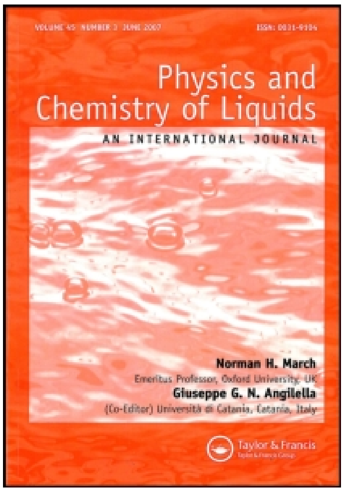

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H. T. Hammel[a]
[a] Physiological Research Laboratory, Scripps Institution of Oceanography, University of California, San Diego, California

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Liquid A As Solution of Polymers: Internal Tensions and Other Thermodynamic Properties

H. T. HAMMEL

Physiological Research Laboratory, Scripps Institution of Oceanography, University of California, San Diego, La Jolla, California 92093.

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The bonding force between a polymer of n molecules in liquid A, $(A)^l_n$, is subject to an internal tension, τ_{An}, attributable to the polymers of all sizes in liquid A. This tension exceeds the internal tension between pure polymer $(A)^{lo}_n$, τ^0_{An}, and this enhanced tension, $\pi_{An} = \tau_{An} - \tau^0_{An}$, changes all partial molar quantities of $(A)^l_n$ within liquid A with respect to the molar quantities of pure $(A)^{lo}_n$, including the chemical potential of polymer $(A)^l_n$ (such that $\mu^l_{An}(T, p^l, x^l_{An})$ is equal to $\mu^{lo}_{An}(T, p^l - \pi_{An})$). When the vapor of A is in equilibrium with liquid A, the vapor of $(A)_n$ must also be in equilibrium with liquid $(A)_n$ for every n from 1 to N. Even when the mole fraction of polymer $(A)^l_n$ is altered by changing the pressure applied to liquid A, its mole fraction must equal the mole fraction of $(A)^v_n$ in the vapor phase with which it is in equilibrium, i.e., $x^l_{An} = x^v_{An}$ for any *T or* p^l. Since water vapor is monomeric, liquid water must also be monomeric.

INTRODUCTION

A liquid A consists of molecules of only one kind. Nevertheless, these molecules may cluster into polymers of varying size. Such a liquid becomes a solution of polymers. Only if the polymers are all of the same number of molecules of A is liquid A a pure liquid and no longer a solution. In this article, we will treat liquid A as a solution of polymers wherein a polymer of a given number of molecules will be considered to be a separate species in the solution. Each species of polymer is a solute, and all other species are the solvent for it. The treatment to follow will be based on the Hulett paradigm[1,2,3,4] in order to describe the thermodynamic properties of each solute in liquid A. We shall find that a modified Hulett Gedanken Experiment requires that the mole fraction of any polymer in liquid A be equal to its mole fraction in the vapor phase for any pressure and temperature applied to liquid A.

Suppose that the liquid consists of $n^l_{\mathrm{A}_1}$ moles of monomers of chemical formula $(\mathrm{A})^l_1$, $n^l_{\mathrm{A}_2}$ moles of dimers of chemical formula $(\mathrm{A})^l_2$, etc. up to and including n^l_{AN} moles of chemical formula $(\mathrm{A})^l_{\mathrm{N}}$. Polymer $(\mathrm{A})_{\mathrm{n}}$ will react with and attain an equilibrium with other polymers in liquid A according to the generalized reaction,

$$(\mathrm{A})^l_{\mathrm{n}} \leftrightharpoons (\mathrm{A})^l_{\mathrm{n-m}} + (\mathrm{A})^l_{\mathrm{m}}$$

where n is an integer such that $1 \leq \mathrm{n} \leq \mathrm{N}$ and where m is an integer such that $0 \leq \mathrm{m} < \mathrm{n}$. The number of equilibria and equilibrium constants is the sum of the factors of n from $\mathrm{n} = 1$ to $\mathrm{n} = \mathrm{N}$.

Polymers may form and co-exist as separate species in liquid A. The equilibrium concentration of liquid polymer $(\mathrm{A})^l_{\mathrm{n}}$, $[(\mathrm{A})^l_{\mathrm{n}}]$, is attained when the rate it is formed equals the rate it is changed by collisions with monomers and other polymers of the system. The coupling force between molecules of liquid A may be one or more of several kinds such as the hydrogen bond or other polar bonds, the ionic bond or such other bonding forces as the London force or induction force. Polymerization implies that the coupling force between molecules within polymer $(\mathrm{A})^l_{\mathrm{n}}$ is greater than that between polymers of $(\mathrm{A})^l_{\mathrm{n}}$. The stronger the bond (the greater the bond energy) between the molecules in polymer $(\mathrm{A})^l_{\mathrm{n}}$, the less frequently the bond is broken at T and the more abundant $(\mathrm{A})^l_{\mathrm{n}}$ will be in liquid A.

All molecules of polymer $(\mathrm{A})^l_{\mathrm{n}}$ move together as a cluster and the center of mass of each $(\mathrm{A})^l_{\mathrm{n}}$ moves randomly with respect to the centers of mass of other $(\mathrm{A})^l_{\mathrm{n}}$ as well as all other polymers. Even though each $(\mathrm{A})^l_{\mathrm{n}}$ may be transient, the molar amount of polymer $(\mathrm{A})^l_{\mathrm{n}}$ remains constant at n^l_{An} at constant T and p^l. The thermal energy of liquid A is partitioned equally between all its polymers regardless of their size from $\mathrm{j} = 1$ to $\mathrm{j} = \mathrm{N}$. These considerations affect the internal tension between each polymer and thereby affect the thermodynamic properties of the polymer.

