					
titanium tetrachloride + anisole	$TiCl_4\cdot C_6H_5OCH_3$	317.19	(b)	congruent	64-goa/ott
titanium tetrachloride + phenetole	$TiCl_4\cdot C_6H_5OCH_2CH_3$	281.95	(b)	congruent	64-goa/ott
tin tetrachloride + phosphorous oxychloride	$SnCl_4\cdot 2POCl_3$	327.92	(b)	congruent	74-shi/goa
Entropy-Stabilized (Favorable Packing Geometry) Compounds					
benzene + hexafluorobenzene	$C_6H_6\cdot C_6F_6$	297.01	(b)	congruent	73-goa/ott
furan + hexafluorobenzene	$C_4H_4O\cdot C_6F_6$	228.21	(b)	incongruent	73-goa/ott
pyridine + hexafluorobenzene	$C_6H_5N\cdot C_6F_6$	236.57	(b)	incongruent	73-goa/ott
thiophene + hexafluorobenzene	$C_4H_4S\cdot C_6F_6$	261.09	(b)	congruent	73-goa/ott
1,5-cyclooctadiene + hexafluorobenzene	$1,5\text{-c-}C_5H_{12}\cdot C_6F_6$	220.86	(c)	incongruent	74-ott/goa
p-dioxane + hexafluorobenzene	$1,4\text{-}C_4H_8O_2\cdot C_6F_6$	260.33	(b)	incongruent	74-goa/ott
N-methylmorpholine + hexafluorobenzene	$\{1,4\text{-c-}C_4H_8ONCH_3\}_2\cdot C_6F_6$	216.19	(b)	congruent	74-ott/goa-1
N-methylpiperidine + hexafluorobenzene	$\text{c-}C_5H_{10}NCH_3\cdot C_6F_6$	189.66	(c)	incongruent	74-ott/goa-1
N,*N*′-dimethylpiperazine + hexafluorobenzene	$1,4\text{-c-}C_4H_8(NCH_3)_2\cdot C_6F_6$	264.84	(b)	congruent	74-ott/goa-1
p-dichlorobenzene + *p*-xylene	$1.4\text{-}C_6H_4Cl_2\cdot\{1,4\text{-}C_6H_4(CH_3)_2\}$	279.24	(b)	incongruent	76-goa/ott
p-dichlorobenzene + *p*-xylene	$1.4\text{-}C_6H_4Cl_2\cdot 2\{1,4\text{-}C_6H_4(CH_3)_2\}$	275.50	(b)	incongruent	76-goa/ott
p-difluorobenzene + mesitylene	$1,4\text{-}C_6H_4F_2\cdot\{1,3,5\text{-}C_6H_3(CH_3)_3\}$	214.19	(b)	incongruent	76-goa/ott
Other Compounds					
acetonitrile + benzene	$CH_3CN\cdot 2C_6H_6$	249.17	(b)	incongruent	61-goa/ott
p-dioxane + anisole	$1,4\text{-}C_4H_8O_2\cdot C_6H_5OCH_3$	248.20	(b)	incongruent	64-man/goa

Table 2 (Continued)

system	formula	T/K	δT	type of melting	ref
		Alkali Metal Compounds			
sodium + potassium	Na_2K	280.07	(b)	incongruent	69-ott/goa
sodium + cesium	Na_2Cs^m	265.26	(c)	incongruent	71-ott/goa

[a] Temperatures were corrected to ITS-90 using eq 1. Temperature uncertainties δT are (a) ±0.05 K, (b) ±0.10 K, (c) ±0.20 K, (d) ±0.50, and (e) ±1.0. [b] Metastable melting temperature. [c] Nonstoichiometric molecular addition compound resulting from a charge-transfer interaction or a freezing temperature maximum due to solid solution formation. [d] Composition of the incongruently melting addition compound is uncertain. [e] Extensive solid solution formation. The stoichiometry of the molecular addition compound is based on a melting temperature maximum at $x = 0.333$. [f] Nonstoichiometric molecular addition compound resulting from a charge-transfer interaction or a freezing temperature maximum due to solid solution formation. [g] Melting temperature of the stable molecular addition compound. [h] Melting temperature of the metastable molecular addition compound. [i] Melting temperature of the congruently melting stable $SO(CH_3)_2 \cdot 2CHCl_3$ molecular addition compound. [j] Melting temperature of the congruently melting metastable $SO(CH_3)_2 \cdot 2CHCl_3$ molecular addition compound. [k] The composition of the (ethyl alcohol + water) hydrate is uncertain. [l] The composition of the (isopropyl alcohol + water) hydrate is uncertain. [m] The composition of the (sodium + cesium) addition compound is uncertain.

