

Topic710

Cohesive Energy Density

The molar enthalpy of vaporisation $\Delta_{\text{vap}}H^*$ is the change in enthalpy for one mole of chemical substance j on going from the liquid to the (perfect) gaseous state. The properties of a given liquid- j are determined by j - j intermolecular forces. By definition, there are no intermolecular forces in a perfect gas. Hence $\Delta_{\text{vap}}H_j^*(\ell)$ offers an insight into the strength of intermolecular forces in the liquid state. We have to be careful not to use the word 'energy'. By definition enthalpy H equals $(U + p \cdot V)$. For phase I at temperature T and pressure p ,

$$U_j^*(\text{I}) = H_j^*(\text{I}) - p \cdot V_j^*(\text{I}) \quad (\text{a})$$

$$\text{Similarly for phase II, } U_j^*(\text{II}) = H_j^*(\text{II}) - p \cdot V_j^*(\text{II}) \quad (\text{b})$$

$$\text{Hence, } U_j^*(\text{II}) - U_j^*(\text{I}) = H_j^*(\text{II}) - H_j^*(\text{I}) - p \cdot [V_j^*(\text{II}) - V_j^*(\text{I})] \quad (\text{c})$$

If phase II is a perfect gas and phase I is the corresponding liquid,

$V_j^*(\text{II}) \gg V_j^*(\text{I})$; for one mole of chemical substance j ,

$$p \cdot V_j^*(\text{II}) = R \cdot T.$$

$$\text{Consequently } \Delta_{\text{vap}}U_j^*(T) = \Delta_{\text{vap}}H_j^*(T) - R \cdot T \quad (\text{d})$$

$\Delta_{\text{vap}}U_j^*(T)$ is the molar thermodynamic energy of vaporisation for liquid j at temperature T . Having calculated $\Delta_{\text{vap}}H_j^*(T)$ from experimental data we obtain $\Delta_{\text{vap}}U_j^*(T)$, a measure of the strength of inter-molecular interactions in the liquid.

The differential quantity $(\partial U / \partial V)_T$ defines the internal pressure $\pi_{\text{int}}(j)$ of chemical substance j . For liquid j ,

$$\pi_{\text{int}}^*(\ell; j) = [\partial U_j^*(\ell) / \partial V_j^*(\ell)]_T \quad (\text{e})$$

The internal pressure for liquids, of the order 10^8 Pa, is an indicator of the strength of intermolecular forces [1]. The structure of the terms in equation (e) prompts a slight rewrite using properties that are either readily measured or calculated, namely $\Delta_{\text{vap}}U_j^*(T)$ and the molar volume of the liquid at temperature T , $V_j^*(T)$ [2,3]. The result is the

cohesive energy density, c.e.d., a measure of the cohesion within a liquid.

$$\text{By definition, c.e.d.} = \Delta_{\text{vap}} U_j^*(T) / V_j^*(\ell) \quad (\text{f})$$

Intuitively, $\Delta_{\text{vap}} U_j^*(T)$ is a measure of cohesive interactions in the liquid whereas volume is a measure of the repulsive interactions, keeping the molecules in the liquid apart. At constant $\Delta_{\text{vap}} U_j^*(T)$, c.e.d decreases with increase in molar volume; c.f. repulsion. But at constant $V_j^*(T)$, c.e.d. increases with increase in $\Delta_{\text{vap}} U_j^*(T)$, the attractive part.

$$\text{If the vapour is a perfect gas, c.e.d.} = [\Delta_{\text{vap}} H_j^*(\ell) - R \cdot T] / V_j^*(\ell) \quad (\text{g})$$

If the molar mass of the liquid j equals M_j and the density equals $\rho_j^*(\ell)$,

$$\text{c.e.d.} = [\Delta_{\text{vap}} H_j^*(\ell) - R \cdot T] \cdot \rho_j^*(\ell) / M_j \quad (\text{h})$$

M_j is expressed in kg mol^{-1} and $\rho_j^*(\ell)$ in kg m^{-3} , consistent with c.e.d. being expressed in $(\text{J mol}^{-1} \text{ m}^{-3})$. At 298.2 K, $R \cdot T = 2.48 \text{ kJ mol}^{-1}$.