Chemical potentials of pure liquid A and its vapor

An important property of pure solvent is its Gibbs molar free energy, its molar Gibbs function. This chemical potential of pure liquid solvent is a function of temperature and the pressure applied to it and is symbolized as $\mu^{lo}_{\mathrm{A}}(T, p^l)$. Likewise, the chemical potential of pure solvent vapor is a function of T and the pressure applied to it and is symbolized as $\mu^{vo}_{\mathrm{A}}(T, p^v)$. The chemical potentials of the pure liquid and pure vapor can be changed by changing the temperature and pressure applied to each according to

$$\mathrm{d}\mu^{lo}_{\mathrm{A}} = -\bar{S}^{lo}_{\mathrm{A}}\,\mathrm{d}T + \bar{V}^{lo}_{\mathrm{A}}\,\mathrm{d}p^l \qquad (1)$$

$$\mathrm{d}\mu^{vo}_{\mathrm{A}} = -\bar{S}^{vo}_{\mathrm{A}}\,\mathrm{d}T + \bar{V}^{vo}_{\mathrm{A}}\,\mathrm{d}p^v, \qquad (2)$$

where $\bar{S}_A^{lo}(T, p^l)$ and $\bar{V}_A^{lo}(T, p^l)$ are the molar entropy and molar volume, respectively, of pure liquid A and both are functions of T and applied pressure p^l. Likewise, $\bar{S}_A^{vo}(T, p^v)$ and $\bar{V}_A^{vo}(T, p^v)$ are the molar entropy and molar volume, respectively, of pure vapor A and both are functions of T and applied pressure p^v.

If, as illustrated in Figure 1A and B, the pressure applied to pure liquid A is slowly decreased from p^l to $p^l - \Delta p^l$ and if the vapor of pure A remains in equilibrium with the liquid of pure A, then the chemical potentials of pure liquid and pure vapor must remain equal, i.e.

$$\int_{\mu_A^{lo}(T,p^l)}^{\mu_A^{lo}(T,p^l-\Delta p^l)} \mathrm{d}\mu_A^{lo} = \int_{\mu_A^{vo}(T,p_A^{vo}(T,p^l))}^{\mu_A^{vo}(T,p_A^{vo}(p^l-\Delta p^l))} \mathrm{d}\mu_A^{vo}. \qquad (3)$$

If the temperature remained constant at T as the pressure applied to the liquid decreased, then according to Eqs (1) and (2)

$$\left.\int_{p^l}^{p^l-\Delta p^l} \bar{V}_A^{lo}\,\mathrm{d}p^l\right|_T = \left.\int_{p_A^{vo}(T,p^l)}^{p_A^{vo}(T,\,p^l-\Delta p^l)} \bar{V}_A^{vo}\,dp^v\right|_T. \qquad (4)$$

This is an exact statement whatever the thermal coefficient of expansion or the compressibility of pure liquid A and whatever the law relating vapor pressure to the molar volume of the vapor or to T. Clearly, $p_A^{vo}(T, p^l - \Delta p^l)$ must be less than $p_A^{vo}(T, p^l)$ depending on the magnitude of $-\Delta p^l$ and always exactly according to Eq. (4). This statement is exact when all molecules of A are of one kind only, pure liquid A.

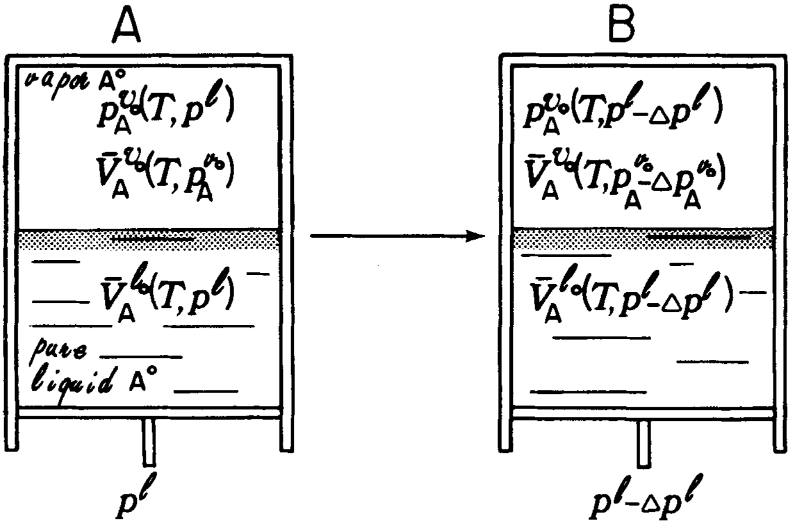

FIGURE 1 Illustrating changes in vapor pressure, molar volume of vapor and molar volume of liquid when pressure applied to pure liquid A^{lo} decreases from p^l to $p^l - \Delta p^l$.

Distribution of pure A between energy states and between its liquid and vapor phases

When pure liquid A is in equilibrium with its vapor, the changes in chemical potentials of the liquid and the vapor remain equal as the pressure applied to the liquid changes. In addition, the chemical potentials of liquid A and vapor A are equal at the limits of integration, Eq. (3). Although their molar internal energies, $\bar{U}^{lo}_{\mathrm{A}}$ and $\bar{U}^{vo}_{\mathrm{A}}$, differ greatly, nevertheless their molar free energies are equal. Thus, at the same T and applied pressure, $\mu^{lo}_{\mathrm{A}}(T, p^{vo}_{\mathrm{A}}(T) = \mu^{vo}_{\mathrm{A}}(T, p^{vo}_{\mathrm{A}}(T))$ where, for example, the pressure applied to liquid A is the pressure of vapor A with which it is in equilibrium, i.e., in Figure 1A, $pl = p^{vo}_{\mathrm{A}}(T, p^{vo}_{\mathrm{A}})$.

The distribution of molecules A between the liquid and the vapor phases in equilibrium is determined by the Boltzmann distribution law, a fundamental law of classical statistical mechanics. If n_2 moles of molecules A in a unit volume are in an energy state 2 with molar energy $\bar{U}_2$ and if they are in equilibrium with n_1 moles of molecules A per unit volume in an energy state 1 with molar energy $\bar{U}_1$ at the same T, then the molecules of A are distributed between the two energy states according to the law

$$n_2/n_1 = \exp - \left(\frac{\Delta\bar{U}}{RT}\right) \tag{5}$$

where $\Delta\bar{U} = \bar{U}_2 - \bar{U}_1$ and where $R = kL$, Boltzmann's constant times Avagadro's constant. The unit volume in each state is a unit of volume available to the centers of the nL molecules of A in each energy state.

