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Thermodynamic Potential Functions for Elastomers

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ABSTRACT: The thermodynamic description of the large principal deformations of elastomers requires four thermodynamic energy functions and their associated free energies. The significance of, and relationship between, these potential functions is discussed and their interrelations are derived. The internal energy contribution to the retractive force or the extension in an elastomer is used as an example of the application of the concepts introduced.

The thermodynamic (more precisely thermostatic) description of the deformation of a solid system is more complex than that of a fluid (gas or liquid) system. In the latter, volume and pressure are the only mechanical parameters to be taken into account. In the former, the set of mechanical parameters must be enlarged, in the general case, to the 6 + 6 = 12 components of the strain and stress tensors.[1] This paper discusses the thermodynamic potential functions which are useful in describing the thermodynamics of large principal deformations of elastomers and the general relations between their differentials and those of various sets of independent variables. Because an elastomer may be regarded as a homogeneous isotropic solid, its deformation can be described more simply than that of a general solid. The potential functions for the thermodynamics of elastomers introduced here are defined in a way which makes them consistent with the definitions of the potential functions in the thermodynamics of fluids. The following discussion aims to provide an exhaustive treatment of the formalism of the thermodynamics of elastomers.

Potential Functions

The first law of thermodynamics gives the change in the internal energy U as

$$\mathrm{d}U = \mathrm{d}Q - \mathrm{d}W \tag{1}$$

where $\mathrm{d}Q$ is the element of heat absorbed, and $\mathrm{d}W$ is the element of work done, by the system on its surroundings. If the process is conducted reversibly

$$\mathrm{d}Q = T\mathrm{d}S \tag{2}$$

where T is the (absolute) temperature and S is the entropy. Flory[2] has shown that the element of elastic work, $\mathrm{d}W$, done by a homogeneous isotropic system in a large principal deformation is given by

$$\mathrm{d}W = -V\sum_{i=1}^{3} t_i \mathrm{d}\ln\lambda_i \tag{3}$$

where V is the deformed volume, the t_i are the principal true stresses, and the λ_i are the principal extension ratios defined as the ratios of the stretched lengths, L_i, to the unstretched lengths, L_{i0}.

Thus, the change in the internal energy is given by

$$\mathrm{d}U = T\mathrm{d}S + V\sum_i t_i \mathrm{d}\ln\lambda_i \tag{4}$$

and the change in the associated (Helmholtz) free energy, defined by

$$A = U - TS \tag{5}$$

becomes

$$\mathrm{d}A = -S\mathrm{d}T + V\sum_i t_i \mathrm{d}\ln\lambda_i \tag{6}$$

The last terms in eq 4 and 6 contain both the work of extension and the work of expansion. The two must be separated because changes in volume may be induced both by the application of forces or extensions and by changes in temperature. We consider that the principal true stresses are

$$t_i = (L_i f_i / V) - P \tag{7}$$

where P is the external pressure and the f_i are the tractions along the three principal directions. Combining eq 4 and 7, recognizing that

$$\sum_i \mathrm{d} \ln \lambda_i = \mathrm{d} \ln V \tag{8}$$

and using the summation convention for repeated indices from this point on, yields

$$\mathrm{d}U = T\mathrm{d}S - P\mathrm{d}V + f_i\mathrm{d}L_i \tag{9}$$

Similarly, from eq 6 and 7

$$\mathrm{d}A = -S\mathrm{d}T - P\mathrm{d}V + f_i\mathrm{d}L_i \tag{10}$$

Equation 9 describes the elemental change in the internal energy, $\mathrm{d}U$, in terms of the extensive parameters S, V, and L_i. By contrast eq 10 has T, V, and L_i as the independent variables. The free energy (here the Helmholtz free energy, or work content), A, therefore, is that partial Legendre transform of U which replaces S by T as the independent variable.

