Thermodynamic Analysis of Isotope Effects on Triple Points and/or Melting Temperatures

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Available literature information on triple point or melting point isotope effects (and related physical properties) is subjected to thermodynamic analysis and consistency checks. New values for the melting point isotope effects for C_6H_6/C_6D_6 and c-C_6H_{12}/c-C_6D_{12} are reported. $^6Li/^7Li$ melting point isotope effects reported recently by Hidaka and Lundén (Z. Naturforsch. **49a**, 475 (1994)) for various inorganic salts are questioned.

1. Introduction

A recent paper by Hidaka and Lundén [1] reports an inverse $^6Li/^7Li$ isotope effect (IE) on the melting temperature of $LiNO_3$, thereby reintroducing an old topic. It affords an opportunity to discuss the thermodynamic basis of triple point or melting point IEs (TPIEs or MPIEs), and to point out relationships between condensed/vapor and solid/liquid fractionation factors and the TPIE/MPIE. It is surprising that in spite of an extensive literature dealing with isotope effects on thermophysical properties (see the reviews by Jancso, Rebelo, and Van Hook [2, 3]), the thermodynamics of the TPIE and its theoretical basis have not been discussed in any detail, even though relationships to accomplish that purpose were implicitly introduced more than thirty years ago [4]. As a consequence the information contained in TPIE/MPIE measurements has not been properly exploited.

2. Some Thermodynamics

To begin, consider the TPIE, $\Delta T_{tr} = T'_{tr} - T_{tr}$. Henceforth the superscript prime, ($'$), will designate the lighter isotope, capital delta, (Δ) will be reserved for isotopic differences (light-heavy), and lower case delta, (δ), will be used to designate difference between phases, usually (solid-liquid). The vapor pressure isotope effect (VPIE) is straightforwardly related to isotopic differences on the standard state partial molar free energy differences between phases [2–4]. For a one component system, the IE on the equilibrium between condensed (c) and gaseous (g) standard states may be described within excellent approximation with

$$\ln(P'/P) = -\delta_{gc}\,\Delta\mu^0/R\,T + (B\,P - B'\,P')/R\,T. \qquad (1)$$

The B's are vapor phase second virial coefficients referring to the pressure expansion, $(P\,V/R\,T) = 1 + B\,P + C\,P^2 \ldots.$ In order to relate thermodynamic IEs to molecular properties it is convenient to rewrite (1) in terms of standard state Helmholtz free energy differences, which, in turn, are expressed in terms of logarithmic partition function ratios,

$$\delta_{cg}\,\Delta A^0 = \delta_{cg}\,\Delta\mu^0 + \delta_{cg}\,\Delta(P\,V)^0 = -\ln(Q'_g\,Q_c/Q_g\,Q'_c). \qquad (2)$$

Combining (1) and (2)

$$\begin{aligned}\delta\ln(P'/P) &= \ln(P'/P)_s - \ln(P'/P)_l = -\,\delta_{sl}\,\Delta\mu^0/R\,T\\ &= \ln(Q'_l\,Q_s/Q_l\,Q'_s) + [(P'\,V' - P\,V)_s\\ &\quad - (P'\,V' - P\,V)_l]/R\,T. \qquad (3)\end{aligned}$$

The development leading to (3) is derivative to one originally given by Bigeleisen [4].

At their respective triple points the vapor pressures of solid and liquid are the same,

$$(\ln P'_s - \ln P'_l)_{T'_{tr}} = (\ln P_s - \ln P_l)_{T_{tr}} = 0. \qquad (4)$$

To transform to a common temperature, say $T_{tr'}$ we write

$$(\ln P'_s - \ln P'_l)_{T_{tr}} = (\ln P'_s - \ln P'_l)_{T'_{tr}} + \int_{T'_{tr}}^{T_{tr}} (\delta H'_{fus}/R\,T^2)\,dT. \qquad (5)$$

The integration extends from T'_{tr} to T_{tr}. The first term to the right of the equality is zero. Adding $(-\ln P_s + \ln P_l)_{T_{tr}} = 0$ to the left side, we obtain

$$\delta\ln(P'_s/P_s)_{T_{tr}} = \int(\delta\,H'_{fus}/R\,T^2)\,dT, \qquad (6)$$

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which is easily integrated, given the temperature dependence of $\delta H'_{\mathrm{fus}}$. Here $\delta H'_{\mathrm{fus}}$ refers to the enthalpy difference, liquid-solid, for the lighter isotope. In the development which follows, $\delta H'_{\mathrm{fus}}$ is taken independent of pressure and expressed, $\delta H'_{\mathrm{fus}} = \delta H^{0\prime}_{\mathrm{fus}} + \delta C'_{\sigma}(\Delta T) + \ldots$. We obtain an implicit expression for ΔT_{tr} by integrating (6). $\delta C'_{\sigma}$ is the difference in condensed phase heat capacities measured along the metastable liquid-vapor and solid vapor equilibrium lines.

$$\Delta T_{\mathrm{tr}} = -\,\delta \ln (P'/P)_{T_{\mathrm{tr}}}/[f(\delta H'_{\mathrm{fus}}, \delta C'_{\sigma})]\,. \tag{7}$$