The energy of a mole of molecules of A can be increased by adding an amount of heat δQ and by performing an amount of work on the molecules δW, i.e. $\Delta\bar{U}_{\mathrm{A}} = \delta Q + \delta W$. If the work is only pressure volume work and if it is performed at constant pressure then $\delta W|_p = -p\Delta\bar{V}_{\mathrm{A}}$ since the volume decreases as work is done on the system. If heat is added to a mole of A at constant p then $\delta Q|_p = \Delta\bar{H}_{\mathrm{A}}|_{\mathrm{p}}$ where $\Delta\bar{H}_{\mathrm{A}}|_p$ is the change in the molar enthalpy of the molecules at constant pressure. Enthalpy of a mole of molecules A is defined as $\bar{H}_{\mathrm{A}} \equiv \bar{U}_{\mathrm{A}} + p\bar{V}_{\mathrm{A}}$ so that a change in the molar enthalpy at constant p is $\Delta\bar{H}_{\mathrm{A}}|_p = \Delta\bar{U}_{\mathrm{A}} + p\Delta\bar{V}_{\mathrm{A}}$ and the change in the molar energy of molecules A is $\Delta\bar{U}_{\mathrm{A}} = \Delta\bar{H}_{\mathrm{A}}|_p - p\Delta\bar{V}_{\mathrm{A}}$ when the volume increases or $\Delta\bar{U}_{\mathrm{A}} = \Delta\bar{H}_{\mathrm{A}}|_p + p\Delta\bar{V}_{\mathrm{A}}$ when the volume decreases. Boltzmann's law may now be applied to obtain the distribution of molecules A between the liquid and vapor phases at T and $p^{vo}_{\mathrm{A}}(T)$. The energy of a mole of vapor $\bar{U}^{vo}_{\mathrm{A}}$ exceeds the energy of a mole of liquid $\bar{U}^{lo}_{\mathrm{A}}$ by an amount $\bar{U}^{vo}_{\mathrm{A}} - \bar{U}^{lo}_{\mathrm{A}} = [\bar{H}^{vo}_{\mathrm{A}}(T, p^{vo}_{\mathrm{A}}(T)) - \bar{H}^{lo}_{\mathrm{A}}(T, p^{vo}_{\mathrm{A}}(T))] - p^{vo}_{\mathrm{A}}(T)[\bar{V}^{vo}_{\mathrm{A}}(T, p^{vo}_{\mathrm{A}}(T)) - \bar{V}^{lo}_{\mathrm{A}}(T, p^{vo}_{\mathrm{A}}(T))]$. Thus, Eq. (5) becomes

$$n^{vo}_{\mathrm{A}}/n^{lo}_{\mathrm{A}} = \exp - \left(\frac{\Delta\bar{H}^{vlo}_{\mathrm{A}} - p^{vo}_{\mathrm{A}}(T)\,\Delta\bar{V}^{vlo}_{\mathrm{A}}}{RT}\right) \tag{5a}$$

where $\Delta\bar{H}_A^{vlo}$ is the enthalpy of evaporating a mole of pure liquid A at T and $p_A^{vo}(T)$ and $\Delta\bar{V}_A^{vlo}$ is the increase in volume of that mole of liquid when it evaporates at T and $p_A^{vo}(T)$. Equation (5*a*) describes the moles of vapor A whose molecular centers move in a unit volume relative to the moles of liquid A whose molecular centers also move in a unit volume. If the volume that one vapor molecule's center occupies is v_A^v then $n_A^{vo}L\mathrm{v}_A^v$ equals a unit volume. Likewise, if v_A^l is the volume that one liquid molecule's center occupies, then $n_A^{lo}L\mathrm{v}_A^l$ equals a unit volume and $n_A^{vo}/n_A^{lo} = \mathrm{v}_A^l/\mathrm{v}_A^v$.

Although the molar energies of the two phases differ, the Gibbs molar free energies of the two phases in equilibrium are equal. Gibbs defined the molar free energy of each phase of A as $\bar{G}_A^{vo} \equiv \bar{H}_A^{vo} - T\bar{S}_A^{vo}$ for the vapor phase and $\bar{G}_A^{lo} \equiv \bar{H}_A^{lo} - T\bar{S}_A^{lo}$ for the liquid phase. Thus, $\Delta\bar{G}_A^{vlo} = \bar{G}_A^{vo} - \bar{G}_A^{lo} = \Delta\bar{H}_A^{vlo} - T\Delta\bar{S}_A^{vlo}$. The molar entropy of vaporization is related to the molar enthalpy of vaporization at constant pressure. From the Second Law of Thermodynamics, adding an amount of heat at constant pressure increases the entropy an amount $\Delta S|_p = \delta Q|p/T$. As stated earlier, $\delta Q|_p = \Delta\bar{H}_A|_p$ when heat is added at constant pressure. Thus, $\Delta\bar{S}_A^{vlo}|_p = \Delta\bar{H}_A^{vlo}/T$ and $\Delta\bar{G}_A^{vlo} = 0$, i.e., the chemical potentials of the liquid and vapor phases are equal in equilibrium.

Pure liquid A in a Hulett column

In a modified Hulett Gedanken Experiment, pure liquid A is supported at its free surface by a matrix at $2h + \Delta h_A^{lo}$ in the left cylinder, Figure 2A. Liquid A is also contained in a cylinder on the right. The pressure applied to the upper surface of liquid A in the left cylinder is $p_A^{vo}(2h + \Delta h_A^{lo})$, while in the right cylinder the applied pressure is $p_A^{vo}(h)$. The pressure applied by both pistons is $p_A^{vo}(h) + \int_0^h \rho_A^{lo}(z)\,\mathrm{d}z$, where the latter term is the weight of a column of liquid A from o to h applied to a unit area of piston surface. Note an opening between the two cylinders which insures that the hydrostatic pressure in liquid A at h in both cylinders is $p_A^{vo}(h)$. The hydrostatic pressure at the upper surface of liquid A at $2h + \Delta h_A^{lo}$ in the left cylinder is $p_A^{vo}(2h + \Delta h_A^{lo}) - \int_h^{2h+\Delta h_A^{lo}} \rho_A^{lo}(z)\,\mathrm{d}z$. The magnitude of Δh_A^{lo} is determined, in part, by the compressibility of liquid A, i.e., liquid A is increasingly distended by increasing tension from h to $2h + \Delta h_A^{lo}$ such that the total distension is Δh_A^{lo}. Similarly, liquid A is increasingly compressed from h to o. Due also to its compressibility, the density of liquid A is a function of z such that $\rho_A^{lo}(2h + \Delta h_A^{lo}) < \rho_A^{lo}(h) < \rho_A^{lo}(o)$. The compressibility also varies with pressure so that it varies with z and $\rho_A^{lo}(2h + \Delta h_A^{lo}) - \rho_A^{lo}(h)$ is not exactly equal to $\rho_A^{lo}(h) - \rho_A^{lo}(o)$.

