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Heat Capacities of Liquids and Vapors

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By the use of an equation previously derived for the energy of vaporization of a liquid: $\Delta E = k(D_l^n - D_g^n)$ (in which k is a constant; $n = 5/3$, and D_l and D_g are the molar densities of liquid and vapor, respectively), an expression is derived relating $(\partial \Delta E / \partial T)_{\text{sat}}$ to the difference in molar heat capacities at constant pressure of the liquid and vapor (ΔC_p). At low pressures this relation can be approximated by the equation $\Delta C_p = (\partial \Delta E / \partial T)_s + R$ (R is the gas constant, 1.986 cal./mole-°A). Under these conditions $(\partial \Delta E / \partial T)_s = (5/3)\Delta E(\partial \ln D_l / \partial T)_s$, and the resulting equation for ΔC_p is $\Delta C_p = (5/3)\Delta E(\partial \ln D_l / \partial T)_s + 1.99$. From known properties of liquids ΔC_p can be calculated using this last equation. These calculated values are found to be in good agreement with observed experimental values.

IN a recent paper¹ it was shown that a cage model of a liquid could be used to derive a simple analytic expression for the configurational energy of the liquid. If the same expression is applied to the configurational energy of the vapor in equilibrium with the liquid, the energy of vaporization is given by the difference between these configurational energies:

$$\Delta E_{\text{vap}} = E_c(\text{liq.}) - E_c(\text{gas}). \quad (1)$$

Since the configurational energies obtained from the cage model are explicit functions only of the density of the particular phase involved, the energy of vaporization becomes an explicit function of these parameters only, and is given by the following equation:

$$\Delta E_{\text{vap}} = k(D_l^n - D_g^n). \quad (2)$$

D_l and D_g are the molar densities of the liquid and gas phases, respectively, k is a constant for any given liquid, and n is a number which may be taken as 5/3 for all liquids.¹ (In the neighborhood of the critical region, the value $n = 2$ gives a better fit with experimental data.)

If we differentiate this expression for the energy of vaporization with respect to temperature at saturation conditions, we will obtain the derivative $(\partial \Delta E / \partial T)_s$,* which may be related thermodynamically to ΔC_p , the difference in the heat capacities of the liquid and its saturated vapor. This latter equation may then be solved explicitly for ΔC_p in terms of experimentally available properties of the liquid and vapor.

RELATION BETWEEN $(\partial \Delta E / \partial T)_s$ AND ΔC_p

From the first and second laws it is possible to derive the following equation for ΔC_p :²

$$\Delta C_p = \left(\frac{\partial \Delta E}{\partial T} \right)_s + \left[\frac{\Delta H}{\Delta V} + P \right] \left(\frac{\partial \Delta V}{\partial T} \right)_p + \frac{P \Delta H}{T \Delta V} \left(\frac{\partial \Delta V}{\partial P} \right)_T. \quad (3)$$

Regrouping the terms in Eq. (3) we find:

$$\Delta C_p = \left(\frac{\partial \Delta E}{\partial T} \right)_s + \frac{\Delta H}{T} \left[\left(\frac{\partial \ln \Delta V}{\partial \ln T} \right)_p + \left(\frac{\partial \ln \Delta V}{\partial \ln P} \right)_T \right] + P \left(\frac{\partial \Delta V}{\partial T} \right)_p. \quad (4)$$

Equation 4 is an exact relation between ΔC_p , $(\partial \Delta E / \partial T)_s$, and the known properties of a liquid and its vapor. The first term on the right-hand side of the equation is the dominant term and negative, a fact in agreement with the observed property that the heat capacity of a liquid is greater than the heat capacity of its vapor.

The third term in Eq. 4 is positive, and the second term is made of two partial derivatives, the first of which is positive and the second negative. If equations of state are available, the second and third terms may be explicitly evaluated and ΔC_p calculated exactly. However, at low vapor pressures the vapor is very dilute and

² F. H. MacDougall, *Thermodynamics and Chemistry*, (John Wiley & Sons, Inc., New York, 1939) third edition, p. 126, contain a derivation from which Eq. 3 may be constructed.

¹ S. W. Benson, J. Chem. Phys. 15, 367 (1947).