In (7)

$$\begin{aligned} f(\delta H'_{\mathrm{fus}}, \delta C'_{\sigma}) &= \{\delta H^{0\prime}_{\mathrm{fus}}/R\,T'^{2}_{\mathrm{tr}}\} * \{1/(1-(\Delta T^{*}_{\mathrm{tr}}/T'_{\mathrm{tr}})\} \\ &\quad - \{\langle \delta C'_{\sigma}\rangle/R\,T'_{\mathrm{tr}}\}\{(1/2)(\Delta T^{*}_{\mathrm{tr}}/T'_{\mathrm{tr}}) \\ &\qquad + (2/3)(\Delta T^{*}_{\mathrm{tr}}/T'_{\mathrm{tr}})^{2} + \ldots\} \\ &\approx \{\delta H^{0\prime}_{\mathrm{fus}}/R\,T'^{2}_{\mathrm{tr}}\}\{1 + (\Delta T^{*}_{\mathrm{tr}}/T'_{\mathrm{tr}}) + (\Delta T^{*}_{\mathrm{tr}}/T'_{\mathrm{tr}})^{2} + \ldots\} \\ &\quad - \{\langle \delta C'_{\sigma}\rangle/R\,T'_{\mathrm{tr}}\}\{(1/2)(\Delta T^{*}_{\mathrm{tr}}/T'_{\mathrm{tr}}) \\ &\qquad + (2/3)(\Delta T^{*}_{\mathrm{tr}}/T'_{\mathrm{tr}})^{2} + \ldots\}\,, \end{aligned} \tag{8}$$

since $\Delta T_{\mathrm{tr}}/T'_{\mathrm{tr}} \ll 1$. In (8) $\delta C'_{\sigma}$, averaged over the temperature range of the integration, is represented as $\langle \delta C'_{\sigma}\rangle$. In deriving (8) we have used $(1-\Delta T_{\mathrm{tr}}/T'_{\mathrm{tr}})^{-1} \approx (1+(\Delta T_{\mathrm{tr}}/T'_{\mathrm{tr}})+\ldots)$ and $\ln(1-\Delta T_{\mathrm{tr}}/T'_{\mathrm{tr}}) \approx -(\Delta T_{\mathrm{tr}}/T'_{\mathrm{tr}} + (1/2)(\Delta T_{\mathrm{tr}}/T'_{\mathrm{tr}})^{2} + \ldots)$. Higher order corrections are easily added. To find ΔT_{tr} using (7) we wrote a routine which took $\Delta T^{*}_{\mathrm{tr}}/T'_{\mathrm{tr}} \approx 0$, (8), as an initial guess, solved (7) for ΔT_{tr}, in the end setting $\Delta T^{*}_{\mathrm{tr}} = \Delta T_{\mathrm{tr}}$, and iteratively continuing until convergence. For $\Delta T_{\mathrm{tr}}/T'_{\mathrm{tr}}$ small enough, the convergence to experimental precision is immediate, higher order terms drop from consideration, and

$$\Delta T_{\mathrm{tr}} = -\,\delta \ln (P'/P)_{T_{\mathrm{tr}}}/\{\delta H^{0\prime}_{\mathrm{fus}}/R\,T'^{2}_{\mathrm{tr}}\}\,. \tag{9}$$

MPIE can be calculated from TPIE given the information on IEs for the molar volume change on melting (since $\partial(\delta \mu/\partial P_m) = \delta V$), and on the solubility difference of air in the two phases (it being assumed the melting points are measured for air saturated solutions at standard pressure). The corrections are negligible in comparison to the experimental precision of TPIE and MPIE data discussed in this paper and will be neglected.

Equations (7)–(9) relate TPIE to the difference in solid/vapor and liquid/vapor fractionation factors for the separated isotopes. We now obtain an expression for TPIE in terms of directly measured solid/liquid fractionations on samples of mixed isotopes, $\alpha = (x'/x)_{\mathrm{s}}/(x'/x)_{\mathrm{l}}$, $x' = (1-x)$ is the mole fraction of the lighter isotope. Van Hook and coworkers [2, 3] show that to sufficient precision

$$R\,T \ln(\alpha) = -\,\delta \Delta A^{0} - R\,T \ln(\gamma)\,. \tag{10}$$

γ is the activity coefficient of the heavy isotope referenced to the Raoult's Law standard state. Assuming ideal solutions for mixtures of isotopes in both solid and liquid phases, and neglecting corrections for molar volume isotope effects in the isotopically separated samples, we have using (3)

$$\delta \ln (P'/P) = \ln(\alpha) = -\,\delta_{\mathrm{sl}}\,\Delta\mu^{0}/R\,T = \ln(Q'_{\mathrm{l}}\,Q_{\mathrm{s}}/Q_{\mathrm{l}}\,Q'_{\mathrm{s}})\,, \tag{11}$$

and by a process analogous to that leading to (7), obtain

$$\begin{aligned} \Delta T_{\mathrm{tr}} &= -\ln(\alpha)_{T_{\mathrm{tr}}}/[f(\delta H'_{\mathrm{fus}}, \delta C'_{\sigma})] \\ &= -\,[\ln(\alpha)_{T'_{\mathrm{tr}}} + \textstyle\int(\delta \Delta H_{\mathrm{fus}}/R\,T^{2})\,\mathrm{d}T]/[f(\delta H'_{\mathrm{fus}}, \delta C'_{\sigma})]\,. \end{aligned} \tag{12}$$

In the cases of present interest $x \ll 1$, and the melting temperature is found close to T'_{tr}. For small enough ΔT_{tr}, small enough $\delta \Delta H_{\mathrm{fus}}$, or both, the correction terms, first in the numerator, then in the denominator can be dropped, and

$$\begin{aligned} \Delta T_{\mathrm{tr}} &= -\,\delta \ln (P'/P)_{T_{\mathrm{tr}}}/\{\delta H^{0\prime}_{\mathrm{fus}}/R\,T'^{2}_{\mathrm{tr}}\} \\ &= -\,\delta \ln (a'/a)_{T_{\mathrm{tr}}}/\{\delta H^{0\prime}_{\mathrm{fus}}/R\,T'^{2}_{\mathrm{tr}}\} \\ &= -\ln(\alpha)/\{\delta H^{0\prime}_{\mathrm{fus}}/R\,T'^{2}_{\mathrm{tr}}\} \\ &= \ln(Q'_{\mathrm{l}}\,Q_{\mathrm{s}}/Q_{\mathrm{l}}\,Q'_{\mathrm{s}})/\{\delta H^{0\prime}_{\mathrm{fus}}/R\,T'^{2}_{\mathrm{tr}}\}\,. \end{aligned} \tag{13}$$

Equation (13) usefully correlates the experimentally observable quantities $\delta \ln (P'/P)$ or $\ln(\alpha)$, and ΔT_{tr} or ΔT_{mp}, with each other, and with l/s partition function ratios which are available from theoretical and spectroscopic considerations [2, 3, 4]. In (13) a'/a denotes the ratio of thermodynamic activities.