Since the molecules of liquid A and vapor A are in a gravity field in Figure 2A, the vertical distribution of the molecules of each will be in accord with the Boltzmann distribution law, Eq. (5). The number of molecules at $z + \mathrm{d}z$ in a

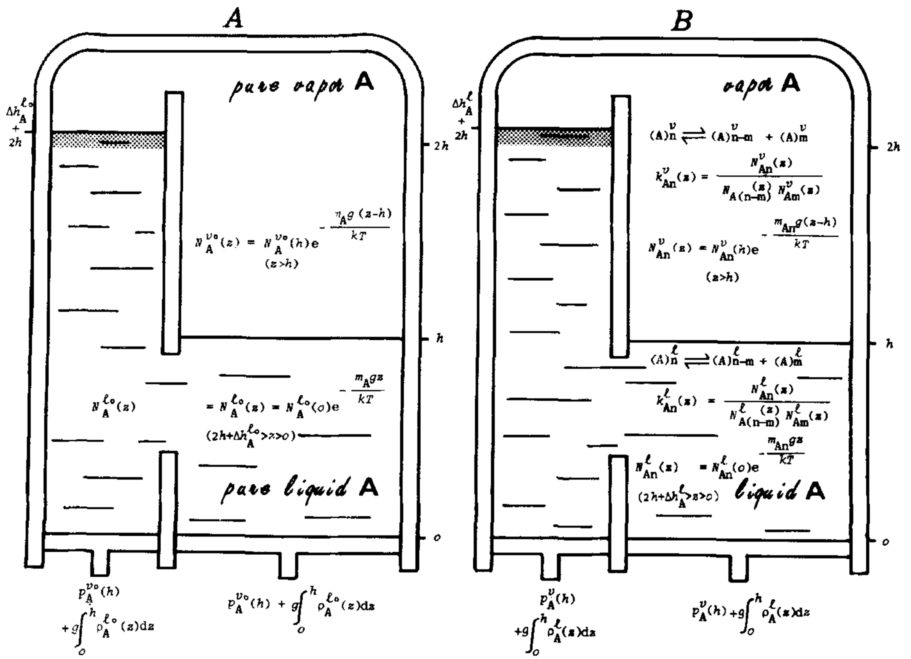

FIGURE 2(A) *Illustrating pure liquid A in a Hulett column in equilibrium with pure vapor A. The distributions of molecules A as a function of z in* both the liquid and vapor phases are illustrated as determined by the Boltzmann distribution law. The surface of liquid A in the left cylinder is held by a matrix at $2h + h_A^{lo}$, implying that the tension in liquid A increases from h to $2h + \Delta h^{lo}$ by an amount $g\int_h^{2h+\Delta h_A^{lo}} \rho_A^{lo}(z)\,dz$. Since the amount of liquid A in the left cylinder between h and $2h + \Delta h_A^{lo}$ equals the amount between o and h, Δh_A^{lo} is the distension of liquid A due to the tension applied by its weight. $\Delta h_A^{lo}/h$ is a measure of the distensibility of pure liquid A[8] and can be correlated with its vapor pressure $p_A^{vo}(2h + \Delta h_A^{lo})$ and therefore with its tension at $2h + \Delta h_A^{lo}$. (B) Illustrating liquid A as a solution of polymers in a Hulett column in equilibrium with a solution of the same polymers in the vapor phase. The distributions of polymer $(A)_n$ as a function of z in the liquid and vapor phases are illustrated as determined by the Boltzmann distribution law and by the law of mass action which establishes the equilibrium constant for polymer $(A)_n$, k_{An}.

volume of unit cross section and thickness dz, $N_{\mathrm{A}}^{0}(z + \mathrm{d}z)$, is less than the number at z, $N_{\mathrm{A}}^{0}(z)$, by

$$N_{\mathrm{A}}^{0}(z + \mathrm{d}z)/N_{\mathrm{A}}^{0}(z) = \exp - \left(\frac{m_{\mathrm{A}} g\, \mathrm{d}z}{kT}\right), \tag{5b}$$

where m_{A} is the mass of a molecule of A and $m_{\mathrm{A}} g\, \mathrm{d}z$ is the gravitational energy the molecule gains from z to $z + \mathrm{d}z$. $m_{\mathrm{A}} g\, \mathrm{d}z$ in Eq. (5*b*) equals $\Delta\bar{U}/L$ in Eq. (5). In Figure 2A, the number of vapor molecules at $z > h$ is

$$N_{\mathrm{A}}^{vo}(z)/N_{\mathrm{A}}^{vo}(h) = \exp - \left(\frac{m_{\mathrm{A}} g(z - h)}{kT}\right). \tag{5c}$$

Likewise, liquid molecules gain the same gravitational energy $m_{\mathrm{A}} g\, \mathrm{d}z$ per molecule so that the number of liquid molecules at $h > z > o$ is

$$N_{\mathrm{A}}^{lo}(z)/N_{\mathrm{A}}^{lo}(o) = \exp - \left(\frac{m_{\mathrm{A}} g z}{kT}\right) \tag{5d}$$

in both the left and right cylinders of Figure 2A. The number of liquid molecules at $(2h + \Delta h_{\mathrm{A}}^{lo}) > z > h$ is

$$N_{\mathrm{A}}^{lo}(z)/N_{\mathrm{A}}^{lo}(h) = \exp \left(\frac{m_{\mathrm{A}} g(z - h)}{kT}\right), \tag{5e}$$

in the left cylinder. In Eq. (5*c*), the ratio of the number of vapor molecules may be replaced by the ratio of the moles of vapor. Likewise, in Eqs (5*d*) and (5*e*), the ratio of the moles of liquid may replace the ratio of the molecules of liquid. m_{A}/k in Eqs (5*c*), (5*d*) and (5*e*) may also be replaced by MW_{A}/R, since $MW_{\mathrm{A}} = Lm_{\mathrm{A}}$ and $R = Lk$, *where* MW_{A} is the molecular weight of A. According to Eq. (5*a*), the molar ratio of vapor to liquid at h will be

$$n_{\mathrm{A}}^{vo}(h)/n_{\mathrm{A}}^{lo}(h) = \exp - \left(\frac{\Delta\bar{H}_{\mathrm{A}}^{vlo}(h) - p_{\mathrm{A}}^{vo}(T, h)\, \Delta\bar{V}_{\mathrm{A}}^{vlo}(h)}{RT}\right), \tag{5f}$$

where $\Delta\bar{H}^{vlo}(h)$ is the enthalpy of evaporating a mole of liquid A at T and $p_{\mathrm{A}}^{vo}(h)$ and where $\Delta\bar{V}_{\mathrm{A}}^{vlo}$ is the increase in volume of that mole of liquid when it evaporates at T and $p_{\mathrm{A}}^{vo}(h)$. Likewise, at $2h + \Delta h_{\mathrm{A}}^{lo}$ the molar ratio of vapor to liquid at the surface of liquid A in the left cylinder will be