The enthalpy

$$H = U + PV \tag{11}$$

is defined as that partial Legendre transform of U which replaces V by P as an independent variable. Taking differentials and using eq 9 gives

$$\mathrm{d}H = T\mathrm{d}S + V\mathrm{d}P + f_i\mathrm{d}L_i \tag{12}$$

The free energy associated with the enthalpy (the Legendre transform of H which replaces S by T) is the free enthalpy (or Gibbs or Lewis free energy) defined as

$$G = H - TS = U + PV - TS \tag{13}$$

Taking differentials and using eq 12 yields

$$\mathrm{d}G = -S\mathrm{d}T + V\mathrm{d}P + f_i\mathrm{d}L_i \tag{14}$$

The potential functions introduced so far differ from those in use in the thermodynamics of fluids in the additional f_iL_i terms. It is because of the presence of these terms that A and G measure the work available in a reversible process from an elastomer at constant temperature (*cf.* eq 33) and at constant temperature and pressure (*cf.* eq 34), respectively. Evidently, the work available at constant *forces* may also be of interest. Thus, we are led to consider those partial Legendre transforms in which L_i is replaced by f_i. As the first we introduce that thermodynamic potential which arises from the internal energy and the products of the forces and lengths. Calling this potential D, we have

$$D = U - f_iL_i \tag{15}$$

which furnishes

$$\mathrm{d}D = T\mathrm{d}S - P\mathrm{d}V - L_i\mathrm{d}f_i \tag{16}$$

Equation 16 describes the elemental change in the thermodynamic potential D in terms of the independent variables S, V, and f_i. The corresponding free energy, in which S is replaced by T as the independent variable, is

$$B = D - TS = U - f_iL_i - TS \tag{17}$$

from which we obtain

$$\mathrm{d}B = -S\mathrm{d}T - P\mathrm{d}V - L_i\mathrm{d}f_i \tag{18}$$

If we assume the volume change to be negligible, we may set $\mathrm{d}V = 0$, and, for the case of simple tension, D and B reduce to the "elastomer enthalpy," K, and its associated free energy, J, introduced by Wall.[3] He derived these starting from the assumption that (in our notation) in simple tension

$$\mathrm{d}W = -f\mathrm{d}L \tag{19}$$

In eq 19, f and L are respectively the uniaxial force and extension. Although the extension of an elastomer may not be accompanied by a noticeable change in volume, such a change may occur as a function of temperature. In addition, at large pressures the incompressibility assumption is no longer tenable. Thus, Wall's potential functions are restricted to purely isochoric deformations. We prefer to disqualify the assumption of incompressibility from the definition of the potential functions.

With eq 11 and 15 we have introduced potential functions which arise from the internal energy and either the PV or the f_iL_i term. The remaining potential to be introduced is

$$M + H - f_iL_i = U + PV - f_iL_i \tag{20}$$

which adds the internal energy to the PV as well as the f_iL_i term. We have

$$\mathrm{d}M = T\mathrm{d}S + V\mathrm{d}P - L_i\mathrm{d}f_i \tag{21}$$

The associated free energy is

$$Z = M - TS = U + PV - f_iL_i - TS \tag{22}$$

from which we obtain

$$\mathrm{d}Z = -S\mathrm{d}T + V\mathrm{d}P - L_i\mathrm{d}f_i \tag{23}$$

We call M the *elasthalpy* and Z the *free elasthalpy*. B and Z measure the work available in a reversible process from an elastomer at constant temperature and forces (*cf.* eq 35) and at constant temperature, pressure, and forces (*cf.* eq 36), respectively. The functions M and Z were briefly discussed earlier by Reiss.[4]

The choice of the appropriate thermodynamic potential with which the system is to be described depends on the experiment or the theoretical point one wishes to discuss. It should be noted, however, that the potentials U, A; H, G; D, B; and M, Z are the only transforms that need to be considered for the thermodynamic description of the principal deformation of an elastomer.