3. Consistency Tests

Table 1 present calculated and measured TPIE's and related thermodynamic data for some isotopically substituted waters, and for hydrogen molecules. We have chosen to discuss these systems separately from some others (Table 2), because the thermodynamic information on the isotopic waters and hydrogen molecules is unusually complete, and the observed TPIE's are large enough to meaningfully illustrate the development in the last section.

Table 1. Triple point isotope effects (TPIEs) for some substituted waters and for hydrogens.

System	T'_m/K	$\Delta H'_{fus}$ $J \cdot mol^{-1}$	$\delta C'_\sigma$ $J \cdot mol^{-1} \cdot K^{-1}$	$10^4 \delta \ln(P'/P)$	ΔT_{calc}/K	ΔT_{exp}/K	Remarks, refs.
$H_2{}^{18}O$	273.16	6001	38.5	35 ± 4	-0.36 ± 0.04	-0.05 ± 0.01	[2, 5, 6, 11]
				35 ± 2	-0.36 ± 0.02	-0.28 ± 0.02	[8, 12]
						(-0.38 ± 0.05)	[2]
D_2O				374 ± 5	-3.88 ± 0.05	-3.815 ± 0.005	Note 1
	Note 2				-3.83 ± 0.02		[2, 5, 14]
T_2O				$500 \pm 15\%$	-5.2 ± 0.8	-4.49	$\delta \ln(P'/P)_s$
	Note 3			(434)	(-4.49)	-4.49	uncertain [9, 15]
$D_2{}^{18}O$					-4.16 ± 0.06	-4.02 ± 0.02	[13]
$p-H_2/n-H_2$	13.813	117	Note 4	99	-0.14	-0.16	[18]
$p-H_2/HD$				1770	-2.68	-2.79	
$p-H_2/n-D_2$				2940	-4.90	-4.91	
$p-H_2/o-D_2$				2920	-4.86	-4.88	
$p-H_2HT$				(2800)		-4.6	
$p-H_2/T_2$				3920	-7.37	-6.81	
$p-H_2/DT$				(3300)		-5.8	

Note 1. The uncertainty in $\Delta T_{tr}(D_2O)$ is smaller than 0.01 K and is approximated here as ±0.005 K.

Note 2. In reference [5] $\ln(P'/P)$ is reported in the solid/solid (a), liquid/liquid (b), and solid/liquid (c) regions. Simultaneous solution of the (a) and (b), and (b) and (c) equations gives the value of ΔT_{tr} reported on this line.

Note 3. The value for $\ln(P'/P)_{TTO,solid}$ reported in [9] is very uncertain. It is more appropriate to use the relatively precise value for $\ln(P'/P)_{liquid}$ reported there together with $(\Delta T_{tr})_{exp}$ to yield a calculated value for $\ln(P'/P)_{solid}$ at T_{tr}, and this value, parenthesized, is reported in this line of the table.

Note 4. For $p-H_2$ following the method outlined in the text we calculate $C'_\sigma/(J \cdot mol^{-1}) = 17.4 - 0.727\,T$.

TPIEs and/or MPIEs of Isotopically Labelled Waters

For water ΔT_{tr} has been measured for a number of isotopomer pairs, including $HH^{16}O/HH^{18}O$, $HH^{16}O/DD^{16}O$, $DD^{16}O/DD^{18}O$, and $HH^{16}O/TT^{16}O$ (top of Table 1) [5–10]. High precision values of the enthalpy and heat capacity of fusion for $H_2{}^{16}O$ are available [11]. Also $\delta \ln(P'/P)$ has been determined with high precision for $HH^{16}O/DD^{16}O$ [5] and $HH^{16}O/HH^{18}O$ [8]. First consider the system $HH^{16}O/DD^{16}O$. The experimental value for $\delta \ln(P'/P)$ [5, 6] yields, (8), $\Delta T_{tr} = 3.88 \pm 0.05$, which is higher than the directly measured TPIE, 3.815 ± 0.005 K, by 1.6%. The uncertainty in TPIE is almost entirely accounted for by the statistical uncertainty in the values reported for $\delta \ln(P'/P)$. The systematic difference between the calculated and observed TPIE is due to the uncertainty involved in extrapolating $\delta \ln(P'/P)_s$ from its last experimental point (near 273.15) to T_{tr}, i.e. over the range $(T'_{tr} \le T \le T_{tr})$. For this integration $HH^{16}O_s$ is represented as a hypothetical superheated solid. For this particular example, however, we are not limited to the use of (7)–(13) to calculate ΔT_{tr} because experimental values for $\ln(P'_l/P_s)$ are available at temperatures between the two triple points $(T'_{tr} \le T \le T_{tr})$ [5]. Therefore an alternate determination of TPIE can be made by equating $\ln(P'/P)_s$ and $\ln(P'_s/P_s)$, and $\ln(P'/P)_l$ and $\ln(P'_l/P_s)$. The result, $\Delta T_{tr} = -3.83 \pm 0.04$ K, is in quantitative agreement with the directly measured value. The exercise points out that the most likely systematic error in the application of (7)–(9) results from imprecision in the extrapolation of $\delta \ln(P'/P)$ between T'_{tr} and T_{tr}, which, in turn, is most likely due to an inaccurate representation of the curvature of $\ln(P'/P)_s$ vs. T in the extrapolated portion of the curve.