$$n_{\mathrm{A}}^{vo}(2h + \Delta h_{\mathrm{A}}^{lo})/n_{\mathrm{A}}^{lo}(2h + \Delta h_{\mathrm{A}}^{lo})$$
$$= \exp - \left(\frac{\Delta\bar{H}_{\mathrm{A}}^{vlo}(2h + \Delta h_{\mathrm{A}}^{lo}) - p_{\mathrm{A}}^{vo}(2h + \Delta h_{\mathrm{A}}^{lo})\Delta\bar{V}_{\mathrm{A}}^{vlo}(2h + \Delta h_{\mathrm{A}}^{lo})}{RT}\right) \tag{5g}$$

where the molar enthalpy increase and molar volume increase pertain to evaporation under the conditions at $2h + \Delta h_{\mathrm{A}}^{lo}$, i.e., where liquid A is under tension and where the pressure-volume work is against a reduced pressure.

In summary, for pure A in Figure 2A: 1) the distribution of its molecules in a gravity field may be described by a fundamental law of classical statistical mechanics, Eq. (5*c*) for the vapor phase and Eqs (5*d*) and (5*e*) for the liquid phase; 2) the distribution of its molecules between the liquid and vapor phases is based on the same law and may be described by Eq. (5*f*) at h and by Eq. (5*g*) at $2h + \Delta h^{lo}_{\mathrm{A}}$; 3) in accordance with a rigorous thermodynamic statement, Eq. (4), at constant T,

$$\int_{p^{vo}_{\mathrm{A}}(h)}^{p^{vo}_{\mathrm{A}}(2h+\Delta h^{lo}_{\mathrm{A}})-\int_h^{2h+\Delta h^{lo}}\rho^{lo}_{\mathrm{A}}(z)\,\mathrm{d}z} \bar{V}^{lo}_{A}\mathrm{d}p^{l} = \int_{p^{vo}_{\mathrm{A}}(h)}^{p^{vo}_{\mathrm{A}}(2h+\Delta h^{lo}_{\mathrm{A}})} \bar{V}^{vo}_{\mathrm{A}}\,\mathrm{d}p^{v}. \qquad (4a)$$

These fundamental statistical mechanical and chemical thermodynamic statements are equally rigorous and completely compatible. They interrelate with each other in the equations of state for the liquid and for the vapor of pure A, i.e., in the relationship between $\bar{V}^{lo}_{\mathrm{A}}$ and p^{l} and T applied to liquid A and between $\bar{V}^{vo}_{\mathrm{A}}$ and p^{v} and T applied to vapor A. The moles of vapor per unit volume at any z equals $1/\bar{V}^{vo}_{\mathrm{A}}(z)$ and depends on $N^{vo}_{\mathrm{A}}(z)$, Eq. (5*c*), or on $n^{vo}_{\mathrm{A}}(z)$ which equals $N^{vo}_{\mathrm{A}}(z)/L$. The relationship between $p^{vo}_{\mathrm{A}}(z)$ and $\bar{V}^{vo}_{\mathrm{A}}(z)$ and T is the gas law (equation of state) for vapor A. Similarly, the moles of liquid per unit volume at any z equals $1/\bar{V}^{lo}_{\mathrm{A}}(z)$ and depends on $N^{lo}_{\mathrm{A}}(z)$, Eq. (5*d*), or on $n^{lo}_{\mathrm{A}}(z)$. The relationship between $p^{lo}_{\mathrm{A}}(z)$ and $\bar{V}^{lo}_{\mathrm{A}}(z)$ and T is the equation of state for liquid A.

We should note, again, that the density of molecules of A in both the liquid and vapor phases diminish exponentially in a gravity field, depending on the mass of the molecule and on the height above the reference. In both phases, this is due to the increased gravitational energy of the molecules at the greater height. In the vapor phase, the distribution relates to the Brownian motion and the pressure-volume work by the molecules. Whereas in the liquid phase, the distribution and increased gravitational energy with z relates to pressure-volume work performed by the cohesive force between the molecules. In both phases in Figure 2A, for $z > h$, the increase in energy per molecule is exactly the same; namely, $m_{\mathrm{A}}g(z - h)$. In the liquid column on the left, the pressure is the weight of the column per unit area, $g\int_h^{z-h}\rho^{lo}_{\mathrm{A}}(z)\,\mathrm{d}z$, and the volume change per unit area is $\Delta h^{lo}_{\mathrm{A}}$ at $z = 2h + \Delta h^{lo}_{\mathrm{A}}$. It is clear, in this example, that the increased tension (negative pressure) in liquid A distends the liquid A so that an amount of negative work is performed on liquid A which exactly equals the increase in the gravitational energy of each molecule of liquid A at z. This exact correspondence of energies ensures the distribution of molecules in liquid A at z will match the distribution of molecules in vapor A and ensures that the vapor pressure of liquid A at z exactly equals the vapor pressure of vapor A at z. In general, any tension applied to pure liquid A lowers its vapor pressure in accord with the negative pressure-volume work performed on the liquid and in accord with the fundamental laws reviewed here, Eqs (4), (5*c*) and (5*e*). Similarly, any positive pressure applied to liquid A varies its vapor pressure in accord with the pressure-volume work performed on the liquid and in accord with the same laws.

Chemical potentials of liquid and vapor of pure polymer $(\mathrm{A})_{\mathrm{n}}^{0}$

The thermodynamic and statistical mechanic statements of the preceding sections also apply when liquid and vapor of A are pure polymer $(\mathrm{A})_{\mathrm{n}}^{0}$. Thus, if the pressure applied to pure liquid polymer $(\mathrm{A})_{\mathrm{n}}^{l\mathrm{o}}$ decreased slowly from p to $p^l - \Delta p^l$ at constant T, Figure 3A and 3B, then the chemical potential of $(\mathrm{A})_{\mathrm{n}}^{l\mathrm{o}}$ decreased an amount

$$-\Delta\mu_{\mathrm{An}}^{l\mathrm{o}} = \mu_{\mathrm{An}}^{l\mathrm{o}}(T, p^l - \Delta p^l) - \mu_{\mathrm{An}}^{l\mathrm{o}}(T, p^l) = \int_{p^l}^{p^l-\Delta p^l} \bar{V}_{\mathrm{An}}^{l\mathrm{o}}\,\mathrm{d}p^l \bigg|_T . \tag{6}$$

