Thermodynamic equations of state of polymers and conversion processing

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Thermal processes, in addition to rheological processes, condition the behaviour of a plastic in processing equipment and the properties and structure of the products. The thermal state of a plastic is determined by the following factors: the pressure $p$, specific volume $ν$ and temperature $T$. An important consideration during processing is the dependence of the specific volume on temperature at atmospheric pressure (Figure 1). The relationship between the pressure, volume and temperature is called the thermodynamic equation of state, or more simply the equation of state. Under equilibrium conditions the equation of state of a single-phase system is given by the equation (1) (ref. 2):

$$F(T, p, ν) = 0$$ (1)

The simplest thermodynamic equation of state is the equation for a perfect gas in the form

$$p ν = nRT$$ (2)

where $R$ is the universal gas constant, $[R = 8314 \text{ J/(kmol.K)}]$, and $n$ is the number of moles of the substance.

This equation assumes that the gas molecules are point masses and hence have no specific volume, and do not interact with each other outside the moment of elastic impact. However, the molecules of real gases do have a specific volume, hence the effective accessible volume for movements of the molecules is less than the total volume of the system. The mutual attraction of the molecules causes a reduction in pressure, so that the molecules not interacting with each other move to the walls of the container in which the gas is located. In order to allow for the specific volume of molecules Van der Waals introduced a correction for the volume of the gas and reduced it to an “active” value, by subtracting the so-called co-volume $b$, equal to the sum of elementary spheres around all of the molecules. In the case of spherical molecules $b$ is equal to four times their volume. The correction for pressure, called the cohesion pressure is according to Van der Waals proportional both to the number of attracted and attracting molecules, and thus is proportional to the square of the gas density $ρ$ (ref. 3); this relationship is shown in equation (3):

$$Δp = ap^2 = \frac{a}{v^2}$$ (3)

where $a$ is a coefficient of proportionality independent of the parameters of state.

Because of this instead of equation (2) in its simplest form ($pν = RT$) we obtain:

$$\left( p + \frac{a}{v^2} \right) \left( v - b \right) = RT$$ (4)

This is an algebraic equation of the third degree with respect to $v$; after transformation it takes the form:

$$v^3 - \frac{bp + RT}{p} v^2 + \frac{a}{p} v - \frac{ab}{p} = 0$$ (5)

In the analysis of physical phenomena it is desirable to employ dimensionless magnitudes since in this way we can avoid the effect of the system of units adopted.

For the thermodynamic dimensionless parameters we can take the ratios of parameters to their values in the critical state (also referred to as the reducing parameters, indicated below by an asterisk). In this way we obtain reduced parameters (indicated by the symbol ~) (refs. 4 and 5):
\[ \tilde{p} = \frac{p}{p^*}; \quad \tilde{v} = \frac{v}{v^*}; \quad \tilde{T} = \frac{T}{T^*} \]  

(6)

On introducing the reduced parameters into the Van der Waals equation we obtain the reduced equation of state in dimensionless form containing only universal constants (without material constants):

\[ \left( \tilde{p} + \frac{3}{\tilde{v}^2} \right)(3\tilde{v} - 1) = 8\tilde{T} \]  

(7)

Equation (7) itself and any other equation of state in dimensionless form is a criterion of thermodynamic similarity; it is called an equation of corresponding states (ref. 3). Different substances are in corresponding states when their reduced parameters have the same numerical values. The critical points of each substance are corresponding states. From this it emerges that if any two fluids have two identical reduced parameters, then their remaining reduced parameter has the same value. The use of the principle of corresponding states in technical calculations is of great importance.

According to the above principle the relationship

\[ F(\tilde{p}, \tilde{v}, \tilde{T}) = 0 \]  

(8)

is the most universal equation of state for real gases and liquids. However, it is found from experimental results (ref. 2) that the state of substances being compared cannot always be described using only three reduced parameters. The theory has therefore been expanded by introducing a fourth parameter, the so-called determining criterion A. Thus:

\[ F(\tilde{p}, \tilde{v}, \tilde{T}, A) = 0 \]  

(9)

The value of \( A \), which characterises the individual properties of bodies, can be defined in various ways. Most commonly the criterion is the coefficient of compression of a substance at the critical point (ref. 2):

\[ Z^* = \frac{\tilde{p} \tilde{v}^*}{RT^*} \]  

(10)

At a later stage we shall show how the \( p\cdot v\cdot T \) relationships can be used to further discover the phenomena occurring during processing and to determine the connections between processing factors.