Values of $\delta \ln(P'/P)$ are available for $H_2{}^{16}O/H_2{}^{18}O$ [5, 8]. The calculated TPIE, -0.36 ± 0.02 K, is in reasonable agreement with the directly measured value [12], -0.28 ± 0.02 K, and establishes it as more reliably than an early crude estimate which was made from the liquid/solid separation factor [10], $(-0.05 \pm 0.01$ K). We see no reason to prefer [12] over [8] and recommend the mean as the best available TPIE, $\Delta T_{tr}(HH^{18}O) = -0.32 \pm 0.03$ K. We applied (9) to $H_2{}^{16}O/D_2{}^{18}O$ by using the VPIE ratios reported by Szapiro and Steckel [13], $[\ln(\alpha_{DD180})/\ln(\alpha_{HH180})]_l = 0.825 \pm 0.022$, which we assumed applicable to both phases. The result, $\Delta T_{tr}(DD^{18}O)_{calc} = -4.16 \pm 0.06$ K, is higher than the measured value, -4.02 ± 0.02 K, and suffers from the same systematic error discussed in the paragraph immediately above. A correction similar

Table 2. TPIEs and MPIEs of various compounds.

System	T'_m	$\Delta H'_{fus}$	$10^4\,\delta\ln(P'/P)$	ΔT_{calc}[a]	ΔT_{exp}	Remarks, refs.
Hydrocarbons						
$^{12}CH_4/^{13}CH_4$	90.675	936	4	-0.03	-0.03	[21, 22] distillation
CH_4/CH_3D			-37	0.27	0.26	[23] VPIE
CH_4/CH_2D_2			-67 ± 2[d]	0.49 ± 0.01[d]	0.50	
CH_4/CHD_3			-98	0.71	0.71	
CH_4/CD_4			-118	0.85	0.88	
C_2H_4/C_2H_3D	103.97	3351	111	-0.30	-0.35	[24]
$C_2H_4/C_2H_2D_2$ (trans)			224	-0.60	-0.62	
$C_2H_4/C_2H_2D_2$ (cis)			217	-0.59	-0.66	
$C_2H_4/C_2H_2C_2$ (gem)			217 ± 4[d]	-0.59 ± 0.01[d]	-0.67	
C_2H_4/C_2HD_3			311	-0.84	-0.91	
C_2H_4/C_2D_4			409	-1.11	-1.16	
$(CH_3)_4C/(CD_3)_4C$	256.69	3258	-128	2.13	2.20	[25]
$(CH_3)_4C/(CD_3)_3(CH_3)C$			-100	1.67	1.60	
$(CH_3)_4C/(CD_3)_2(CH_3)_2C$			-58	0.97	1.06	
$(CH_3)_4C/(CD_3)(CH_3)_3C$			-29 ± 5[d]	0.49 ± 0.09[d]	0.60	
$(CH_3)_4C/(CH_2D)(CH_3)_3C$			-5	0.08	0.18	
$(CH_3)_4C/(CH_2D)_4C$			-28	0.47	0.71	
C_6H_6/C_6D_6	278.68	9951	152 ± 10	-0.99 ± 0.06	-1.2 ± 0.1	[14], this paper[b]
			148 ± 5	-0.96 ± 0.03		[27]
C_6H_{12}/C_6D_{12}	279.75	2630	-170 ± 50	4.1 ± 1.1	4.6 ± 0.1	[14], this paper[c]
			0 ± 20	0 ± 0.5		[27]
Halocarbons						
$CHBr_3/CDBr_3$	281.65	11184	280 ± 30	-1.7 ± 0.2	-0.30 ± 0.05	[28], van't Hoff
Polymers						
$C_{36}H_{74}/C_{36}D_{74}$	348.9				3.9	[29–33]
Polyethylene	407.9				4.9	
i-polystyrene	488.2				5.5	
i-polypropylene	440.2				0	
Noble gases, inorganic molecules						
$^{20}Ne/^{22}Ne$	24.58	335	150 ± 25	-0.23 ± 0.04	-0.15	[34]
$^{36}Ar/^{40}Ar$	82.7	1058	11.5 ± 0.6	-0.062 ± 0.003	-0.059	[35]
$^{80}Kr/^{84}Kr$	115.78	1640	2.4 ± 0.6	-0.016 ± 0.004	-0.01	[36
$^{14}N^{14}N^{16}O/^{14}N^{14}N^{18}O$	182.259	6537	18 ± 2	-0.075 ± 0.008	-0.065	[37]
$^{14}N^{14}N^{16}O/^{14}N^{15}N^{16}O$			17 ± 2	-0.074 ± 0.008	-0.070	
$^{14}N^{14}N^{16}O/^{15}N^{14}N^{16}O$			13 ± 2	-0.057 ± 0.008	-0.052	
$^{12}CO_2/^{13}CO_2$	216.55	7950	-0.5 ± 0.5	0.002 ± 0.002		[38]
$C^{16}O_2/C^{18}O_2$			32 ± 4	-0.16 ± 0.02		
$C^{16}O_2/C^{18}O^{16}O$			11 ± 4	-0.05 ± 0.02		
$^{12}C^{16}O/^{13}C^{16}O$	68.14	841	13 ± 2	-0.060 ± 0.10	-0.061	[22]
$^{12}C^{16}O/^{12}C^{18}O$			9 ± 2	-0.040 ± 0.10	-0.047	
NH_3/ND_3	195.45	5974	615 ± 30	-3.23 ± 0.15	-3.55	[39]
$^{14}NH_3/^{15}NH_3$			6 ± 4	-0.03 ± 0.02	-0.17	[39]
HCN/DCN	259.83	8410	164 ± 40	-1.1 ± 0.3		[42]
$HCN/HC^{15}N$			-49 ± 40	0.4 ± 0.3		
H_2S/D_2S	187.66	2378	(-98)	–	0.47	[40, 41, 43, 44]
HCl/DCl	159.03	1971	-47 ± 9	0.50 ± 0.16	0.65	[45]
			$+33\pm?$	-0.36		[46]
			-19 ± 40	0.20 ± 0.50		[47]
HBr/DBr	186.50	2399	(-72)		0.86	[45]
				0.01		[48]
HI/DI	222.50	2855	(-69)		0.99	[45]
				-0.02		[48]