Up to now we have considered a closed system. Extension to an open system is straightforward. Consideration of an open single component system further elucidates the significance of the free energies associated with the deformation of a homogeneous isotropic solid. For an open single component system the Euler relation for an elastomer is

$$U = TS - PV + f_iL_i + \mu N \tag{24}$$

where μ is the chemical potential and N is the number of moles of the component. Inserting the Euler relation into eq 5, 13b, 17b, and 22b gives

$$A = -PV + f_iL_i + \mu N \tag{25}$$

$$G = f_iL_i + \mu N \tag{26}$$

$$B = -PV + \mu N \tag{27}$$

and

$$Z = \mu N \tag{28}$$

in turn. Thus, while the chemical potential is equal to the molar enthalpy in a fluid system, it is equal to the molar elasthalpy in a homogeneous isotropic solid.

The Gibbs–Duhem relation for an elastomer in a closed system becomes

$$S\mathrm{d}T - V\mathrm{d}P + L_i\mathrm{d}f_i = 0 \tag{29}$$

and for an open single component system we have

$$\mathrm{d}\mu = -s\mathrm{d}T + v\mathrm{d}P - (L_i/N)\mathrm{d}f_i \tag{30}$$

where s and v are the molar entropy and molar volume, respectively.

Since experimental studies on the thermodynamics of elastomers are usually carried out in simple tension, it is convenient to specialize at this point. Thus, for simplicity, we shall henceforth consider simple tension only, for which $i = 1$. Also, we write f, L, and λ for f_1, L_1, and λ_1. Thus the expressions for the various thermodynamic potentials in simple tension are obtained by deleting the subscript i in the corresponding relations given above.

General Relations

Inspection of the thermodynamic potentials shows that S, V, and L are natural variables for U; T, V, and L are natural variables for A; etc. The differentials for these eight potential functions for a closed system may, however, be expressed in terms of variables other than the natural ones and are often needed in such terms. Only the four sets (T, V, L), (T, V, f), (T, P, L), and (T, P, f) need to be considered for each of the eight potential functions since the entropy, S, is not a practical variable. Of these four sets, the first two are required to correlate observations with theoretical considerations, whereas the last two are convenient from the experimental standpoint. The relations contain certain partial derivatives which are defined below. These are

(a) the specific heat at constant x and y

$$c_{x,y} \equiv T\frac{\partial S}{\partial T}\bigg|_{x,y} \tag{31}$$

where x represents either V or P and y represents either f or L

(b) the volumetric expansion coefficient at constant P and y

$$\beta_{P,y} \equiv \frac{1}{V}\frac{\partial V}{\partial T}\bigg|_{P,y} \tag{32}$$

(c) the linear expansion coefficient at constant x and f

$$\alpha_{x,f} \equiv \frac{1}{L}\frac{\partial L}{\partial T}\bigg|_{x,f} \tag{33}$$

(d) the isothermal compressibility at constant y

$$\kappa_{T,y} \equiv -\frac{1}{V}\frac{\partial V}{\partial P}\bigg|_{T,y} \tag{34}$$

(e) the linear isothermal compressibility at constant f

$$\chi_{T,f} \equiv -\frac{1}{L}\frac{\partial L}{\partial P}\bigg|_{T,f} \tag{35}$$

(f) the pressure–temperature coefficient at constant V and y

$$\gamma_{V,y} \equiv \frac{\partial P}{\partial T}\bigg|_{V,y} = \beta_{P,y}/\kappa_{T,y} \tag{36}$$

(g) the force–temperature coefficient at constant x and L

$$\psi_{x,L} \equiv \frac{\partial f}{\partial T}\bigg|_{x,L} \tag{37}$$

(h) the force–pressure coefficient at constant T and L

$$\phi_{T,L} \equiv \frac{\partial f}{\partial P}\bigg|_{T,L} \tag{38}$$

(i) the force–length coefficient at constant T and x

$$\mu_{T,x} \equiv \frac{\partial f}{\partial L}\bigg|_{T,x} \tag{39}$$

Using the definitions given above, general relations for the change in the various thermodynamic potentials can be derived easily. The results for one set of independent variables (T, V, L) are listed in Appendix I. From these the results for the remaining three sets are readily obtained through the use of eq A-1.9 through A-1.16. The Maxwell relations are tabulated in Appendix II for convenience.

Application

We now consider the application of the equations developed earlier to the problem of the decomposition of the force or length into entropic and energetic components.