**USE OF THE THERMODYNAMIC EQUATION OF STATE IN THE CONVERSION OF POLYMERS**

The use of the equation of state in the conversion of polymers will be characterised using as an example one of the commonest processing methods, namely injection moulding.

The main factors in injection moulding are temperature, pressure and time. These may vary widely. Variable external pressure affects e.g. the density of the plastic and the shape and dimensions of the moulding. By using a predetermined program of change in external pressure many properties of the moulding are optimised (refs. 6–10).

Simultaneous recording of pressure and temperature at the same site in the moulding cavity makes it possible to plot their changes on a \( p\cdot v\cdot T \) graph (Figures 1 and 2). The theoretical curve of the process (Figure 1) marks out simple lines: the isotherm of pressure A, the isobar corresponding to the pressure phase B and the isochore of cooling C (refs. 11 and 12).

![Figure 1](image1.png)

*Figure 1. p-n-T graphs representing a theoretical injection moulding cycle for polystyrene; isobars corresponding to pressure (in MPa): a – 0.1, b – 20, c – 40, d – 60, f – 160 (for further explanations see test) (refs. 7 and 8)*

![Figure 2](image2.png)

*Figure 2. p-n-T graph of a real injection moulding cycle for polystyrene; for meaning of isobar symbols see Figure 1) (refs. 7 and 8)*
At point 0 on the isotherm A the plastic reaches the pressure sensor. Point 1 denotes complete volume filling of the moulding cavity under low pressure conditions. Rapid compression of the liquid plastic in the cavity is shown by lines 1 – 2. The plastic compressed to a pressure with a value defined by the isobar passing through point 2 and cooled remains fixed at the same isobar until it reaches a temperature at which solidification of the plastic at the narrowest point occurs (point 3). This is a very important point in the injection moulding process, which goes on spontaneously to the stage when the pressure of the plastic reaches a value defined by the isobar as 0.1 MPa (point 4). Further cooling of the plastic causes a decrease in its volume and hence the occurrence of processing shrinkage.

The actual curve of the injection moulding process (Figure 2) deviated from the theoretical assumptions. Obtaining a constant value for shrinkage \( \Delta \nu_s \) is difficult because of the variation in position of the point where the plastic solidifies at the narrow point and because of later uncontrolled changes in the specific volume (ref. 11).

The \( p-n-T \) relationship can be used to analyse the processes taking place in the moulding cavity during different types of injection moulding, such as injection-compression moulding (refs. 13 and 14). This method of moulding has come to be used for making high-quality mouldings (e.g. components of optical devices, CDs). The volume processing shrinkage of the moulding when cooled in a tightly closed mould is compensated by a reduction in the dimensions of the mould cavity during the compression phase. This process requires two-stage closing of the mould and an additional compression force. The injection and compression phase of the mould are shown in Figure 3.

The processing shrinkage of the mouldings accompanying compression can be determined using \( p-n-T \) graphs (Figure 4).

![Figure 3. Diagram of injection-compression moulding process: a – injection phase; b – compression phase (\( s_p \) – compression gap compensating for volume contraction) (ref. 9)](image)

Point 1 in Figure 4 corresponds to the filling of the cavity. During flow of the plastic a slight pressure is maintained which is just higher than atmospheric pressure (point 2) until the mould is spontaneously sealed (point 3). Then the volume of the mould cavity is reduced as a result of the pressure, which causes a rise in pressure in the mould (point 4). The conclusion of cooling of the moulding (point 5) occurs at the isobar corresponding to atmospheric pressure. A small amount of processing shrinkage \( \Delta \nu_s \) occurs on opening the mould and cooling the moulding to ambient temperature.

An important parameter is the time of delay in compression \( t_p \) determined from the \( p-n-T \) graph. The end of compression (point 3) should occur when the mould is sealed, otherwise the plastic may pass through into the runner or further, in the direction of the nozzle.