Likewise, the chemical potential of pure vapor polymer $(\mathrm{A})_{\mathrm{n}}^{v\mathrm{o}}$ decreased an amount

$$\begin{aligned}-\Delta\mu_{\mathrm{An}}^{v\mathrm{o}} &= \mu_{\mathrm{An}}^{v\mathrm{o}}(T, p_{\mathrm{An}}^{v\mathrm{o}}(T, p^l - \Delta p^l)) - \mu_{\mathrm{An}}^{v\mathrm{o}}(T, p_{\mathrm{An}}^{v\mathrm{o}}(T, p^l))\\ &= \int_{p_{\mathrm{An}}^{v\mathrm{o}}(T,p^l)}^{p_{\mathrm{An}}^{v\mathrm{o}}(T,p^l-\Delta p^l)} \bar{V}_{\mathrm{An}}^{v\mathrm{o}}\,\mathrm{d}p_{\mathrm{An}}^{v}\bigg|_T \end{aligned} \tag{7}$$

as the vapor pressure in equilibrium with pure liquid $(\mathrm{A})_{\mathrm{n}}^{l\mathrm{o}}$ decreased from $p_{\mathrm{An}}^{v\mathrm{o}}(T, p^l)$ to $p_{\mathrm{An}}^{v\mathrm{o}}(T, p^l - \Delta p^l)$.

Since $-\Delta\mu_{\mathrm{An}}^{l\mathrm{o}}$ must equal $-\Delta\mu_{\mathrm{An}}^{v\mathrm{o}}$, it follows from Eqs (6) and (7) that at constant T

$$\int_{p^l}^{p^l-\Delta p^l} \bar{V}_{\mathrm{An}}^{l\mathrm{o}}\,\mathrm{d}p^l = \int_{p_{\mathrm{An}}^{v\mathrm{o}}(T,p^l)}^{p_{\mathrm{An}}^{v\mathrm{o}}(T,p^l-\Delta p^l)} \bar{V}_{\mathrm{An}}^{v\mathrm{o}}\,\mathrm{d}p_{\mathrm{An}}^{v}. \tag{8}$$

Equation (8) is valid because the molar free energy of pure polymer $(\mathrm{A})_{\mathrm{n}}^{0}$ decreased the same amount in both the liquid and vapor phases as the pressure applied to pure liquid $(\mathrm{A})_{\mathrm{n}}^{l\mathrm{o}}$ decreased slowly from p^l to $p^l - \Delta p^l$ at constant T.

Chemical potential and vapor pressure of polymer $(\mathrm{A})_{\mathrm{n}}$ in liquid A

When liquid A is a mixture of polymers, we may treat it thermodynamically as a solution. The chemical potential, other partial molar quantities and the colligative properties of each polymer $(\mathrm{A})_{\mathrm{n}}$ may be considered in relation to these quantities and properties of pure polymer $(\mathrm{A})_{\mathrm{n}}^{0}$. The chemical potential and the other properties of polymer $(\mathrm{A})_{\mathrm{n}}^{l}$ in a mixture of polymers in liquid A

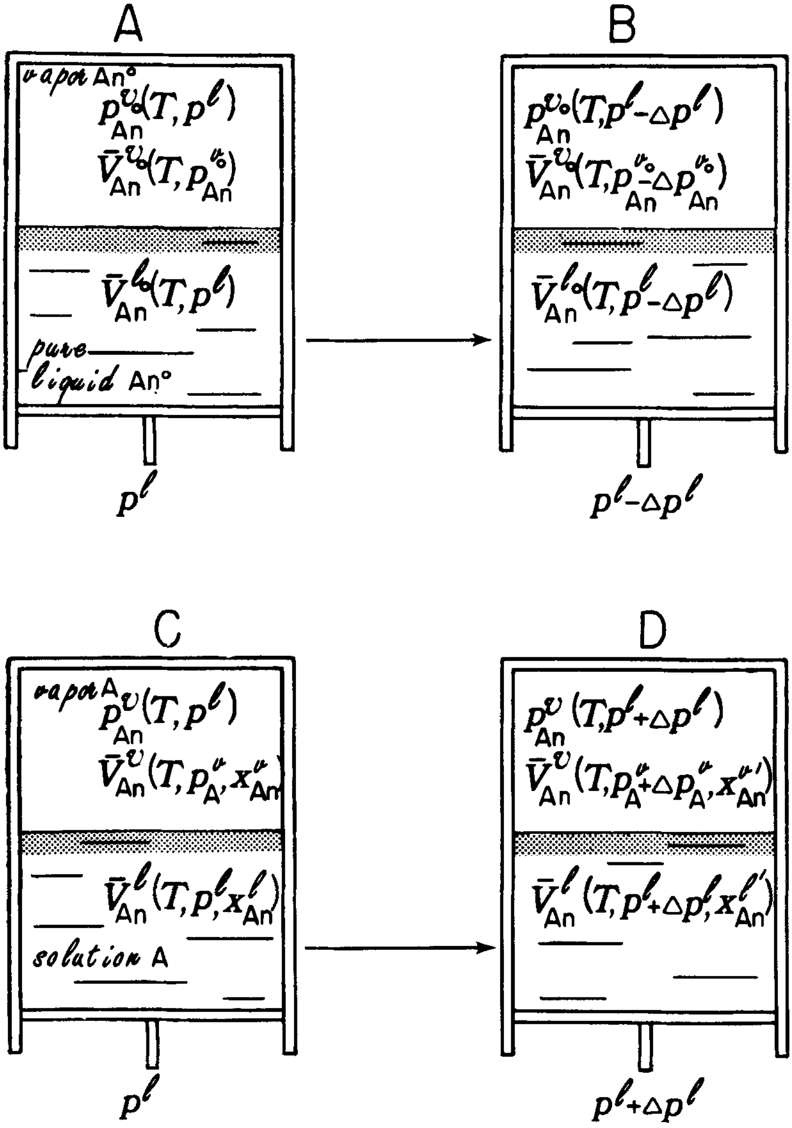

FIGURE 3(A,B) Illustrating changes in vapor pressure, molar volume of vapor and molar volume of liquid when pressure applied to pure liquid polymer $(A)_n^{l\circ}$ decreases from p^l to $p^l - \Delta p^l$. (C,D) Changes in partial vapor pressure, partial molar volume of polymer vapor $(A)_n^v$ and partial molar volume of polymer liquid $(A)_n^l$ in liquid A^l (a solution of polymers of A) when pressure applied to the solution increases from p^l to $p^l + \Delta p^l$. $p_A^v(T, p^l) = \sum_j p_{A_j}^v(T, p^l)$ and $p_A^v(T, p^l + \Delta p^l) = \sum_j p_{A_j}^v(T, p^l + \Delta p^l)$.

can be stated with respect to pure liquid polymer $(\mathrm{A})_\mathrm{n}^{l\circ}$, even when, at T and applied pressure p^l, pure polymer $(\mathrm{A})_\mathrm{n}^{l\circ}$ cannot be realized.