Notes: [a] (7) to (9). [b] At ≈10% melted. Melting range ≈0.2 to 0.4 K. [c] Melting range ≈0.1 K. [d] ± refers to all members of the group.

Table 3. Calculated and measured triple points, $\Delta T_{tr} = (T'_{tr}(HH^{16}O) - T_{tr})$ and calculated and measured separation factors for the isotopically labelled waters. See Table 1, (9) and [16, 17].

Isotopomer		^{16}O		^{17}O		^{18}O	
		ΔT_{tr}	$\delta \ln (P'/P)$	ΔT_{tr}	$\delta \ln (P'/P)$	ΔT_{tr}	$\delta \ln (P'/P)$
HHO	calc.			-0.20	0.0020	-0.36	
	exp.					-0.28 ± 0.02	0.0035
HDO	calc.	-2.16		-2.36	0.023	-2.52	0.024
	exp.		0.0209				
DDO	calc.	-3.88 ± 0.05		-4.07	0.039	-4.16 ± 0.04	
	exp.	-3.815 ± 0.005	0.0374			-4.02 ± 0.02	0.0402
HTO	calc.	-3.08	0.030	-3.27	0.032	-3.43	0.033
	exp						
TTO	calc.	(-4.49)		-4.69	0.045	-4.86	0.047
	exp.	-4.49 ± 0.02?	(0.043)				
DTO	calc.	-4.73	0.046	-4.93	0.048	-5.08	0.049

to that used for $DD^{16}O$ yields, $\Delta T_{tr}(DD^{18}O)_{calc} = -4.11$ K. It is interesting that for both $HH^{18}O$ and $DD^{18}O$ the thermophysically calculated TPIEs lie consistently about 0.09 K above the measured MPIEs [12]. Again, with no reason to choose between the two results we recommend the mean value $\Delta T_{tr}(DD^{18}O) = -4.06 \pm 0.06$ K.

Jones [15] has reported the melting point of $TT^{16}O$ as 4.49 K and also reports [9] $\ln (P'/P)_l$ at good precision. However he measured just a few data points for the vapor pressure of solid TTO, and those at low precision. Therefore the value for $\Delta T_{tr}(TT^{16}O)$ calculated from (9), 5.2 ± 0.8 K, is too imprecise to be useful. It makes more sense to employ the observed melting point, 4.49 °C, in the reverse calculation to yield a best available value for $\delta \ln (P'/P)$. That value is reported in Table 1. Combining with $\ln (P'/P)_l$ [9, 15] one can obtain the VPIE of the solid at its freezing point.

With 18 isotopomers of water there are 17 TPIE or MPIEs, but only four have been directly measured. Van Hook [16, 17] has reported correlating equations for $\ln (P'/P)_l$ and $\ln (P'/P)_s$ for all 17 isotopomer pairs. These correlating equations have been employed to determine the ratios $\{\ln (P'/P)_{l\,or\,s}/\ln (P'/P)_{l\,or\,s,\,DDO}\}$, and thence self-consistent $\delta \ln (P'/P)$ values, and TPIEs for the 13 water isotopomer pairs not included in Table 1 or discussed above. These are reported in Table 3.

Molecular Hydrogen TPIE's

The vapor pressures, triple points, and related properties for some isotopomers and nuclear spin isomers of molecular hydrogen are available [18]. Using heats of fusion and vapor pressures from Landolt-Bornstein [18], and C_σ obtained as described below, we employed (7) and (8) to calculate the TPIE's reported in Table 1. The IEs are referenced to $p-H_2$. The range of the integration is very large, ($\Delta T_{tr}/T'_{tr}$ reaches 0.5 for $T_2/p-H_2$). For that reason the excellent agreement between calculated and observed TPIEs for all isotopomers is especially gratifying, (although for T_2 the agreement deteriorates). The poor agreement for T_2 most likely reflects inaccuracy in the extrapolated curvature for $[\ln (P')_s]$ close to $\Delta T_{tr}/T'_{tr} \approx 0.5$.

To evalute $\delta C'_{\sigma,fus}$ we employed C'_σ for saturated liquid $p-H_2$ as reported by Younglove and Diller [19] together with C'_v data for solid $p-H_2$, Ahlers [20]. The latter author reported C'_vs and Debye θ's as functions of molar volume and temperature ($0 \leq T/K \leq 20$). We used the Ahlers data to estimate $C'_{v,solid}$ along the sv equilibrium line, including the extrapolated portion, then converted to C'_p using $(C'_p - C'_v) \approx (C'_\sigma - C'_v) = (\alpha^2 V T/\varkappa)'$. $(C'_{\sigma,s} - C'_{\sigma,l})$ was fit graphically to obtain $C'_{\sigma,fus} = 17.405 - 0.727$ T.