Usually the relations between pressure, specific volume and temperature of the polymers are determined experimentally. We can also use for this purpose mathematical equations (theoretical and experimental) which are an extension of the thermodynamic equation of state.

**THEORY OF THEORETICAL EQUATIONS**

The theoretical equations are based mainly on the equation known from statistical mechanics relating the pressure to specific volume and temperature (ref. 15):

\[
p = kT \left( \frac{\partial \ln Z}{\partial \nu} \right)_r
\]

where \( k \) is the Boltzmann constant and \( Z \) is a distribution function defined at the atomic level.

Direct determination of the distribution function is very difficult, requiring certain assumptions regarding the structure of the macromolecules and intermolecular forces.
THE SIMHA-SOMCYNCKY EQUATION

Simha and Somcynsky (ref. 16) modified the cellular model proposed by Lennard-Jones and Devonshire (ref. 17). They defined the magnitude \( y \) which is independent of temperature, taking the volume of free spaces ("holes") in the system as \((1 - y)\). Simha and Somcynsky's "hole" theory made it possible to define equations describing the reduced variables. The reducing variables \( \nu^*, T^* \) and \( p^* \) characterising each polymer were defined as follows (refs. 18–21):

\[
\nu^* = \frac{Nsv'}{M} \quad (12)
\]

\[
T^* = \frac{(z - 2)se^*}{ck} \quad (13)
\]

\[
p^* = \frac{(z - 2)e^*}{\nu'} \quad (14)
\]

where \( \nu' \) is the volume of a macromolecular segment, \( N \) is the number of macromolecules of the polymer, \( N_A \) is the Avogadro number, \( M \) is the molecular weight of a segment of the macromolecule, \( e^* \) is the minimum intersegmental potential energy, \( s \) is the number of segments in the macromolecule, \( z \) is the coordination number, \( k \) is Boltzmann's constant, and \( c \) is the number of external degrees of freedom of the macromolecule.

The equation of state for the reduced variables takes the form:

\[
\ln \frac{p}{T} = \frac{1}{\nu^*} \left[ 1 - 2 \frac{1}{\delta} y \left( \nu^* \right)^{\frac{1}{3}} \right]^{-1} + \left( \frac{2y}{T} \right) \left( \nu^* \right)^{-2} \ldots \left[ 1.01 \left( \nu^* \right)^{-2} - 1.2045 \right] \quad (15)
\]

According to the Simha-Somcynsky theory \( y \) defines the units of the quasi-crystalline network occupied by segments of the macromolecules; hence \((1 - y)\) is the region of "free" spaces between the segments and thus when \( s \to \infty \) equation (15) can be written in the form:

\[
\begin{align*}
\frac{\delta \nu}{T} &= \left[ 1 - 2 \frac{1}{\delta} y \left( \nu^* \right)^{-\frac{1}{3}} \right]^{-1} + \left( \frac{2y}{T} \right) \left( \nu^* \right)^{-2} \\
&= \left[ 1.01 \left( \nu^* \right)^{-2} - 1.2045 \right]
\end{align*}
\]

The experimental points of the relationship \( \log \nu_p \) vs. \( \log T \) are displaced parallel to the axis according to the method of superimposition, until satisfactory results are obtained. Using this method we can use Figure 5 to determine the reducing parameters: \( T^* = 7906K \) and \( \nu^* = 0.424 \times 10^{-3} \) m\(^3\)/kg. The reducing parameter of pressure \( p^* \) was determined using the Simha-Somcynsky theory for each value of reduced pressure.

ISING'S EQUATION

Most equations of state of polymers use a cellular model that requires separation of the internal and external degrees of freedom. The external degrees of freedom attributed to the chain segment of the polymer are lower than in the case of a low-molecular compound. Since Ising's model does not involve a cellular model, there is no need to separate the internal and external degrees of freedom (ref. 22).

