An Equation of State for Liquids

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A comparatively simple and accurate equation of state has been developed for the liquid state. The proposed equation has the form

$$P - P_0 = K \left[\frac{1}{v_R^4} - \frac{1}{v_R^2} \right]^q$$

where K and q are constants dependent on temperature. The equation is tested for validity against P-V-T data for aldehydes obtained in the course of this investigation. Literature data on alkanes, alcohols, and water were also utilized to confirm the validity of the equation. A critical comparison of the proposed equation with the Hudleston equation reveals the former to yield more satisfactory prediction of P-V-T behavior of liquids.

On a mis au point et proposé une équation d'état relativement simple et précise pour l'état liquide, à savoir:

$$P - P_0 = K \left[\frac{1}{v_R^4} - \frac{1}{v_R^2} \right]^q$$

où K et q sont des constantes qui dépendent de la température. On a vérifié l'exactitude de la dite équation en comparant ses résultats avec ceux qu'on a obtenus pour des aldéhydes, au cours de l'étude, par rapport aux facteurs pression, volume et température. On a aussi utilisé, dans le même but, des renseignements publiés sur les alcanes, les alcools et l'eau.

Une comparaison critique de l'équation proposée avec celle d'Hudleston a indiqué que la première permettait de prédire, d'une manière plus satisfaisante, le comportement des liquides par rapport aux facteurs pression, volume et température.

For a number of years, P-V-T behaviour of liquids has been investigated by numerous researchers in order to develop a suitable equation of state[1-6]. Since the molecular phenomenon involved are quite complex, a theoretical equation of state is difficult to establish. The cell theory of liquids, particularly as developed by Lennard-Jones and Devonshire, has had fair success for low temperature and high density conditions[7,8]. The most encouraging approach seems to utilize theoretical guidelines with experimental data. Past efforts in this direction include works by Tait[9] and Hudleston[10].

The Tait equation is

$$v - v_0 = C \log \left(\frac{D + P}{D + P_0} \right) \quad \dots \dots \dots (1)$$

where v_0 and v are specific volumes at pressures P_0 and P respectively. Even though the theoretical basis of Tait equation is somewhat obscure, the equation has had considerable success in correlating data for a wide range of liquids. Among the investigators who have utilized this equation are Wohl[11], Carl[12], Gibson[13], and Eduljee[14].

Hudleston proposed the following equation of state

$$\log [P\, v_R{}^{2/3}/(1 - v_R{}^{1/3})] = A + B\,[1 - v_R{}^{1/3}] \quad \dots (2)$$

where A and B are empirical constants. The Hudleston equation is based on an intermolecular force law of the form

$$f = a\,(l - l_0) \exp b\,(l_0 - l) \quad \dots \dots \dots \dots (3)$$

The testing of Hudleston equation has been mainly confined to alkanes[14-18]. It has been found that the equation is not satisfactory for water and acetone[10].

None of the existing equations of state is completely satisfactory for prediction of P-V-T behavior of liquids. In this paper, a new equation of state is developed and compared to the Hudleston equation.

Development of the Equation of State

It has been found that for most liquids, the viscosity varies with inverse of temperature[19].

$$\mu = A' \exp (B'/RT) \quad \dots \dots \dots \dots \dots (4)$$

The constant B' is a function of the intermolecular force potential. The Lennard-Jones 12–6 potential, which has been used widely for gases, as well for liquids[20], may be assumed to hold for roughly spherical molecules. The potential function is

$$\Phi(r) = 4\epsilon\,[(\sigma/r)^{12} - (\sigma/r)^6] \quad \dots \dots \dots \dots (5)$$

where σ is the collision diameter and ϵ is the minimum energy of interaction. If it is assumed that the molecular volume is proportional to the cube of the collision diameter, then it follows that

$$\Phi(v) \; \alpha \; [(v_0/v)^4 - (v_0/v)^2] \quad \dots \dots \dots \dots (6)$$

Since the constant B' in the Equation (4) is some function of $\Phi(v)$, one may assume that

$$B' = h\,[(v_0/v)^4 - (v_0/v)^2]^q \quad \dots \dots \dots \dots (7)$$

where h and q are arbitrary constants.

As a rule, the viscosity of liquids is an exponentially increasing function of pressure[21].

$$\mu = \exp sP \quad \dots \dots \dots \dots \dots \dots (8)$$