Table 3. Transition Temperature T/K of Pure Substances Obtained from Two-Phase (Solid + Liquid) Phase Equilibria Studies[a]

substance	formula	T/K	ref
	Plastic Crystal Transition		
cyclohexane	$c\text{-}C_6H_{12}$	186.13 ± 0.1	79-goa/ott
carbon tetrachloride	CCl_4	225.3 ± 0.3	83-ott/goa
trichlorobromomethane	$CBrCl_3$	259.0 ± 0.3	66-goa/ott
1,1,1-trichloroethane	CH_3CCl_3	223.5 ± 0.5	66-goa/ott
1,1,1-trichlorotrifluoroethane	CCl_3CF_3	148 ± 2	87-ott/woo
p-dioxane	$p\text{-}C_4H_8O_2$	272.79 ± 0.2	64-goa/ott-1
tertiary butyl alcohol	$C(CH_3)_3OH$	285.6 ± 0.5	79-ott/goa
2,2-dimethyl-1,3-propanediol	$C(CH_3)_2(CH_2OH)_2$	310.14 ± 0.2	82-ott/goa
	Other Transitions		
acetonitrile	CH_3CN	215 ± 1	61-goa/ott
N,*N*-dimethylformamide	$HCON(CH_3)_2$	197.00 ± 0.2	66-goa/ott
N,*N*-dimethylacetamide	$CH_3CON(CH_3)_2$	223.1 ± 0.3	66-ott/goa
p-difluorobenzene	$1,4\text{-}C_6H_4F_2$	194 ± 4	76-moe/ott

Temperatures were corrected to ITS-90 using eq 1.

from the fact that $TiCl_4$ does not form a molecular addition compound with benzene. An interesting interaction must be occurring, however, in the liquid mixture when $TiCl_4$ is mixed with aromatics, including benzene. Colored solutions are formed, with the color changing from yellow to orange to red as the electron density on the aromatic ring increases. {The (titanium tetrachloride + benzene) mixture is orange-red in color, while the (titanium tetrachloride anisole) mixture is a deep blood red.} We have made −visible light absorption studies on these liquid solutions (65-ott/goa) and found that no specific complexes are formed in (titanium tetrachloride + benzene) mixtures that would explain the color, but did find complexes in (titanium tetrachloride + anisole) and (titanium tetrachloride + diphenyl ether) mixtures. The formulas of the complexes in these liquid mixtures are $TiCl_4 \cdot C_6H_5OCH_3$, $TiCl_4 \cdot 2C_6H_5OCH_3$, and $TiCl_4 \cdot (C_6H_5)_2O$. It is expected that these complexes result from Lewis acid−base interactions similar to those that cause the formation of the solid molecular addition compounds in the (titanium tetrachloride + anisole) and (titanium tetrachloride + phenetole) systems.

X-ray studies (63-bra) show that in $SnCl_4 \cdot 2POCl_3$(s) the oxygen of $POCl_3$ is bonded directly to Sn in $SnCl_4$. This supports the conclusion (74-shi/goa) that bonding in this molecular addition compound is due to a Lewis acid−base interaction.

Entropy-Stabilized (Favorable Packing Geometry) Compounds. Calorimetric methods suggest that the formation of $C_6F_6 \cdot C_6H_6$(s) results principally from favorable packing geometry, with no specific interaction contributing to the stability (76-ott/goa). For example, the enthalpy change for the formation of the solid addition compound from the solid components (reaction 2) was measured calorimetrically for $C_6H_6 \cdot C_6F_6$(s) and determined to be $+0.08\ \mathrm{kJ \cdot mol^{-1}}$ (76-ott/goa). This value can be compared with the result for a similar calorimetric determination of the enthalpy change for the formation of $1,4\text{-}C_6H_4(CH_3)_2 \cdot CCl_4$(s) from the solid components of $-10.09\ \mathrm{kJ \cdot mol^{-1}}$ (76-ott/goa). (This calorimetric result differs slightly from the value of $-9.43\ \mathrm{kJ \cdot mol^{-1}}$ described earlier that was calculated from the phase equilibria results.) (We attributed the stability of this latter addition compound to a charge-transfer interaction.) We were able to identify molecular addition compounds with hexafluorobenzene in a number of systems in which the second component has a ring structure. It is possible that the stabilities of the (hexafluorobenzene + cyclic molecule) solid addition compounds summarized in Table 2 result principally from favorable packing geometry. That is, these compounds are entropy stabilized rather than energy stabilized. For stable compounds to form, a negative free energy change ΔG must occur for reaction 2. Since $\Delta G = \Delta H - T\Delta S$, and ΔH is nearly zero for the formation of these addition compounds, the stability of the addition compound results primarily from the large positive ΔS that occurs in the packing process.