Ising's equation relating to the reduced parameters of polymers in the liquid state takes the form:

\[
\bar{p}^2 + \bar{p} + T \left[ \ln(1 - \bar{p}) + \left( 1 - \frac{1}{r} \right) \bar{p} \right] = 0 \quad (17)
\]
where \( r \) is the number of units in the crystalline network occupied by the \( r \)th mer.

The reducing parameters can be related to the molecular weight by the equation:

\[
\frac{RT}{\tilde{\rho}} = \frac{M}{r} \tag{18}
\]

Since the parameter \( r \) appears in the reduced equation of state (17), the basic requirement of self-similar states is not fulfilled. However, for a polymer in the liquid state the value \( r \rightarrow \infty \), and equation (17) reduces to the form:

\[
\tilde{\rho}^2 + \tilde{\rho} + T\left[\ln(1-\tilde{\rho}) + \rho\right] = 0 \tag{19}
\]

Thus polymers in the liquid state with a correspondingly high molecular weight must fulfil the basic requirement of corresponding states. This was confirmed experimentally by I.C. Sanchez and R.H. Lacombe (ref. 22).

In the graph (Figure 6) it can be seen that in the case of the ten polymers studied the principle of corresponding states is fulfilled over a wide range of temperature and pressure. The lines are theoretical isobars calculated from equation (19) on the basis of the reduced pressure and experimental density measurements correspondingly reduced by the reducing parameters. The maximum error in the density calculations is 1.2%, and the average is 0.2%. Experimental errors in the determination of the density are in the range 0.01 – 0.05%.

Ising’s equation approximates to the experimental data much more closely than the complex equations based on a cellular model. In addition, it can describe the properties of fluids with a low molecular weight.

PASTINE AND WARFIELD’S EQUATION

A three-parameter equation of state expressed with the use of reduced variables was proposed by D.J. Pastine and R.W. Warfield (ref. 23). This was designed for polymers in the liquid state on the basis of the theory of a vibrating chain in a rigid cylinder. It can be represented by the general relationship:

\[
p(v, T) = p_0(v) + A(v) T^{3/2} \tag{20}
\]

where \( A \) is a volume function, \( p_0 \) is the internal pressure, dependent on the internal energy of the polymer.

Using the Simha-Somcynsky relationship under conditions of atmospheric pressure this equation of state can be rewritten in the form:

\[
\ln v(0, T) = \ln v(0, 0) + \left( \frac{T}{T_0} \right)^{3/2} \tag{21}
\]

In equation (21) the values \( v(0,0) \) later referred to as \( v_0 \) and \( T_0 \) represent the coefficients of this equation. Assuming that

\[
A(v) = \frac{f(v)}{T_0^{3/2}} \tag{22}
\]

and using equations (20) and (21) we obtain the relationship:

\[
\frac{p(v, T)}{f(v)} = \left( \frac{T}{T_0} \right)^{3/2} - \ln \frac{v}{v_0} \tag{23}
\]

in which \( f(v) \) has the pressure dimension.

Pastine and Warfield studied polymers in the pressure range 0 – 200 MPa, at a temperature exceeding (up to 1000°C) the temperature of the corresponding phase change of the given polymer.

From experimental data they determined \( f(v) \) in the form:

\[
f(v) = B \left( \frac{v}{v_0} \right)^5 \tag{24}
\]

where \( B \) is a parameter showing the pressure magnitude.

Figure 6. Graphical representation of the principle of corresponding states for 10 polymers. The lines are theoretical isobars calculated from equation (19) for various values of \( \tilde{\rho} \): 1 – 0.25, 2 – 0.10, 3 – 0 (ref. 18).
The above-mentioned authors defined $B^*$, $\nu^*$ and $T^*$ as reducing parameters, determining them by extrapolation to a temperature of 0°C and a pressure of zero. Substituting $f(\nu)$ into equation of state (23) we obtain:

$$\left(\frac{p}{B^*}\right)\left(\frac{\nu}{\nu^*}\right)^5 = \left(\frac{T}{T^*}\right)^{\frac{3}{2}} - \ln\left(\frac{\nu}{\nu^*}\right)$$

(25)

Introducing the reduced variables $\tilde{p} = p/B^*$, $\tilde{\nu} = \nu/\nu^*$, $\tilde{T} = T/T^*$ simplifies equation (25) to the form:

$$\tilde{p}\tilde{\nu}^5 = \tilde{T}^{\frac{3}{2}} - \ln\tilde{\nu}$$

(26)

which fulfils the principle of corresponding states.

