On the Entropy of Fusion and Its Separation into Configurational and Volume-Change Contributions

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ABSTRACT: The basis and implications of the well-known separation of the fusion entropy into configurational and volume-change contributions are discussed. For thermodynamic and other reasons the concept is shown to be incorrect; additional support for this conclusion is afforded by relevant calculations for several polymers.

The entropy of fusion of polymers has frequently been analyzed in terms of two distinct contributions: (1) a constant volume, purely configurational, entropy change, followed by (2) a volume change of the disordered solid. The configurational contribution has been postulated to be a consequence of the constant volume disordering of the crystalline state at the melting point. The remaining part of the total entropy of fusion is then associated with the volume change (generally positive) of the resulting disordered crystal to the liquid. In terms of the above ideas the formal expression

$$\Delta S_f = (\Delta S_c)_V + \Delta S_V \tag{1}$$

is obtained where ΔS_f denotes the total entropy of fusion, $(\Delta S_c)_V$ the above-mentioned configurational entropy change, and ΔS_V the nonconfigurational volume change entropy contribution. All the quantities are commonly normalized so as to refer to fusion of the completely crystalline state.

The entropy separation concept seems consistent with those solid-based models of the melting process which divide the total partition function into configurational and thermal terms.[1] The concept for polymers appears to follow such a development for metals suggested by Eucken[2] and Slater[3] and elaborated upon by Kubaschewski[4] and Oriani.[5] It is the purpose of this paper to demonstrate that such a separation cannot be performed.

The concept rests on the assumption that the volume change contribution to the total entropy of fusion, the term ΔS_V in eq 1, may be calculated from the integration of a thermodynamic identity. Fullest discussion of the concept and its use necessitates the following rehearsal of arguments by which ΔS_V is "calculated". One method of calculation proceeds from the Maxwell relation

$$(\partial S/\partial V)_T = (\partial P/\partial T)_V \tag{2}$$

which in the present context has been integrated along the melting curve (cf. eq 2, ref 5) to yield:

$$\Delta S_V = (\partial P/\partial T)_V \Delta V_f$$
$$= \frac{\alpha}{\beta} \Delta V_f \tag{3}$$

where α and β are respectively the isobaric expansivity and isothermal compressibility of the solid at the melting temperature, T_m. Such an integration with the appearance of ΔV_f, the volume of fusion, in eq 3 rests on the assumption that none of the volume change on melting is connected with configurational changes.

The volume-related entropy increment of eq 3 is, if the entropy separation concept is valid, a state function and thus path independent. However, if equilibrium freezing (crystallization) of the liquid is considered, an immediate difficulty arises. The above rationale demands that the ratio α/β now refers to the respective properties of the liquid at T_m. This important point, although recognized by Oriani,[5] seems to have received scant critical attention. If the concept is correct then the ratio α/β is required to have the same numerical value for the crystalline solid, at T_m, as for the liquid. There is no thermodynamic basis for such a general condition. This then implies that ΔS_V and hence $(\Delta S_c)_V$ are not uniquely determined but are functions of the direction of the phase change. As will be shown, the experimental evidence confirms that there can be, in fact, considerable differences between the values of the ratios (α/β) at T_m and thus reflects a basic difficulty with the concept. Indeed it would seem that this point has not received much attention because the entropy separation concept has been *assumed* to be valid.

The difficulties brought out above are emphasized upon the consideration of a second thermodynamic process. The process we have considered above is an overall isothermal one with an exchange of heat $T_m \Delta S_f$ with the surroundings; the entropy change ΔS_V is occasioned or suppressed by the application of a pressure[5] of appropriate sign and the configurational entropy changes $(\Delta S_c)_V$ are given by the difference $\Delta S_f - \Delta S_V$. This process is that appropriate to 2 and 3. Suppose now that the path between the initial and final states is chosen so that the overall change is an isobaric one at a pressure P_m. Following this approach the conjugate relation $(\partial S/\partial V)_{P_m} = C_p/TV\alpha$ is integrated to yield[4]

$$\Delta S_V = C_p \Delta V_f / TV\alpha \tag{4}$$

where C_p, the isobaric heat capacity, α, and V, the molar volume of the crystal (or melt, see below), are all evaluated at P_m. We note that if in this description the entropy separation concept is valid it is again equally acceptable to use all crystal or liquid parameters in eq 4; the phase for which the parameters are to be evaluated is dictated by the direction of the phase change.

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Table I
Volume Properties

Polymer	ΔS_f, cal mol^{-1} K^{-1}	ΔS_V, cal mol^{-1} K^{-1}			
		a	*b*	*c*	*d*
Polyethylene (linear)	2.29 (7)	0.64	1.2	3.80	5.68
Polystyrene (isotactic)	3.92 (25)	2.10	1.74	24.8	48.9
Poly(methyl methacrylate) (isotactic)	4.65 (10)	1.48	0.96	13.9	28.3
Poly(dimethyl siloxane)	2.58 (15)	0.98		6.8	26.7
Polypropylene (isotactic)	4.22 (17)	1.45	0.91	11.2	21.9

[a] $(\alpha/\beta)_l \Delta V_f$. [b] $(\alpha/\beta)_s \Delta V_f$. [c] $(C_p/T_m \alpha V_m)_l \Delta V_f$. [d] $(C_p/T_m \alpha V_m)_s \Delta V_f$.