We have also proposed (76-goa/ott) that the formation of the (dihalobenzene + substituted benzene) solid molecular addition compounds that we have identified also result from favorable packing geometry, rather than a specific interaction. As further support for this conclusion, mixtures of fluorobenzene, chlorobenzene, or bromobenzene with *p*-xylene follow very closely the ideal freezing curve (76-goa/ott), suggesting that strong and specific interactions are not present.

Alkali Metal Compounds. The Na_2K addition compound (69-ott/goa) is known to be a Laves Phase of the $MgZn_2$ type (42-lav/wal), with the Na atoms stacked in tetrahedra that fill holes in the hexagonal K lattice. The radius ratio r_K/r_{Na} is 1.23. This is very close to the ideal radius ratio for a Laves phase of $\sqrt{3}/\sqrt{2} = 1.225$. Laves phases, like the favorable packing geometry molecular addition compounds described previously, form principally as a result of entropy stabilization, with the smaller atom filling the hole in the lattice of the larger atom without any specific interactions required to hold the structure together.

The (sodium + cesium) addition compound probably has the empirical formula Na_2Cs, although the reaction leading to the formation is sluggish and long time periods of annealing at a temperature just below the incongruent melting temperature failed to completely convert the stoichiometric mixture to the solid compound (71-ott/goa). Na_2Cs is probably not a Laves phase, since the radius ratio $r_{Cs}/r_{Na} = 1.41$ is significantly larger than the ideal radius ratio. (Sodium + rubidium) does not form an addition compound (70-goa/ott), and neither do any of the binary mixtures of potassium, rubidium, and cesium, where complete miscibility occurs in the solid state with freezing temperature minima (71-goa/ott, 71-goa/ott-1).

(b) Solid Solution Formation. Solid Solution Maxima. Extensive solid solutions form in mixtures of -dioxane + carbon tetrachloride) and (*p*-dioxane + trichlorobromomethane) (64-ott/goa), and in the (pyridine + carbon tetrachloride) system (86-che/ott-2). Two eutectics are present in each system that extend over a narrow composition range near the eutectic composition. Maximum melting temperatures occur between the eutectics. For (*p*-dioxane + carbon tetrachloride), the maximum occurs at a stoichiometric composition corresponding to the molecular addition compound $1,4\text{-}C_4H_8O_2{\cdot}2CCl_4(s)$. For the other two mixtures, the maximum occurs at a nonstoichiometric ratio, which could be the result of the formation of a nonstoichiometric solid molecular addition compound or, simply, a solid solution maximum without specific compound formation. It is especially likely that a solid solution maximum, rather than compound formation, occurs in the -dioxane + trichlorobromomethane) system, where a second eutectic, if present at all, would be at a mole fraction very near that of pure $CBrCl_3$. This lack of solid compound formation is in spite of the fact that a charge-transfer interaction is probably present in liquid mixtures of (*p*-dioxane + trichlorobromomethane).

(c) Solid Phase Transitions. Plastic Crystal Formation. The solid phase transitions in carbon tetrachloride, trichlorobromomethane, 1,1,1-trichloroethane, 1,1,1-trichlorotrifluoroethane, cyclohexane, and *p*-dioxane result from a change from a "normal" crystal at low temperatures to a "plastic" crystal at higher temperatures, in which the solid is soft, tacky, and has a small enthalpy of fusion. This transition, which involves the onset of molecular rotation in the solid phase, usually occurs at a temperature not far below the melting temperature. An exception is 1,1,1-trichlorotrifluoroethane, where the plastic crystal transition occurs at approximately 140 K below the melting temperature (87-ott/woo). Molecules that have a plastic crystal transition are nearly spherical or globular in shape. Tertiary butyl alcohol and 2,2-dimethyl-1,3-propanediol molecules are nearly spherical, and the transitions we observed in these substances (79-ott/goa, 82-ott/goa) probably result in a plastic crystal, although the enthalpies of fusion for these alkanols are larger than for the other plastic crystals.

Slow Transitions. As mentioned earlier, many slow and sluggish transitions occur more easily when a liquid solution is present. As an example, a solid phase transition in *N*,*N*-dimethylformamide could not be obtained in the pure substance (66-goa/ott). In the mixture, it was difficult to initiate the conversion from the high-temperature form to the low-temperature form. Once started, however, the conversion was rapid, with a large increase in volume. On two occasions the conversion shattered the glass melting temperature apparatus. The reverse conversion from the low-temperature form to the high-temperature form was rapid.