In order to compare the values obtained from equation (26) with the experimental data (ref. 23), first of all the specific volume $\nu_0$ and temperature $T_0$ by substituting into equation (25) $p = 0$. Then the parameter $B_0$ was determined, plotting the relationship $p = f(\nu^{3/2})$ for a constant specific volume. The reducing parameters were established by comparing the values of the specific volumes found experimentally with the values calculated from equation (26). The results for PE-HD in the form of graphs of the theoretical and experimental isotherms are shown in Figure 7. Corresponding results for the isobars are shown in Figure 8. In both these cases the accuracy of comparison between the experimental and theoretical data is about 0.001 cm³/g.

**Figure 7.** HDPE isotherms corresponding to temperature:

- a - 142.1°C,
- b - 152.9°C,
- c - 165.4°C,
- d - 171.1°C,
- e - 180.9°C,
- f - 189.6°C,
- g - 199.7°C (the circles denote experimental data, and the continuous line are theoretical, determined using equation (26) (ref. 19)

**Figure 8.** HDPE isobars corresponding to pressure (in MPa):

- a - 0.1,
- b - 40,
- c - 80,
- d - 120,
- e - 160,
- f - 200 (the circles indicate experimental data; the lines are theoretical, determined using equation (26) (ref. 19)

**WHITAKER AND GRISKEY’S EQUATION**

This equation was evolved on the basis of the theory of corresponding states (ref. 24). Considering the coefficient of compression:

$$Z = \frac{p\nu}{RT}$$

(27)

it was observed that the relationship between $Z$ and the reduced temperature ($T/T_g$) shows a set of corresponding curves (displaced parallel to themselves) determined for different polymers under atmospheric pressure (Figure 9).

**Figure 9.** Graph of compressibility coefficient ($Z$) vs. reduced temperature ($T/T_g$) at atmospheric pressure for 11 different polymers (ref. 20)
From the data in Figure 9 we obtained the following general relationship between the temperature \((T \text{ in K})\), pressure \((p \text{ in Pa})\) and specific volume \((V \text{ in m}^3)\):

\[
V = \left( \frac{0.01205}{\rho_0^{0.9421}} \right)^{-1} \left( \frac{T}{T_g} \right)^{m+1} R
\]

(28)

where \(\rho_0\) is the density at 25°C and pressure 0.1 MPa, \(T_g\) is the glass transition temperature, \(R\) is the universal gas constant in J/(kg.K), and \(m\) and \(n\) are equation parameters.

The mean error of the data calculated from equation (28) and the experimental data is 2%. It is only in the melting region of the polymers that equation (28) does not correspond to the experimental data – there is a discontinuity in the case of all of the studied polymers having a clearly defined melting range.

Finally, on differentiating the Whitaker-Griskey equation and taking definite values of the constants and exponents, we get the relationship:

\[
V = K \left( \frac{T}{T_g} \right)^x \rho^y
\]

(29)

where \(x\) and \(y\) are exponents representing pressure functions, \(K\) is a function of density at 25°C and at pressure of 0.1 MPa (refs. 24).

**REVIEW OF EXPERIMENTAL EQUATIONS**

**The Spencer-Gilmore equation**

A thermodynamic equation of state of polymers arising from the Van der Waals equation was proposed by Spencer and Gilmore (refs. 25–30) in the form:

\[
(p + \pi) \left( \nu_M - \omega_M \right) = RT
\]

(30)

where \(p\) is the external absolute pressure, \(\pi\) is the internal pressure (cohesion pressure) taken as being independent of the volume, \(\nu_M\) is the specific volume of a single kilomole of polymer under pressure \(p\) and at temperature \(T\), \(\omega_M\) is a coefficient representing the constant volume of the polymer macromolecules at a temperature of absolute zero.