The elastic force f is the change in the (Helmholtz) free energy with a change in length at constant temperature and volume and is given by

$$f = \frac{\partial A}{\partial L}\bigg|_{T,V} = \frac{\partial U}{\partial L}\bigg|_{T,V} - T\frac{\partial S}{\partial L}\bigg|_{T,V} \tag{40}$$

The total force f is thus resolved into energetic and entropic components defined by

$$f_u \equiv \frac{\partial U}{\partial L}\bigg|_{T,V} \tag{41}$$

and

$$f_s \equiv -T\frac{\partial S}{\partial L}\bigg|_{T,V} = T\psi_{V,L} \tag{42}$$

To determine these components it is necessary to measure the changes in force with temperature at constant volume and length. Achievement of the constant volume condition requires applying hydrostatic pressure during the force–temperature measurements. This experiment is difficult in practice. To obtain a usable expression for f_s and f_u we make use of the equations collected in Appendix I. Thus

$$f_s = T\psi_{P,L} + T\gamma_{V,L}\phi_{T,L} \tag{43}$$

and

$$f_u = f - T\psi_{P,L} - T\gamma_{V,L}\phi_{T,L} \tag{44}$$

Although traditionally the thermodynamic treatment of the deformation of an elastomer has centered on the force it can equally be discussed in terms of length. In such an experiment a constant force is applied to the test piece and the changes in the equilibrium length are studied at various conditions of temperature and pressure. This application provides an instance of the use of the concept of the elasthalpy and free elasthalpy which we have introduced.

From eq 23, the stretched length in simple tension at constant temperature and pressure is obtained as

$$L = -\frac{\partial Z}{\partial f}\bigg|_{T,P} \tag{45}$$

i.e., as the negative partial derivative of the free elasthalpy with respect to force. From eq 22a then

$$L = -\frac{\partial M}{\partial f}\bigg|_{T,P} + T\frac{\partial S}{\partial f}\bigg|_{T,P} \tag{46}$$

The stretched length can, therefore, be resolved into elasthalpic and entropic components

$$L_M = -\frac{\partial M}{\partial f}\bigg|_{T,P} \tag{47}$$

and

$$L_S = T\frac{\partial S}{\partial f}\bigg|_{T,P} = T\frac{\partial L}{\partial T}\bigg|_{P,f} = LT\alpha_{P,f} \tag{48}$$

Thus, the elasthalpic component of the stretched length becomes

$$L_M = L(1 - T\alpha_{P,f}) \tag{49}$$

Similar decompositions can be made from eq 14 and 18. The first gives

$$f = \frac{\partial G}{\partial L}\bigg|_{T,P} = \frac{\partial H}{\partial L}\bigg|_{T,P} - T\frac{\partial S}{\partial L}\bigg|_{T,P} \tag{50}$$

Using Appendix II, the entropic component of the restoring force becomes

$$f_S = T\psi_{P,L} \tag{51}$$

and the enthalpic component follows as

$$f_H = f - T\psi_{P,L} \tag{52}$$

From eq 18 we find

$$L = -\frac{\partial B}{\partial f}\bigg|_{T,V} = -\frac{\partial D}{\partial f}\bigg|_{T,V} + T\frac{\partial S}{\partial f}\bigg|_{T,V} \tag{53}$$

The two components of the stretched length are thus obtained as

$$L_s = T\frac{\partial S}{\partial f}\bigg|_{T,V} = LT(\alpha_{P,f} - \gamma_{V,f}\chi_{T,f}) \tag{54}$$

and

$$L_d = -\frac{\partial D}{\partial f}\bigg|_{T,V} = L(1 + T\gamma_{V,f}\chi_{T,f} - T\alpha_{P,f}) \tag{55}$$

