Contrary to Equation (11), where the pressure drop is a function of five variables, Equation (14) gives the pressure drop in terms of only four variables, i.e., feed rate, reactor diameter, temperature, and pressure, or

$$-\frac{\partial p}{\partial L} = \psi(W, D, t, p) \quad (15)$$

It seems to the author that using Equation (14) instead of Equation (11) should simplify the programming of the problem and also reduce the time needed for the machine computation.

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Adiabatic-temperature Change

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The following equation may be derived from thermodynamics and is applicable to all states of matter:

$$\left(\frac{\partial T}{\partial p}\right)_s = \frac{T\alpha}{C'_p\rho} = \frac{TV\alpha}{C'_p} \quad (1)$$

where

T = temperature, °K.
p = pressure, atm.
$\alpha = 1/V(\partial V/\partial T)_p$ = cubical coefficient of expansion, °K.$^{-1}$
ρ = density, g./ml.
V = specific volume, ml./g.
C'_p = specific heat, ml. (atm.)/(g.)(°K.) = 41.3 cal./,g.)(°K.) = $41.3C_p$
S = entropy

Equation (1) may be written as

$$d\ln T = \frac{\alpha\, dp}{41.3\, C_p\, \rho} \quad (2)$$

For a liquid α, C_p, and ρ will not change greatly with pressure; therefore, integration of Equation (2) gives

$$\Delta T = T_1\left[{}_e\left(\frac{\alpha_{avg}\,\Delta_p}{41.3\, C_{pA}\,\rho_A}\right)_{-1}\right] \quad (3)$$

where the subscripts 1 and *avg* represent initial and average values respectively, and the subscript A represents values at atmospheric pressure.

A simpler relation between ΔT and Δp may be obtained by use of the following approximate form of Equation (1):

$$\Delta T = \frac{T_1\,\alpha_{avg}\,\Delta_p}{C_{pA}\,\rho_A} \quad (4)$$

Thus it is possible to calculate the adiabatic-temperature change of a liquid produced from a given change in pressure by use of Equation (3) or (4). In most cases Equation (4) is sufficiently accurate.

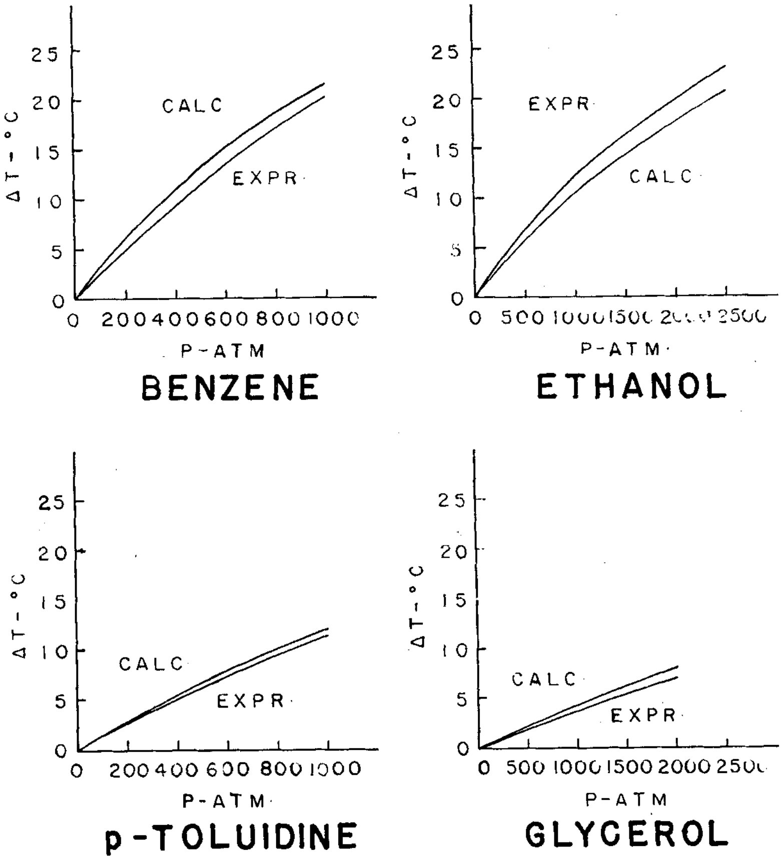

Fig. 1.