The ratio of internal pressure $\pi_{\text{int}}(j)$ to c.e.d. defines a property n using equation (i).

$$n = [\partial U_j^*(\ell) / \partial V_j^*(\ell)]_T / [\Delta_{\text{vap}} U_j^*(\ell) / V_j^*(\ell)] \quad (\text{i})$$

The dimensionless ratio n has been used to comment on the strength of intermolecular forces in a liquid [4].

In the context of the properties of liquid mixtures, using the definition of enthalpy $H (= U + p \cdot V)$ we can write the following equation for a given phase I containing n_1 moles of substance 1 and n_2 moles of substance 2.

$$U(\text{I}; n_1 + n_2) = H(\text{I}; n_1 + n_2) - p \cdot V(\text{I}; n_1 + n_2) \quad (\text{j})$$

We assert that phase I is an ideal binary liquid mixture. Then,

$$U(\text{I}; n_1 + n_2; \text{mix}; \text{id}) = n_1 \cdot H_1^*(\ell) + n_2 \cdot H_2^*(\ell) - p \cdot V(\text{I}; n_1 + n_2; \text{mix}; \text{id}) \quad (\text{k})$$

We assert that phase II is a perfect gas comprising n_1 moles of substance 1 and n_2 moles of substance 2. Then

$$U(\text{II}; n_1 + n_2; \text{pfg}) = n_1 \cdot H_1^*(\text{pfg}) + n_2 \cdot H_2^*(\text{pfg}) - p \cdot V(\text{II}; n_1 + n_2; \text{pfg}) \quad (\text{l})$$

$$\text{For a perfect gas, } p \cdot V(\text{II}; n_1 + n_2; \text{pfg}) = (n_1 + n_2) \cdot R \cdot T \quad (\text{m})$$

We express the thermodynamic energy of vaporisation for $(n_1 + n_2)$ moles passing from phase I to phase II.

$$\begin{aligned} \Delta_{\text{vap}} U(\text{id}, n_1 + n_2) = \\ n_1 \cdot \Delta_{\text{vap}} H_1^* + n_2 \cdot \Delta_{\text{vap}} H_2^* - (n_1 + n_2) \cdot R \cdot T \\ + p \cdot V(\text{I}; n_1 + n_2; \text{mix}; \text{id}) \end{aligned} \quad (\text{n})$$

Therefore for one mole,

$$\Delta_{\text{vap}} U_m(\text{id}) = x_1 \cdot \Delta_{\text{vap}} H_1^* + x_2 \cdot \Delta_{\text{vap}} H_2^* - R \cdot T + p \cdot V_m(\text{I}; \text{mix}; \text{id}) \quad (\text{o})$$

Suppose however that the thermodynamic properties of the liquid mixture are not ideal. We rewrite equation (k) in the following form (for one mole of mixture) where H_m^E and V_m^E are the excess molar enthalpies and excess molar volumes of mixing.

$$\begin{aligned} U_m(\text{I}, \text{mix}) = \\ [x_1 \cdot H_1^*(\ell) + x_2 \cdot H_2^*(\ell) + H_m^E] - p \cdot [x_1 \cdot V_1^*(\ell) + x_2 \cdot V_2^*(\ell) + V_m^E] \end{aligned} \quad (\text{p})$$

$$\text{Or } U_m(\text{I}, \text{mix}) = [x_1 \cdot H_1^*(\ell) + x_2 \cdot H_2^*(\ell) + H_m^E] - p \cdot V_m(\text{mix}) \quad (\text{q})$$

Therefore the molar thermodynamic energy of vaporisation on going from the real mixture to the perfect gas is given by equation (r).