It should be noted that

$$f_S - f_s = -T\gamma_{V,L}\phi_{T,L} \tag{56}$$

and

$$L_S - L_s = LT\gamma_{V,f}\chi_{T,f} \tag{57}$$

We have derived these relations by differentiating A and G with respect to L, and B and Z with respect to f. It is, of course, also possible to derive relations by differentiating A and G with respect to f, and B and Z with respect to L. Thus, *e.g.*, the portion of the stretched length contributed by internal energy is similarly obtained as

$$L_U = \frac{\partial U}{\partial f}\bigg|_{T,P} = TL\alpha_{P,f} + f\mu_{T,P}^{-1} - PL\chi_{T,f} \tag{58}$$

The expressions involving changes with length and changes with force are interchangeable and, in principle, would yield exactly the same molecular information. However, the choice of one set of independent variables over the other may be dictated by experimental convenience. With the recent development of new techniques for measuring dimensional changes[5] the constant force experiment may prove to be of importance. Shen and coworkers[6,7] have made a partial study of thermoelastic behavior at constant force.

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Appendix I

This appendix lists the expressions for the differentials of the eight elastomeric potentials in terms of the variables T, V, and L, choosing the coefficients which are most convenient from the experimental standpoint. Specifically, the coefficients of the differentials dT, dV, dP, dL, or df in the following equations are obtainable from experiments at constant temperature, pressure, length, or force.

$$\begin{aligned} dU = {} & (c_{P,L} - TV\beta_{P,L}\gamma_{V,L})dT + (T\gamma_{V,L} - \\ & P)dV + (f - T\psi_{P,L} - T\gamma_{V,L}\phi_{T,L})dL \end{aligned} \tag{A-1.1}$$

$$dA = -SdT - PdV + fdL \tag{A-1.2}$$

$$\begin{aligned} dM = {} & [c_{P,L} + (1 - T\beta_{P,L})V\gamma_{V,L} - L\psi_{P,L} - \\ & L\gamma_{V,L}\phi_{T,L}]dT + (T\gamma_{V,L} - \kappa_{T,L}^{-1} + \\ & L\phi_{T,L}/V\kappa_{T,L})dV - [T\psi_{P,L} + L\mu_{T,P} + (T\gamma_{V,L} - \\ & \kappa_{T,L}^{-1} + L\phi_{T,L}/V\kappa_{T,L})\phi_{T,L}]dL \end{aligned} \tag{A-1.3}$$

$$\begin{aligned} dZ = {} & (V\gamma_{V,L} - S - L\psi_{P,L} - L\gamma_{V,L}\phi_{T,L})dT - \\ & \kappa_{T,L}^{-1}(1 - L\phi_{T,L}/V)dV + [\phi_{T,L}(1 - \\ & L\phi_{T,L}/V)/\kappa_{T,L} - L\mu_{T,P}]dL \end{aligned} \tag{A-1.4}$$

$$\begin{aligned} dH = {} & (c_{P,L} - TV\beta_{P,L}\gamma_{V,L} + V\gamma_{V,L})dT + \\ & (T\gamma_{V,L} - \kappa_{T,L}^{-1})dV + [f - T\psi_{P,L} - \\ & \phi_{T,L}(T\gamma_{V,L} - \kappa_{T,L}^{-1})]dL \end{aligned} \tag{A-1.5}$$

$$\begin{aligned} dG = {} & (-S + V\gamma_{V,L})dT - \kappa_{T,L}^{-1}dV + \\ & (f + \phi_{T,L}/\kappa_{T,L})dL \end{aligned} \tag{A-1.6}$$

$$\begin{aligned} dD = {} & [c_{P,L} - \gamma_{V,L}(TV\beta_{P,L} + L\phi_{T,L}) - \\ & L\psi_{P,L}]dT + (T\gamma_{V,L} - P + L\phi_{T,L}/V\kappa_{T,L})dV - \\ & [T\psi_{P,L} + L\mu_{T,P} + \phi_{T,L}(T\gamma_{V,L} + \\ & L\phi_{T,L}/V\kappa_{T,L})dL \end{aligned} \tag{A-1.7}$$

$$\begin{aligned} dB = {} & -(S + L\psi_{P,L} + L\phi_{T,L}\gamma_{V,L})dT + \\ & (L\phi_{T,L}/V\kappa_{T,L} - P)dV - (L\mu_{T,P} + \\ & L\phi_{T,L}^{2}/V\kappa_{T,L})dL \end{aligned} \tag{A-1.8}$$