This method of calculation is simple as long as α values are available as a function of pressure. Thus for water the calculated values of ΔT are in agreement with those calculated from experimental values of $(\partial T/\partial p)_s$ obtained from Dorsey (*2*). α values as a function of pressure are not available for most substances; however, values of the compressibility coefficient β as a function of pressure are known for many substances. The following discussion shows a useful relation between the cubical coefficient of expansion and the compressibility coefficient.

For the variables pressure, temperature, and volume, it has been shown mathematically that

$$\left(\frac{\partial p}{\partial T}\right)_V\left(\frac{\partial V}{\partial p}\right)_T\left(\frac{\partial T}{\partial V}\right)_p = -1 \quad (5)$$

Equation (5) may be written as

$$\alpha = \beta\left(\frac{\partial p}{\partial T}\right)_V \quad (6)$$

where

$\beta = -1/V(\partial V/\partial p)_T$ = compressibility coefficient, atm.$^{-1}$

When Equation (6) is differentiated, temperature constant

$$\left(\frac{\partial\alpha}{\partial p}\right)_T = \beta\frac{\partial}{\partial p}\left[\left(\frac{\partial p}{\partial T}\right)_V\right]_T + \frac{\alpha}{\beta}\left(\frac{\partial\beta}{\partial p}\right)_T \qquad (7)$$

Further consideration of Equation (7) will simplify the relation between $(\partial\alpha/\partial p)_T$ and $(\partial\beta/\partial p)_T$. It will now be shown that the first term on the right side of Equation (7) is negligible compared with the second term.

Differentiation of the first term on the right side of Equation (7) may be accomplished by applying the equation of state for liquids proposed by Benson(*1*):

$$p = \frac{RT}{V - bV^{-\frac{1}{2}}} - \frac{a}{V^{5/3}\,T^{2/3}} \qquad (8)$$

where

$a = 0.9099RT_c^{5/3}V_c^{2/3}$

$b = 0.1567V_c^{2/3}$

Differentiation of Equation (8) gives

$$\left(\frac{\partial p}{\partial T}\right)_V = \frac{R}{V - bV^{-\frac{1}{2}}} + \frac{2a}{3\,(TV)^{5/3}} \qquad (9)$$

Differentiation of Equation (9) gives

$$\frac{\partial}{\partial p}\left[\left(\frac{\partial p}{\partial T}\right)_V\right]_T = -\beta\left[RV\frac{(1+0.5bV^{-3/2})}{(V-bV^{-\frac{1}{2}})^2} + 1.11\,a\,(TV)^{-5/3}\right] \qquad (10)$$

Substitution of Equation (10) into Equation (7) gives

$$\left(\frac{\partial\alpha}{\partial p}\right)_T = -\beta^2\left[RV\frac{(1+0.5\,bV^{-3/2})}{(V-b\,V^{-\frac{1}{2}})^2} + 1.11\,a\,(TV)^{-5/3}\right] + \frac{\alpha}{\beta}\left(\frac{\partial\beta}{\partial p}\right)_T \qquad (11)$$

It will now be shown that the first term on the right side of Equation (11) is negligible compared with the second term.

The following approximations will be made for a typical liquid:

$R = 1/$(ml.) (atm.) (g.) (°K.)

$V_c = 3$ ml./g.

$T_c = 600$°K.

$\alpha = 10^{-4}$ °K.$^{-1}$

$\beta = 10^{-6}$ atm.$^{-1}$

$(\partial\beta/\partial p)_T = -10^{-9}$ atm.$^{-2}$

$V = 1$ ml./g.

$T = 300$°K.