If we consider the relation between the specific volume for one kilomole, or

\[
\nu_M = M_0 \nu
\]

(31)

where \(M_0\) is the molar mass in g/mol, then equation (30) takes the form:

\[
(p + \pi) \left( \nu - \omega \right) = \frac{RT}{M_0}
\]

(32)

in which \(\omega\) is a constant value for one kilogram of the polymer (m³/kg).

Substituting in equation (32) the expression

\[
\frac{R}{M_0} = R'
\]

(33)

where \(R'\) is the individual gas constant expressed in J/(kg.K), we obtain a thermodynamic equation of state of polymers in the following form:

\[
(p + \pi) \left( \nu - \omega \right) = R'T
\]

(34)

Equations (32) and (34) are extremely important as regards measurement possibilities. The Spencer-Gilmore model is of course one of the oldest models, but it still continues to be used in studies of polymers (refs. 27–32).

**Tait’s equation**

Tait’s equation presents the change in specific volume along the isotherm as a function of two variable parameters \(B(T)\) and \(C(T)\) (refs. 19 and 20):

\[
\nu(p, T) = \nu(0, T) \left[ 1 - C \ln \left( 1 + \frac{p}{B(T)} \right) \right]
\]

(35)

where \(\nu(p, T)\) is the specific volume at pressure \(p\) and temperature \(T\), \(C\) is a universal constant equal to 0.0984, and \(B(T)\) is a parameter defined by the relation

\[
B(T) = B_0 \exp(-B_1 T)
\]

(36)

where \(B_0\) and \(B_1\) are characteristic constants of the given polymer.

The volume under atmospheric pressure denoted by \(\nu(0, T)\) and determined by extrapolation can be represented as a polynomial at a temperature \(T < T_m\)

\[
\nu(0, T) = A_0 + A_1 T + A_2 T^2 + A_3 T^3 + \ldots
\]

(37)

or as an exponent, where \(T > T_m\)

\[
\nu(0, T) = \nu_0 \exp(\alpha_0 T)
\]

(38)

where \(\nu_0\) is the specific volume at atmospheric pressure, \(\alpha_0\) is the coefficient of volume expansion at atmospheric pressure.

The authors of ref. 19 have determined the parameter \(B\) of several polymers in the liquid and solid states. Table 1 shows average values of this parameter in a temperature corresponding to the liquid state of the selected polymers.
The maximum deviations between the theoretical calculations in Table 1 and the experimental results for PS, PMMA and PVC are 1.96%, 0.05% and 0.8% respectively.

CONCLUSION

There are many mathematical forms of the thermodynamic equation of state of polymers. The reason for this variety is the various approaches to the problem and its solution. Also, an equation of this kind must correspond to the criteria listed below, which are difficult to meet at the same time (ref. 24):

- it must be valid over a wide range of pressure and temperatures;
- its mathematical form must be generalised so that it can be used for many polymers differing in their properties and states of aggregation;
- it must be relatively simple and easy to use;
- it must also enable the calculation of thermodynamic relationships of the polymer when only physical properties that are relatively easy to measure are known, such as the glass transition temperature or melting point at atmospheric pressure and density at 20°C and under atmospheric pressure.

Equations fulfilling all these criteria usually relate to particular groups of polymers either in the solid or liquid state, but it is rarely possible to describe the behaviour of a particular polymer in both these states. For this reason the existing equations are continually modified and improved in order to obtain the most universal models.

In the field of processing use has been made of experimental equations, mainly Gilmore and Spencer’s equation and Tait’s equation, in which the constants have been employed for he conditions of a particular conversion process. The relations between these conditions are highly complex, and for this reason the use of the equations continues to be restricted, and the literature covering these problems is inadequate.

In conversion processes it is also important to know the derivatives of the specific volume as a function of pressure and temperature. Using the first derivative we can determine the coefficients of volume expansion and the coefficients of compressibility which play an important part in the designing of dimensions of injection mouldings. The experimental equations of state on differentiation determine the values of these coefficients.

Examination of the literature shows among other things the continuously poor knowledge of the relationship between equations of state and the fundamentals of high-molecular plastics processing. In connection with this results will be presented in another article of our own investigations into the effect of cooling of injection mouldings on the thermodynamic equation of state.

REFERENCES

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(Received 19/3/2001)