The expressions for the remaining sets of independent variables are easily derived by using the relations for the set T, V, and L together with the following relations

$$\mathrm{d}L = L(\alpha_{P,f} - \gamma_{V,f}\chi_{T,f})\mathrm{d}T + (L\chi_{T,f}/V\kappa_{T,f})\mathrm{d}V + (\mu_{T,P}{}^{-1} - L^2\chi_{T,f}{}^2/V\kappa_{T,f})\mathrm{d}f \quad \text{(A-1.9)}$$

$$\mathrm{d}V = V\beta_{P,f}\mathrm{d}T - V\kappa_{T,f}\mathrm{d}P + L\chi_{T,f}\mathrm{d}f \quad \text{(A-1.10)}$$

$$\mathrm{d}V = V\beta_{P,L}\mathrm{d}T - V\kappa_{T,L}\mathrm{d}P + \phi_{T,L}\mathrm{d}L \quad \text{(A-1.11)}$$

$$c_{V,L} = c_{P,L} - TV\beta_{P,L}\gamma_{V,L} \quad \text{(A-1.12)}$$

$$c_{V,f} = c_{P,f} - TV\beta_{P,f}\gamma_{V,f} \quad \text{(A-1.13)}$$

$$c_{P,L} = c_{P,f} + TL\alpha_{P,f}\psi_{P,L} \quad \text{(A-1.14)}$$

$$\beta_{P,L} = \beta_{P,f} + L\chi_{T,f}\psi_{P,f}/V \quad \text{(A-1.15)}$$

$$\kappa_{T,L} = \kappa_{T,f} - L\chi_{T,f}\phi_{T,L}/V \quad \text{(A-1.16)}$$

For example, to obtain an expression for the potential D in terms of independent variables T, P, and f, we substitute eq A-1.9 and A-1.10 into eq A-1.7 and simplify using eq A-1.14, A-1.15, and A-1.16.

Appendix II

This appendix lists the useful Maxwell relations according to the potential function from which they are derived.

$$U\!:\quad \left.\frac{\partial T}{\partial V}\right|_{S,L} = -\left.\frac{\partial P}{\partial S}\right|_{V,L} \qquad \left.\frac{\partial T}{\partial L}\right|_{S,V} = \left.\frac{\partial f}{\partial S}\right|_{V,L} \qquad -\left.\frac{\partial P}{\partial L}\right|_{S,V} = \left.\frac{\partial f}{\partial V}\right|_{S,L}$$

$$A\!:\quad \left.\frac{\partial S}{\partial V}\right|_{T,L} = \left.\frac{\partial P}{\partial T}\right|_{V,L} \qquad -\left.\frac{\partial S}{\partial L}\right|_{T,V} = \left.\frac{\partial f}{\partial T}\right|_{V,L} \qquad -\left.\frac{\partial P}{\partial L}\right|_{T,V} = \left.\frac{\partial f}{\partial V}\right|_{T,L}$$

$$H\!:\quad \left.\frac{\partial T}{\partial P}\right|_{S,L} = \left.\frac{\partial V}{\partial S}\right|_{P,L} \qquad \left.\frac{\partial T}{\partial L}\right|_{S,P} = \left.\frac{\partial f}{\partial S}\right|_{P,L} \qquad \left.\frac{\partial V}{\partial L}\right|_{S,P} = \left.\frac{\partial f}{\partial P}\right|_{S,L}$$

$$G\!:\, -\left.\frac{\partial S}{\partial P}\right|_{T,L} = \left.\frac{\partial V}{\partial T}\right|_{P,L} \qquad -\left.\frac{\partial S}{\partial L}\right|_{T,P} = \left.\frac{\partial f}{\partial T}\right|_{P,L} \qquad \left.\frac{\partial V}{\partial L}\right|_{T,P} = \left.\frac{\partial f}{\partial P}\right|_{T,L}$$