When liquid A is a mixture of polymers from j = 1 to N, the mole fraction of polymer $(\mathrm{A})_\mathrm{n}^l$ is $x^l_{\mathrm{An}} = n^l_{\mathrm{An}}/\sum_\mathrm{j} n^l_{\mathrm{Aj}}$. Since $\sum_\mathrm{j} x^l_{\mathrm{Aj}} = 1$, where j may be every integer from 1 to N, there will be N − 1 independent x^l_{Aj}. The chemical potential of polymer $(\mathrm{A})_\mathrm{n}^l$ in liquid A is, by definition, the partial molar Gibbs function of liquid A,

$$\mu^l_{\mathrm{An}} \equiv \left(\frac{\partial G^l_\mathrm{A}}{\partial n^l_{\mathrm{An}}}\right)_{T,p^l,n^l_{\mathrm{Aj}\neq\mathrm{An}}}, \tag{9}$$

where G^l_A is the Gibbs function of liquid A. G^l_A is an extensive property of liquid A and is a function of the intensive quantities T and p^l as well as a function of the extensive quantities n^l_{Aj}, i.e., G^l_A is $G^l_\mathrm{A}(T, p^l, n^l_\mathrm{j})$. An infinitesimal change of state of liquid A can be expressed by $\mathrm{d}G^l_\mathrm{A}$ due to an infinitesimal change in T or in p^l or in the moles of any or all polymers in liquid A. A fundamental thermodynamic equation for the change $\mathrm{d}G^l_\mathrm{A}$ is[5]

$$\mathrm{d}G^l_\mathrm{A} = -S^l_\mathrm{A}\,\mathrm{d}T + V^l_\mathrm{A}\,\mathrm{d}p^l + \sum_\mathrm{j} \mu^l_{\mathrm{Aj}}\,\mathrm{d}n^l_{\mathrm{Aj}}, \tag{10}$$

where S^l_A is the entropy and V^l_A is the volume of liquid A.

The third term on the right side of Eq. (10) states that the Gibbs function of A^l will increase, at constant T and p^l, when there is an infinitesimal increase in the amount of any polymer $(\mathrm{A})_\mathrm{j}^l$ so that

$$(\mathrm{d}G^l_\mathrm{A})_{T,p^l} = \sum_\mathrm{j} \left(\frac{\partial G^l_\mathrm{A}}{\partial n^l_{\mathrm{Aj}}}\right)_{T,p^l,n^l_{\mathrm{Ai}\neq\mathrm{Aj}}} \mathrm{d}n^l_{\mathrm{Aj}}, \tag{11}$$

where the increase in the moles of polymer $(\mathrm{A})_\mathrm{j}^l$ is made without changing the amount of any other polymer $(\mathrm{A})_\mathrm{i}^l$. Equation (11) may also be written[6]

$$(\mathrm{d}\bar{G}^l_\mathrm{A})_{T,p^l} = \sum_\mathrm{j} \left(\frac{\partial G^l_\mathrm{A}}{\partial n^l_{\mathrm{Aj}}}\right)_{T,p^l,n^l_{\mathrm{Ai}\neq\mathrm{Aj}}} \mathrm{d}x^l_{\mathrm{Aj}}. \tag{11a}$$

where $\mathrm{d}\bar{G}^l_\mathrm{A}$ is the total infinitesimal change in the molar Gibbs function due to infinitesimal changes in the mole fractions of all polymers $(\mathrm{A})_\mathrm{j}^l$ at constant T, p^l and all other $n^l_{\mathrm{Ai}\neq\mathrm{Aj}}$. For all n^l_{Aj} constant, $\mathrm{d}G^l_\mathrm{A}$ in Eq. (10) may be written

$$(\mathrm{d}\bar{G}^l_\mathrm{A})_{n^l_{\mathrm{Aj}}} = -\bar{S}^l_\mathrm{A}\,\mathrm{d}T + \bar{V}^l_\mathrm{A}\,\mathrm{d}p^l_\mathrm{A}$$

so that Eq. (10) becomes

$$\mathrm{d}\bar{G}^l_\mathrm{A} = -\bar{S}^l_\mathrm{A}\,\mathrm{d}T + \bar{V}^l_\mathrm{A}\,\mathrm{d}p^l + \sum_\mathrm{j} \mu^l_{\mathrm{Aj}}\,\mathrm{d}x^l_{\mathrm{Aj}}. \tag{10a}$$

The chemical potential of polymer $(\mathrm{A})_\mathrm{n}^l$, μ^l_{An}, the molar Gibbs function of liquid A, $\bar{G}^l_\mathrm{A}$, the molar entropy $\bar{S}^l_\mathrm{A}$ and the molar volume $\bar{V}^l_\mathrm{A}$ of liquid A, are functions of the intensive variables T, p^l and x^l_{Aj}. According to the rule of partial differentiation, the total differential of μ^l_{An} is

$$\mathrm{d}\mu^l_{\mathrm{An}} = \left(\frac{\partial \mu^l_{\mathrm{An}}}{\partial T}\right)_{p^l, x^l_{\mathrm{Aj}}} \mathrm{d}T + \left(\frac{\partial \mu^l_{\mathrm{An}}}{\partial p^l}\right)_{T, x^l_{\mathrm{Aj}}} \mathrm{d}p^l + \sum_{\mathrm{j}} \left(\frac{\partial \mu^l_{\mathrm{Aj}}}{\partial x_{A j}}\right)_{T, p^l, n_{\mathrm{Ai} \neq \mathrm{Aj}}} \mathrm{d}x^l_{\mathrm{Aj}}. \quad (12)$$