Vapor pressures for solid HT and DT are not available in [18] although TPIEs for these isotopomers are reported there. We have estimated TPIE from $\delta \ln (P'/P)$ for HT and DT, reporting the results parenthetically in Table 1. Since liquid phase vapor pressures are available for HT and DT [18], values for $\ln (P'/P)_s$ can be calculated.

Hydrocarbons/Deuterocarbons

Table 2 reviews literature TPIE data on hydrocarbons. The most complete data are for the methane/deuteromethane/$^{13}CH_4$ [21–23], ethylene/deuteroethylene [24], and neopentane/deuteroneopentane [25] systems. For these molecules ΔT_{tr} and $\Delta T_{tr}/T'_{tr}$ are generally smaller than for water or hydrogen. Also because $C_{\sigma,fus}$ and the range of integration are small, terms containing $C_{\sigma,fus}$ can be dropped. For the methanes, ethylenes, and neopentanes the agreement between calculated and observed TPIEs is very good. It is often within 0.03 K or so, and is rarely larger than 0.1 K. Our estimates of the experimental uncertainties in $\delta \ln(P'/P)$ and the related uncertainties in ΔT_{calc} are included in the Table when possible. The sign of TPIE, as expected, correlates uniformly with $\delta \ln(P'/P)$. The excellent agreement speaks for the high quality of both the VPIE and TPIE measurements for these three sets of compounds.

VPIE data for liquid [26] and solid [14, 27] isotopomers of C_6H_6/C_6D_6 and C_6H_{12}/C_6D_{12} are available, and this permits calculation of TPIEs for these molecules. The results are in Table 2. Although there is reasonable agreement for VPIEs from different laboratories for benzene, the cyclohexane results show significant differences between the $\ln(P'/P)_s$ values reported by Kiss, Jakli, and Illy [27] and by Rabinovich [14]. This obviously leads to different predictions for TPIE. The Russian data for the VPIE of solid cyclohexane are imprecise. The Hungarian, while showing better precision, exhibits little or no difference between the solid and liquid VPIEs. This unusual behaviour led to the earlier speculation [2] that the vapor pressure measurements were actually carried out on the glassy, not the crystalline, solid state. We chose to resolve the matter by measurement ΔT_{mp} for protio- and deutero-benzenes and -cyclohexanes. Our results are included in Table 2 and show good agreement with the Russian [14] data. For melting point measurements we sealed samples in capillary tubes, froze at 273.15 K, then allowed the samples in a stirred bath to warm slowly. The melting point was observed visually using a mercury thermometer graduated in steps of 0.01 degree.

Halocarbons

VPIEs and TPIEs have been determined for $CHBr_3/CDBr_3$ by Jakli, Juhasz, and Jancso [28]. There is a large difference between the TPIE calculated from (9) using a V'ant Hoff determined value for $\Delta H'_{fus}$, and that determined by the authors.

Protio/Deutero Polymers

Bates, Kieth and McWhan [29] have reported MPIE data for perprotio/perdeutero isotopomer pairs of hexatriacontane and polystyrene and have summarized literature MPIE data on other polymers [30–33]. The data are found in Table 2. The MPIEs are all positive, $T'_{mp} > T_{mp}$, and large (except for i-polypropylene [33], where the effect is anomalously small).

Noble Gases and Low Boiling Inorganic Gases

Bigeleisen and coworkers [34–36] have reported TPIEs and $\delta \ln(P'/P)$ values for Ne, Ar and Kr. Calculated, (9), and observed TPIEs are in reasonable agreement, differences are 0.08 K for Ne (where the effect is largest) decreasing to a few mK for Ar and Kr, which show smaller isotope effects. The same research group reported TPIE and $\delta \ln(P'/P)$ for nitrous oxide. ^{18}O and ^{15}N effects were studied [37]. The largest difference between calculated and observed TPIEs is 0.01 K (but the "observed" TPIEs were obtained in [37] by fits to the vapor pressure data). Rotational effects were studied by comparing $^{14}N^{15}N^{16}O/^{14}N^{14}N^{16}O$ and $^{15}N^{14}N^{16}O/^{14}N^{14}N^{16}O$ pairs, the expected order for TPIE, i.e. that predicted from the $\delta \ln(P'/P)$ results, is the one observed experimentally. Both TPIE and $\delta \ln(P'/P)$ are smaller for the more rotationally symmetric $^{15}N^{14}N^{16}O$ (than for $^{14}N^{15}N^{16}O$). Bigeleisen has also reported ^{13}C and ^{18}O $\delta \ln(P'/P)$ effects for CO_2 molecules but without reporting TPIE's. The data [38] are summarized in Table 2, we have employed then to calculate TPIEs. The ^{13}C and ^{18}O VPIEs, $\delta \ln(P'/P)$'s and TPIEs are of opposite sign, this observation agrees with the spectroscopically based dynamical analysis using the theory of condensed phase isotope effects [2–4].