Table II
Data Used in Calculations[a]

	Polyethylene (linear)	Polystyrene (isotactic)	Poly(methyl methacrylate) (isotactic)	Poly(dimethyl siloxane)	Polypropylene (isotactic)
$\alpha V_m(l) \times 10^4$, ml mol^{-1} K^{-1}	156 (22)	562 (23)	530 (11,22)	653 (24)	386 (14)
$\alpha V_m(s) \times 10^4$, ml mol^{-1} K^{-1}	86 (22)	260 (8)	225 (11,21)	152 (13)	168 (14)
$\beta V_m(l) \times 10^5$, ml mol^{-1} atm^{-1}	170 (22)	810 (23)	520 (22)	680 (24)	460 (20)
$\beta V_m(s) \times 10^5$, ml mol^{-1} atm^{-1}	50 (22)	452 (23)	340 (22)		320 (20)
$C_p(l)$ at T_m, cal mol^{-1} K^{-1}	8.5 (7)	57 (9)	53 (10)	26.2 (15)	27.3 (16)
$C_p(s)$ at T_m, cal mol^{-1} K^{-1}	7.0 (7)	53 (9)	46 (10)	24 (15)	23.1 (17)
T_m, K	411 (6)	510 (9)	433 (10)	248 (15)	449 (26)
ΔV_f, ml mol^{-1}	2.87 (6,18)	12.5 (19)	6.0 (12)	4.2 (19)	7.14 (14)

[a] References given in parentheses.

freezing) as a state function implies that there is in no sense a choice in the use of either eq 3 or 4; either equation should provide a unique value of ΔS_V. This would imply the existence of relations between parameters on the right-hand sides of eq 3 and 4. The isobaric process was used implicitly by Kubaschewski[4] in his discussion of the fusion entropy of metals. Oriani[5] recognized but did not elaborate on the large numerical discrepancies which emerge as a consequence of the calculations of ΔS_V by the two different paths. These two paths provide four possible calculations of ΔS_V [i.e., from eq 3 and 4, in each case the phase change considered in either direction]. Table I contains such values calculated from the base data presented in Table II; large differences are evident. We acknowledge that problems with imprecise data, the necessity for extrapolation, and so forth may cause some uncertainty in some values presented in Table I. Nevertheless the differences in these results for any given polymer seem to us far too large to be attributed to this source. Of particular note is that in all cases the use of eq 4 yields values of ΔS_V larger than the entire entropy of fusion ΔS_f. This anomalous inversion, which clearly compromises the basis and appeal of the entropy separation concept, was found also in the study of metals.[4,5]

Notwithstanding the difficulty we have noted and the lack of any proof of the hypothesis this concept has been fairly widely used and the values of ΔS_V that have been calculated for polymers (usually based on the more readily available liquid state data) have been considered reasonable in that such values are mostly in the range of 0.2 to $0.8\Delta S_f$.

As the entropy separation concept is ostensibly based on elementary thermodynamic principles the development presented above indicates the possible misuse of these principles and specifically that neither eq 3 nor eq 4 is used correctly. While eq 3 and 4 may be used in a one-phase system arbitrarily close to a phase change they may not be correctly employed to calculate differences which arise as a consequence of phase changes.

Thermodynamic considerations applied to that part of the entropy separation concept amenable to such discussion implies that it is not, as seems to be commonly accepted, an approximation; it is incorrect. One obvious criticism is that it ignores the Gibbs–Duhem relation. If ΔV_f is positive any pressure reduction at T_m necessary to increase the volume of the solid to that of the same amount of liquid, as was envisaged in ref 5, Figure 1, will clearly melt the solid. Similarly, the pressure increase necessary during freezing to alter the liquid volume to that of the crystal will increase the equilibrium crystallization temperature. Precisely analogous difficulties with respect to the necessary temperature changes arise when considering the isobaric process.

In summary, none of the proposed calculations of ΔS_V appears to be thermodynamically sound, however intuitively appealing; it is not possible to separate ΔS_f into configurational and volume change terms, nor indeed is it possible to construct any thermodynamic process or cycle to accomplish this separation. Furthermore, the seemingly intuitive concept of the separation of ΔS_f into two components is less attractive on closer examination. The volume change associated with fusion does not depend for its existence on an expansion of the lattice due to changes in vibrational modes but rather enters "intrinsically" because of the occurrence of a metastable region in P,S (or P,V) space at the melting point. We are led therefore to conclude that the entropy and volume of fusion are indissolubly linked.

Thus, notwithstanding the quantitative success of calculations which employ the entropy separation concept, we are led to conclude that the basis of the concept is unsound and, thus, a critical reexamination of conclusions that may have been drawn from its use is merited.

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