$$\Delta_{\text{vap}} U_m = [x_1 \cdot \Delta_{\text{vap}} H_1^*(T) + x_2 \cdot \Delta_{\text{vap}} H_2^*(T) - H_m^E] - R \cdot T + p \cdot V_m(\text{mix}) \quad (\text{r})$$

The cohesive energy density, c.e.d., for a real binary liquid mixture is given by equation (s).

$$\begin{aligned} \text{c.e.d.} = \{ [x_1 \cdot \Delta_{\text{vap}} H_1^*(T) + x_2 \cdot \Delta_{\text{vap}} H_2^*(T) - H_m^E] / V_m(\text{mix}) \} \\ - \{ R \cdot T / V_m(\text{mix}) \} + p \end{aligned} \quad (\text{s})$$

The c.e.d. for a given binary mixture is given by the molar enthalpies of vaporisation of the pure components, the excess molar enthalpy of mixing and the molar volume of the mixture. For the corresponding ideal binary mixture, c.e.d.(id) is given by equation (t).

$$\begin{aligned} \text{c.e.d.}(\text{id}) = \{ [x_1 \cdot \Delta_{\text{vap}} H_1^*(T) + x_2 \cdot \Delta_{\text{vap}} H_2^*(T)] / V_m(\text{mix}; \text{id}) \} \\ - \{ R \cdot T / V_m(\text{mix}; \text{id}) \} + p \end{aligned} \quad (\text{t})$$

The difference between $\Delta_{\text{vap}} U_m / V_m(\text{mix})$ and $\Delta_{\text{vap}} U_m / V_m(\text{mix}; \text{id})$ is the excess cohesive energy density, (c.e.d.)^E. The sign of (c.e.d.)^E is controlled to a significant extent by the excess molar volume V_m^E and the

excess molar enthalpy H_m^E [6]. In fact equations (s) and (t) lead to equation (u).

$$(\text{c.e.d.})^E = \frac{-[x_1 \cdot \Delta_{\text{vap}} H_1^*(T) + x_2 \cdot \Delta_{\text{vap}} H_2^*(T) - R \cdot T]}{V_m(\text{mix}) \cdot V_m(\text{mix}; \text{id})} - \frac{H_m^E}{V_m(\text{mix})} \quad (\text{u})$$

Recently the cohesive energy density of a liquid has been described as a 'solvation pressure' acting on, for example, ethanol in ethanol + water and ethanol + trichloromethane liquid mixtures [7].

Footnotes

[1] M. R. J. Dack, *Aust. J. Chem.*, 1976, **27**, 779.

[2] $\text{c.e.d.} = [\text{J mol}^{-1}] / [\text{m}^3 \text{ mol}^{-1}] = [\text{J m}^{-3}] = [\text{N m}^{-2}]$; the unit of pressure.

$$R \cdot T = [\text{J K}^{-1} \text{ mol}^{-1}] \cdot [\text{K}] = [\text{J mol}^{-1}]$$

[3] A variety of units are used for cohesive energy densities. Despite the fact that there are good grounds for using the unit J m^{-3} , the commonly used unit is calories per cm^3 , cal cm^{-3} .

For liquids 298.15 K and ambient pressure.

Liquid	c.e.d./cal cm^{-3}
water	547
methanol	204
benzene	85
tetrachloromethane	74

[4] A. F. M. Barton, *J. Chem. Educ.*, 1971, **48**, 156.

[5] For comments on the role of cohesive energy densities of solvents and rates of disproportionation, see A.P. Stefani, *J. Am. Chem. Soc.*, 1968, **90**, 1694.

[6] For comments on cohesive energy densities of binary aqueous mixtures see,

(a) D. D. Macdonald and J. B. Hyne, *Can. J. Chem.*, 1971, **49**, 611, 2636.

(b) D. D. Macdonald, *Can. J. Chem.*, 1976, **54**, 3559.

[7] N.W. A. van Uden, H. Hubel, D. A. Faux, A. C. Tanczos, B. Howlin and D. J. Dunstan, *J. Phys.: Condens. Mater.*, 2003, **15**, 1577.