TPIE's and $\delta \ln(P'/P)$ were reported for the ^{13}C and ^{18}O isotopomers of CO by Johns [22]. The calculated and observed TPIE's agree within the experimental error. H/D and $^{15}N/^{14}N$ TPIEs and VPIEs for ammonia were reported by Ishida and coworkers [39]. The H/D effects are in good agreement with measurements published in 1962 by Kiss et al. [40], Ishida et al. determined $(\ln(P'_l/P_s))_{NH_3/ND_3}$ in the region between the triple points. TPIE calculated from the intersections of that fit with the ones for $\ln(P'/P)_s$ and $\ln(P'/P)_l$ is -3.19 ± 0.15 K, in good agreement with the value calculated from Table 2, -3.23 ± 0.15 K. Both results, however, are significantly below the directly observed TPIE, -3.55 K [39, 41], and we find no apparent reason for the discrepancy. Calculated and observed $^{15}N/^{14}N$ effects also disagree by more than 10^{-1} K. Appleton and Van Hook [42] reported $\delta\ln(P'/P)$ for HCN/DCN and $HC^{14}N/HC^{15}N$ isotopomer pairs but did not measure TPIE. The authors discuss reasons for the relatively poor precision of VPIE measurements for hydrogen cyanides. Measured values for the H_2S/D_2S TPIE [41] and $\ln(P'/P)$ for liquid [41, 43] and solid [40] are available. Kiss, Matus and Opausky [40] determined $\ln(P'/P)$ in both phases, but TPIE calculated from their data is in poor agreement with the observed value ($-0.13\ \mathrm{K_{calc}}$ vs. $0.47\ \mathrm{K_{obs}}$). Moreover, calculated values of $\ln(P'/P)_l$ near the triple point from 3 sources [40, 43, 44] do not agree well. For these reasons it seems best to employ the measured TPIE to calculate $\delta\ln(P'/P)$. That result can then be combined with the most reliable value for $\ln(P'/P)_l$ to yield an estimate for $\ln(P'/P)_s$, see Table 2.

Chihara and Inaba [45] have reported a series of careful measurements of H/D IEs on the thermodynamic properties of liquid and solid hydrogen chloride, and solid hydrogen bromide and iodide near their triple points. $\delta\ln(P'/P)$ values for HCl/DCl calculated from our least-squares fits to there data, and calculated and observed TPIEs are reported in Table 2. The agreement is within experimental error and confirms the careful nature of the Japanese measurements. Earlier Lewis et al. [46] reported $\delta\ln(P'/P)$ for HCl, but these results are much less precise and give an unreliable value for TPIE. Extrapolation of the liquid phase results given by Lopes, Calado and Jancso [47] from their lowest temperature (≈ 170 K) to the triple point, and combination with the solid data from [45] yields a calculated TPIE which is consistent with experiment (Table 2), but rather less precise than the one calculated from [45] itself because of the uncertainty introduced by the extrapolation. Turning to the HBr/DBr and HI/DI pairs we comment that it is unfortunate that Chihara and Inabe [45] did not measure $\ln(P'/P)_l$ for a sufficient number of points to permit $\delta\ln(P'/P)$ to be determined with useful precision (only one data point is reported for P_l(DBr), and but two for P_l(HI)). For that reason we have employed the measured TPIEs [45] to calculate $\delta\ln(P'/P)$ for HBr/DBr and HI/DI and report those values (parenthesized) in Table 2. Table 2 also shows TPIEs calculated from the very early results of Bates, Halford and Anderson [48]. These are in poor agreement with the measured values and are not recommended.

Discussion

The thermodynamic analysis correlating extant data on TPIE and $\delta\ln(P'/P) \approx \delta\ln(a'/a)$ which are summarized in Tables 1 to 3, and discussed above, unequivocally establishes TPIE as a sensitive and accurate measure of the IE on the change in the ratio of thermodynamic activities across the phase change. We have seen that TPIE sometimes can be employed to calculate $\delta\ln(a'/a)$; the result is sometimes more reliable than that determined from vapor pressure measurements. Alternatively, the now well developed theory of isotope effects in condensed phases [2–4] can be employed to calculate $\delta\ln(a'/a)$ from spectroscopic and phase frequency shifts. In this way observed TPIEs can be checked for theoretical and spectroscopic consistency. It is this latter approach which is adopted in the discussion of the data of Hidaka and Lundén [1] which follows.

MPIEs of Some Inorganic Salts

We now consider the results of Hidaka and Lundén (HL) [1] which originally stimulated our interest in the TPIE/MPIE because of the large inverse $^6LiNO_3/^7LiNO_3$ effects they reported. MPIE data for $LiNO_3$ and several other salts are reviewed in Table 4. The table includes a synopsis of the principal features of the theoretical analysis presented below. In that analysis we elect to discuss the plausibility of the HL TPIEs in terms of an harmonic oscillator model for the isotope effects on the activity ratio [2, 3, 4]:

$$\delta\ln(a'/a) = \sum\ln\frac{\{(u_i/u_i')_s\exp[(u_i'-u_i)_s/2]*[1-\exp(-u_i')_s]/[1-\exp(-u_i)_s]}{(u_i/u_i')_l\exp[(u_i'-u_i)_l/2]*[1-\exp(-u_i')_l]/[1-\exp(-u_i)_l]}\,. \tag{14}$$

Table 4. Melting point isotope effects for some salts. See [1, 49–51].

System	T'_m	$\Delta H'_{fus}$	$10^4\,\delta \ln (a'/a)$	ΔT_{exp}	Model freq. shift, $3 \times$ deg.	Remarks
$^6LiNO_3/^7LiNO_3$	537	25400	(−85)	0.8	$\nu_s^* = 750 \rightarrow \nu_l^* = 820$	Inconsistent with spec. data. Observed MPIE erroneously large.
			(−3)	0.03	$\nu_s^* = 750 \rightarrow \nu_l^* = 752$	Spectroscopically plausible. Observed MPIE possible.
$^6Li_2SO_4/^7Li_2SO_4$	1133	12700	(1)	−0.5	$\nu_s^* = 200 \rightarrow \nu_l^* = 130$	Spectroscopically implausible. Observed MPIE erroneously large.
$Na^{14}NO_3/Na^{15}NO_3$	580	15700	(17)	−0.3	$\nu_s^* = 1000 \rightarrow \nu_l^* = 760$	Inconsistent with spec. data. Observed MPIE erroneously large.
$Na^{35}Cl/Na^{37}Cl$	1074	30200	(16)	−0.5	$\nu_s^* = 350 \rightarrow \nu_l^* \approx 0$	Inconsistent with spec. data. Observed MPIE erroneously large.