$$D\!:\quad \left.\frac{\partial T}{\partial V}\right|_{S,f} = -\left.\frac{\partial P}{\partial S}\right|_{V,f} \qquad \left.\frac{\partial T}{\partial f}\right|_{S,V} = -\left.\frac{\partial L}{\partial S}\right|_{V,f} \qquad \left.\frac{\partial P}{\partial f}\right|_{S,V} = \left.\frac{\partial L}{\partial V}\right|_{S,f}$$

$$B\!:\quad \left.\frac{\partial S}{\partial V}\right|_{T,f} = \left.\frac{\partial P}{\partial T}\right|_{V,f} \qquad \left.\frac{\partial S}{\partial f}\right|_{T,V} = \left.\frac{\partial L}{\partial T}\right|_{V,f} \qquad \left.\frac{\partial P}{\partial f}\right|_{T,V} = \left.\frac{\partial L}{\partial V}\right|_{T,f}$$

$$M\!:\quad \left.\frac{\partial T}{\partial P}\right|_{S,f} = \left.\frac{\partial V}{\partial S}\right|_{P,f} \qquad \left.\frac{\partial T}{\partial f}\right|_{S,P} = -\left.\frac{\partial L}{\partial S}\right|_{P,f} \qquad \left.\frac{\partial V}{\partial f}\right|_{S,P} = -\left.\frac{\partial L}{\partial P}\right|_{S,f}$$

$$Z\!:\quad \left.\frac{\partial V}{\partial T}\right|_{P,f} = -\left.\frac{\partial S}{\partial P}\right|_{T,f} \qquad \left.\frac{\partial S}{\partial f}\right|_{T,P} = \left.\frac{\partial L}{\partial T}\right|_{P,f} \qquad \left.\frac{\partial L}{\partial P}\right|_{T,f} = -\left.\frac{\partial V}{\partial f}\right|_{T,P}$$

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Copolymerization with Depropagation. IX. Molecular Weights in Copolymerization with Depropagation

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ABSTRACT: A method is described for calculating number and weight average molecular weights of copolymers polymerizing under conditions where reversibility of the propagation reaction must be considered. Generating functions combined with our diad model were used for derivation of equations which yielded leading moments of macromolecular weight distribution. The resulting equations were tested experimentally by using the copolymerizing system, styrene-α-methylstyrene. Rapid decrease of molecular weight with increasing α-methylstyrene feed concentration can be explained by relating the molecular weight decrease to a progressive increase of the apparent termination rate constant.

Molecular weight distribution (MWD) in copolymers was previously discussed by Simha and Branson[1a] and Stockmayer[1b] for irreversible polymerization at zero conversion. Zeman and Amundson[2] applied the continuous variable technique to copolymerization in batch reactors. The effect of the depropagation reaction was also discussed, but the penultimate unit effect on the depropagation steps of copolymerization was neglected.

In the fourth paper of this series[3] the use of the Monte Carlo method for calculating composition and chain length distribution was demonstrated. Recently, the theory of linear kinetics has been used by Horn and Klein[4] to derive asymptotic expressions for the dynamic behavior of the molecular weight distribution moments for living copolymerization systems. Ray, *et al.*,[5] have applied generating functions to determine the moments of the MWD in irreversible copolymerization in various reactors.

In the eighth paper of this series[6] a general solution for composition behavior was presented for multicomponent reversible polymerization using a probability approach for a diad model. By combining Ray's generating function technique for calculating moments of the MWD of irreversible copolymerization and our diad model for reversible copolymerization, we show in this paper that the moments of the MWD of reversible copolymerization can be calculated.

In this paper numerical calculations of average molecular weights from the resulting equations are compared with data obtained experimentally using the free radical copolymerization system of styrene (ST) and α-methylstyrene (AMS) at 60 and 100°. Molecular weights were experimentally found to decrease very rapidly as AMS feed concentration increases. We attribute this phenomenon to a progressive decrease of the apparent termination constant as AMS feed concentration increases. Therefore, we propose that the effect of depropagation reactions on both the copolymer molecular weight and the copolymerization rate is due to an increasing termination rate rather than a decrease of the net propagation rate.