* The subscript s will refer to saturation.

may be assumed to obey the ideal gas laws. In such regions the following approximations may be made:

$$\left(\frac{\partial \ln \Delta V}{\partial \ln T}\right)_p \sim \left(\frac{\partial \ln V_g}{\partial \ln T}\right)_p \sim 1, \quad (5)$$

$$\left(\frac{\partial \ln \Delta V}{\partial \ln P}\right)_T \sim \left(\frac{\partial \ln V_g}{\partial \ln P}\right)_T \sim -1, \quad (6)$$

and

$$\left(\frac{\partial \Delta V}{\partial T}\right)_p \sim \left(\frac{\partial V_g}{\partial T}\right)_p \sim R/P. \quad (7)$$

Substituting these values into Eq. 4 we have, finally,

$$\Delta C_p \sim \left(\frac{\partial \Delta E}{\partial T}\right)_s + R. \quad (8)$$

EVALUATION OF $(\partial \Delta E / \partial T)_s$

If we take the derivative with respect to temperature of ΔE (at saturation) as given by Eq. 2, we have

$$\left(\frac{\partial \Delta E}{\partial T}\right)_s = knD_l^{n-1} \left(\frac{\partial D_l}{\partial T}\right)_s - knD_g^{n-1} \left(\frac{\partial D_g}{\partial T}\right)_s. \quad (9)$$

Rearranging the terms this becomes

$$\left(\frac{\partial \Delta E}{\partial T}\right)_s = \frac{nkD_l^n}{D_l} \left[\left(\frac{\partial D_l}{\partial T}\right)_s - \left(\frac{D_g}{D_l}\right)^{n-1} \left(\frac{\partial D_g}{\partial T}\right)_s \right]. \quad (10)$$

At the pressures which are under consideration (in the neighborhood of the boiling point or lower), $(\partial D_g / \partial T)_s$ is never greater than 1/10 of $(\partial D_l / \partial T)_s$. In this same region D_g is usually less than 1/200 of D_l . We can, therefore, make the following approximations in this pressure region:

$$\left(\frac{D_g}{D_l}\right)^{n-1} \left(\frac{\partial D_g}{\partial T}\right)_s \ll \left(\frac{\partial D_l}{\partial T}\right)_s, \quad (11)$$

and

$$\Delta E = kD_l^n. \quad (12)$$

Making the substitutions from Eqs. 11 and 12 into Eq. 10 we find:

$$\left(\frac{\partial \Delta E}{\partial T}\right)_s \sim n\Delta E \left(\frac{\partial \ln D_l}{\partial T}\right)_s. \quad (13)$$

TABLE I. ΔC_p of liquids and their saturated vapors.

Compound	Mole Wt.	t ($^{\circ}\text{C}$)	ΔC_p (obs.) cal./mole $^{\circ}\text{C}$	ΔC_p (calc.) cal./mole $^{\circ}\text{C}$
Ethyl ether	74	35	14.0	14.2
Carbon tetrachloride	154	20	11.2	12.1
Benzene	78	80	14.9	14.4
<i>n</i> -hexane	86	80	16.5	15.6
Sulfur dioxide	64	15	11.4	12.7
Water	18	100	9.31	9.21

Further substitution from Eq. 13 into 8 finally yield

$$\Delta C_p = n\Delta E(\partial \ln D_l / \partial T)_s + R. \quad (14)$$

COMPARISON OF EQ. 14 WITH EXPERIMENTAL DATA

Equation 14 gives us a method of calculating ΔC_p at low pressures from the energy of vaporization of a liquid and its coefficient of expansion. If data are lacking for the energy of vaporization, ΔE may be approximated at the boiling point by Trouton's rule or by Hildebrand's rule. In any case, all of the quantities in the first term on the right-hand side of Eq. 14 are either well known or easily measured experimentally. On the other hand, it is very difficult to obtain reliable experimental values for ΔC_p . Heat capacities for liquids have been measured, but heat capacities at constant pressure for saturated vapors are difficult to obtain.

In Table I experimental values of ΔC_p are compared with values calculated with the aid of Eq. 14 ($n = 5/3$).

The experimental values for the heat capacities of liquids and vapors were taken from values listed in Landolt-Bornstein and the *International Critical Tables*. For the calculated values of ΔC_p , Eq. 14 was used, with the value of n taken as 5/3. Values of the energy of vaporization and the thermal coefficient of expansion of the liquid were calculated from the data of Young³ and tables found in Landolt-Bornstein. The agreement between the observed and experimental values of ΔC_p (Table I) are quite satisfactory and probably within the limits of error of the experimental values for the molar heat capacities. The agreement lends further support to the value of $n = 5/3$ which was proposed in the previous paper.¹

³ Young, Proc. Roy. Dublin Soc. 12, 374 (1910).