In (14) the sum is over all isotope sensitive frequencies and $u_i = h c \nu_i / k T$. In the material which follows we approximate (14) and model the system with one three-fold degenerate characteristic frequency chosen to describe the motion of the isotopically substituted atom of interest.

For $^6LiNO_3/^7LiNO_3$ the MPIE reported by HL is equivalent to $\delta \ln (a'/a) = -0.0085$, which translates, (14), to $a \approx 70\ \text{cm}^{-1}$ blue shift on fusion in the $\approx 750\ \text{cm}^{-1}$ mode assigned to the pairwise $Li^+NO_3^-$ interaction, taken here as triply degenerate. The spectra of the molten salts treated in this section have been discussed in considerable detail by Devlin [49] and Brooker and Papatheodorou [50]. The spectroscopic data support the idea of a specific $Li^+NO_3^-$ interaction in the fused salt correlating with a small blue shift on fusion in lattice modes. Thus the sign of MPIE reported by HL is consistent with spectroscopic analysis. However the magnitude of the blue shift required to rationalize the MPIE, ($\approx 3 \times 70\ \text{cm}^{-1}$), is far and away too large to be supported by the spectroscopic information. It is highly implausible. On the other hand, the earlier and much smaller $^6Li/^7Li$ TPIE reported by Jansson and Lundén [51] for this compound turns out to be equivalent to a much smaller blue shifts on fusion, ($\approx 3 \times 2\ \text{cm}^{-1}$), and is consistent with the spectroscopic analysis. We conclude that it is the latter MPIE [51] which is the more reliable.

We turn now to results on other salts reported by HL. For $^6Li/^7Li$, Li_2SO_4 their reported value for MPIE, $\Delta T_{tr} = -0.5$ K, corresponds to an implausibly large shift in the characteristic lattice frequency on melting. Similarly, the other effects they report, MPIE for $Na^{14}NO_3/Na^{15}NO_3 = -0.3$ K, and MPIE for $Na^{35}Cl/Na^{37}Cl = -0.5$ K are equivalent to red shifts of $\approx 250\ \text{cm}^{-1}$ in the nitrogen breathing modes of $NaNO_3$, and $\approx 350\ \text{cm}^{-1}$ in the lattice translational modes of NaCl. These are impossibly large. They lead to the conclusion that the MPIEs reported by HL are in error. HL themselves comment that their DSC measurements yield MPIEs which are an order of magnitude or more larger than earlier reports based on measurements of solid/liquid fractionations [51]. The present discussion indicates that it is those earlier results which are more likely correct. We pause to remark that DSC experiments involve dynamic measurements. The shape of the observed endotherms is critically dependent on the temperature scan rate, and on the enthalpy of transition. Possibly the IE on δH_{fus}, together with a too-rapid scan, may have caused enough distortion in peak shapes to lead to the errors under discussion.

Hydrate/Deuterate MPIEs

There exists a significant amount of data on MPIEs of hydrate/deuterate systems, e.g. [1, 14, 52, 53], which we have chosen not to analyze in the present paper. The complete treatment, which will be deferred to a later publication, will involve theoretical consideration of the IE on solubility for the water/salt-hydrate systems (i.e. the determination of the concentration IE at common temperature), as well as analyses of the MPIE itself (for those hydrates/deuterates which melt), and VPIEs for the hydrate deuterate system (especially for salts which deliquesce).

4. Discussion

In the material above we have reviewed the thermodynamic correlation between triple point or melting point isotope effects and the discontinuous change in vapor pressure isotope effect which occurs across the phase change. The agreement between predicted and observed TPIE/MPIEs is excellent for most of the cases reviewed in the Tables, and this speaks to the high quality of these thermodynamic data. By using the statistical theory of condensed phase isotope effects [2–4] it is possible to reformulate the correlation and predict TPIE/MPIEs in terms of the discrete differences in reduced partition function ratios (RPFRs) which occur on phase change, or, moving further along, in terms of the frequency shifts in lattice and internal vibrational modes which occur on the phase change. Many of the compounds discussed in the tables and text above have been subjected to statistical thermodynamic analysis, and agreement between measured VPIEs and the available spectroscopic information is generally satisfactory. It is in that context that we were able to conclude that some of the MPIE results reported in [1] cannot be correct, they are incomensurate with the spectroscopic information.

It is clear that, could one deduce general rules to predict RPFR and/or spectroscopic frequency shifts on phase change, this would be equivalent to predicting TPIE and δ VPIE. Unfortunately, that course of action appears to be difficult, at least for polyatomic molecules. About twenty-five years ago Jeevanandam [54] tried to apply significant structures theory [55] to the problem, but without quantitative success. The attempted correlation via significant structures theory is with the volume of fusion, δV, but individual normal modes show radically different dependences on δV. In the end one concludes the net effect on δ RPFR is complicated and virtually impossible to predict, except for very simple cases. Significant structures theory does not contain the detail which is required for an accurate calculation of TPIE/MPIE. More recently Bates, Keith and McWhan [29] correlated MPIE (and thus δ RPFR) for nonpolar polymer molecules with a linear combination of isotope effects on core volume and polarizability. The correlation is limited to large molecules and polymers where the contribution of lattice modes and other low lying frequencies to RPFR can be neglected. It fails dramatically for smaller molecules where lattice vibrations and/or internal rotations contribute significantly. It also fails for those larger molecules, including polymers, where internal rotations of pendant groups contribute to RPFR. We conclude that a need exists for an improved theory to correlate δ RPFR (and therefore TPIE/MPIE) with simple physical parameters which describe the phase change (such as ΔV and $\Delta \delta V$, ΔH and $\delta \Delta H$, etc.).

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