Therefore

$a \approx (600)^{5/3}\,(3)^{2/3} = 9 \times 10^4$

$b \approx 0.15\,(3)^{2/3} = 0.3$

Substitution of these approximate values into Equation (11) gives

$$\left(\frac{\partial\alpha}{\partial p}\right)_T \approx -(10^{-6})^2\left[\frac{(1+0.15)}{(1-0.30)_2} + \frac{(1.11\times9\times10^4)}{(300)^{5/3}}\right] - \left[\frac{10^{-4}}{10^{-6}}\times10^{-9}\right]$$

$$\approx -10^{-13} - 10^{-7} = 10^{-7}$$

Since numbers of the order of 10^{-13} are negligible compared with numbers of the order of 10^{-7}, Equation (11) may be simplified as follows:

$$\left(\frac{\partial\alpha}{\partial p}\right)_T = \frac{\alpha}{\beta}\left(\frac{\partial\beta}{\partial p}\right)_T \qquad (12)$$

Equation (12) shows a simpler relation between $(\partial\alpha/\partial p)_T$ and $(\partial\beta/\partial p)_T$ than Equation (7). Therefore α values may now be obtained for use in Equation (3) or (4).

A sample calculation will illustrate the entire procedure. It is desired to find the adiabatic temperature change produced when liquid benzene, initially at 90°C. and 1 atm., is subjected to a pressure of 1,000 atm.

$C_{pA} = 0.475$ cal./ (g.) (°K.)

The specific volume vs. temperature is

T, °C.	V, ml./g.
80	1.230
90	1.245
100	1.263

From these data

$$\alpha\,(90^\circ\text{ C., 1 atm.}) = \frac{(1.263-1.230)}{1.245\times20}$$

$$= 1.34\times10^{-3}\ ^\circ\text{K.}^{-1}$$

β values at 20°C. and at various pressures are obtainable from Perry(*3*). β (20°C., 1 atm.) is 8.9 × 10^{-5} atm.$^{-1}$ By graphical integration

$$\beta_{mean} = \frac{\int_{p=1}^{p=1{,}000}\beta\,dp}{1{,}000-1} = 6.2\times10^{-5}\text{ atm.}^{-1}$$

Therefore

$$\alpha_{mean}\text{ at }90^\circ\text{ C.} = \left(\frac{\beta_{mean}}{\beta}\right)_{\substack{20^\circ\text{ C.}\\(1\text{ atm.})}}\times$$

$$\alpha\,(90^\circ\text{ C., 1 atm.}) = \frac{6.2\times10^{-5}}{8.9\times10^{-5}}\times$$

$$1.34\times10^{-3} = 9.33\times10^{-4}\ ^\circ\text{K.}^{-1}$$

From Equation (4)

$$\Delta T = \frac{363\times9.33\times10^{-4}\times(1{,}000-1)\times1.245}{41.3\times0.475}$$

$$= 21.6\ ^\circ\text{C.}$$

Graphical integration of Equation (3) of the data of Pushin(*4*) gives

$$\Delta T = \int_{p=1}^{p=1{,}000}\left(\frac{\partial T}{\partial p}\right)_s dp = 20.5\ ^\circ\text{C.}$$

Close agreement is obtained although the α and β values were not at the same temperature.

Similar calculations were made for benzene, ethanol, *p*-toluidine, and glycerol; the results were compared with those calculated from the experimental data of Pushin (*4*). β values for glycerol at high pressures were not available. It was assumed that $(\partial\beta/\partial_p)_T$ values were proportional for glycerol and glycol. The assumption proved to be valid. The results are given in Table 1 and plotted in Figure 1. It is seen that close agreement between calculated and experimental values is obtained.

TABLE 1

T, °C.	*p*₂, atm. (*p*₁ is 1 atm.)	Δ*T*, °C. Calc.	Δ*T*, °C. Expr.
	Benzene		
90	500	13.1	11.5
90	750	17.9	16.1
90	1,000	21.6	20.5
	Ethanol		
30	500	6.28	6.70
30	1,000	10.6	12.0
30	1,500	14.5	16.5
30	2,500	21.0	23.7
	p-Toluidine		
80	500	6.59	6.21
80	750	9.50	8.97
80	1,000	12.2	11.7
	Glycerol		
25	500	2.28	2.14
25	1,000	4.18*	4.12
25	2,000	7.98*	7.70

*Based on extrapolated β values *for glycol.*

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