We also reported a solid phase transition in *N*,*N*-dimethylacetamide (66-ott/goa). A reversible conversion was impossible to obtain, even in our apparatus. The samples always supercooled upon cooling or superheated on warming to the degree that conversion always occurred at too low or too high a temperature. Melting temperatures could be obtained above and below the transition temperature in mixtures of $C_6H_5CF_3$ with both the high-temperature and low-temperature forms of the *N*,*N*-dimethylacetamide. The intersection of these melting temperature against composition curves gave the transition temperature for *N*,*N*-dimethylacetamide. As with *N*,*N*-dimethylformamide, conversion from the high-temperature form to the low-temperature form resulted in a large volume increase. On two occasions, the melting temperature apparatus shattered during the conversion process.

(d) Slow Equilibrium. Phase changes sometimes occurred so slowly and were so sluggish that equilibrium temperatures could not be obtained from time against temperature cooling or warming curves. The following are examples.

A phase transition was observed in *p*-difluorobenzene (76-moe/ott), and two transitions occurred in *p*-dichlorobenzene (76-moe/ott). All three transitions were of low energy and so sluggish that the transition temperature could not be accurately determined.

The freezing of pseudocumene (62-ott/goa) was so slow and sluggish that it was not possible to keep the solid and liquid phases in equilibrium. Hence, it was not possible to obtain the purity from the change in melting temperature with the fraction melted.

(e) Metastable Melting Temperatures. In a number of instances, supercooling allowed a metastable solid phase to crystallize from solution rather than the stable phase. An example already described is the freezing of solid ethylene glycol or ice from the (water + ethylene glycol) system when the solid hydrate should form instead (72-ott/goa). Other examples are as follows.

Metastable Addition Compounds. The $2CCl_2{\cdot}C_6H_6(s)$ addition compound melts incongruently. However, supercooling of the $CCl_4{\cdot}C_6H_6(s)$ addition compound allows a metastable melting temperature to be determined for the $2CCl_4{\cdot}C_6H_6(s)$ addition compound (62-ott/goa).

Chloroform forms metastable and stable addition compounds with dimethyl sulfoxide (72-goa/ott) and with 1,2-dimethoxyethane (86-che/ott). The formulas are $(CHCl_3)_2{\cdot}SO(CH_3)_2$ and $(CH_3OCH_2)_2{\cdot}2CHCl_3$. These are the only examples we found in which metastable addition compounds form along with stable addition compounds of the same composition.

Metastable Solid Components. *N*-Methylpiperidine has a stable and two metastable melting temperatures (74-ott/goa-1). Depending on the cooling and warming procedures followed, three different melting temperatures can be obtained for pure *N*-methylpiperidine and for mixtures in which *N*-methylpiperidine freezes from solution.

Mesitylene (mesitylene is 1,3,5-trimethylbenzene) also has two metastable melting temperatures (76-goa/ott) and the same effects occur as described above for *N*-methylpiperidine, but with a complication. Cooling usually caused the lowest melting (and least stable) form to crystallize from solution. Alternate cooling and warming with stirring of this (solid + liquid) mixture at a temperature just below the melting temperature caused conversion to the higher temperature (more stable) metastable form of mesitylene. The highest temperature (stable) form could only be obtained by seeding with a crystal of this phase. These crystals were prepared in the manner described by Mair and Schicktanz (33-mai/sch). In the procedure followed, a brass rod (Mair and Schicktanz report that only brass would do) was cooled to liquid nitrogen temperatures and plunged into supercooled liquid mesitylene held at a temperature below the stable melting temperature but above the melting temperature of the low-temperature metastable form. Almost always, this procedure resulted in the formation of the stable solid. In phase equilibria studies, kinetic effects and thermodynamic stability effects sometimes are in conflict because of supercooling and slow transition times. Phase equilibria measurements are often challenging, but interesting and usually satisfying, though experience, luck, and sometimes even a bit of black magic, seem to help.

Acknowledgment

We acknowledge the work of 25 individuals (undergraduate students, graduate students, and faculty associates) who assisted with the measurements and interpretation of the results and became co-authors on the papers.

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Received for review March 18, 1996. Accepted May 1, 1996.⊗ The authors acknowledge the support of these studies by the Brigham Young University Chemistry Department and several granting agencies.

JE9601063

⊗ Abstract published in *Advance ACS Abstracts,* June 15, 1996.