In Eq. (12),

$$\frac{\partial \mu^l_{\mathrm{An}}}{\partial T} = \frac{\partial^2_{\mathrm{A}} G^l_{\mathrm{A}}}{\partial T\, \partial n^l_{\mathrm{An}}} \quad (13)$$

and

$$\frac{\partial \mu^l_{\mathrm{An}}}{\partial p^l} = \frac{\partial^2 G^l_{\mathrm{A}}}{\partial p^l\, \partial n^l_{\mathrm{An}}}, \quad (14)$$

according to Eq. (9). The partial derivatives of G^l_{A} with respect to T and with respect to p^l are, from Eq. (10), $\partial G^l_{\mathrm{A}}/\partial T = -S^l_{\mathrm{A}}$ and $\partial G^l_{\mathrm{A}}/\partial p^l = V^l_{\mathrm{A}}$, respectively. Thus, Eq. (13) becomes

$$\frac{\partial \mu^l_{\mathrm{An}}}{\partial T} = -\frac{\partial S^l_{\mathrm{A}}}{\partial n^l_{\mathrm{An}}} \equiv -\bar{S}^l_{\mathrm{An}} \quad (13a)$$

and Eq. (14) becomes

$$\frac{\partial \mu^l_{\mathrm{An}}}{\partial p^l} = \frac{\partial V^l_{\mathrm{A}}}{\partial n^l_{\mathrm{An}}} \equiv \bar{V}^l_{\mathrm{An}}. \quad (14a)$$

Evaluation of the last term in Eq. (12) is subject to two constraints: 1) as x^l_{Aj} changes, i.e., as n^l_{Aj} changes, all $n^l_{\mathrm{Ai} \neq \mathrm{Aj}}$ must remain constant; and 2) the partial change in μ^l_{An} with respect to changing x^l_{Aj} is subject to the condition that all n^l_{Aj}, except n^l_{An}, must remain constant, according to Eq. (9). So the last term in Eq. (12) is only $\partial \mu^l_{\mathrm{An}}/\partial x^l_{\mathrm{An}\,T, p^l, n^l_{\mathrm{Aj} \neq \mathrm{An}}}\, \mathrm{d}x^l_{\mathrm{An}}$. Using Eqs (13$a$) and (14$a$), Eq. (12) becomes

$$\mathrm{d}\mu^l_{\mathrm{An}} = -(\bar{S}^l_{\mathrm{An}})_{p^l, x^l_{\mathrm{Aj}}}\, \mathrm{d}T + (\bar{V}^l_{\mathrm{An}})_{T, x^l_{\mathrm{Aj}}}\, \mathrm{d}p^l + \left(\frac{\partial \mu^l_{\mathrm{An}}}{\partial x^l_{\mathrm{An}}}\right)_{T, p^l, n^l_{\mathrm{Aj} \neq \mathrm{An}}} \mathrm{d}x^l_{\mathrm{An}}. \quad (15)$$

Slowly increasing the pressure applied to liquid A from p^l, Figure 3C, to $p^l + \Delta p^l$, Figure 3D, at constant T, increases the chemical potential of polymer $(\mathrm{A})^l_{\mathrm{n}}$ an amount

$$\int_{\mu^l_{\mathrm{An}}(T, p^l, x^l_{\mathrm{An}})}^{\mu^l_{\mathrm{An}}(T, p^l + \Delta p^l, x^l_{\mathrm{An}})} \mathrm{d}\mu^l_{\mathrm{An}} = \int_{p^l}^{p^l + \Delta p^l} \bar{V}^l_{\mathrm{An}}\, \mathrm{d}p^l, \quad (16)$$

when the composition of liquid A remains constant. However, even when there is no exchange between liquid A and its surrounding, the moles of $(\mathrm{A})^l_{\mathrm{n}}$ may vary and its mole fraction, x^l_{An}, may vary. For example, when a polymer is formed from its constituents, if there is a change of volume, then the ratio of moles of that polymer to the sum of moles of all polymers will be altered by changing the pressure applied to liquid A. As we shall discuss in the next section, distribution of polymers in a gravity field will also alter their mole fractions.

If x^l_{An} is altered to $x^{l'}_{\mathrm{An}}$ as the pressure applied to liquid A is changed from p^l to $p^l + \Delta p^l$ at constant T, then the chemical potential of liquid $(\mathrm{A})^l_{\mathrm{n}}$ would increase an amount

$$\begin{aligned}\Delta\mu^l_{\mathrm{An}} &= \mu^l_{\mathrm{An}}(T, p^l + \Delta p^l, x^{l'}_{\mathrm{An}}) - \mu^l_{\mathrm{An}}(T, p^l, x^l_{\mathrm{An}}) \\ &= \int_{p^l}^{p^l+\Delta p^l} \bar{V}^l_{\mathrm{An}}\,\mathrm{d}p^l\bigg|_{T, x^l_{\mathrm{An}}} + \int_{\mu^l_{\mathrm{An}}(T, p^l, x^l_{\mathrm{An}})}^{\mu^l_{\mathrm{An}}(T, p^l, x^{l'}_{\mathrm{An}})} \frac{\partial\mu^l_{\mathrm{An}}}{\partial x^l_{\mathrm{An}}}\,\mathrm{d}x^l_{\mathrm{An}}. \qquad (17)\end{aligned}$$

As illustrated in Figure 3C and D, the vapor pressure of each polymer in the vapor phase, p^v_{An}, remains in equilibrium with its liquid polymer $(\mathrm{A})^l_{\mathrm{n}}$ as the pressure applied to the latter increased from p^l to $p^l + \Delta p^l$, that is, as $p^v_{\mathrm{An}}(T, p^l)$ in Figure 3C increased to $p^v_{\mathrm{An}}(T, p^l + \Delta p^l)$ in Figure 3D. The chemical potential of polymer $(\mathrm{A})^v_{\mathrm{n}}$ in the vapor phase, $\mu^v_{\mathrm{An}}(T, p^v_{\mathrm{A}}, x^v_{\mathrm{An}})$, is also a function of T, total vapor pressure and the mole fraction of polymer $(\mathrm{A})^v_{\mathrm{n}}$ in the vapor in equilibrium with liquid A. Both $p^v_{\mathrm{A}}(T, p^l)$ and the moles of $(\mathrm{A})^v_{\mathrm{n}}$, $n^v_{\mathrm{An}}(T, p^l)$, are functions of T and pressure applied to liquid A, p^l. The chemical potential of the vapor of polymer $(\mathrm{A})^v_{\mathrm{n}}$ changes according to

$$\mathrm{d}\mu^v_{\mathrm{An}} = -\bar{S}^v_{\mathrm{An}}\,\mathrm{d}T + \bar{V}^v_{\mathrm{An}}\,\mathrm{d}p^v_{\mathrm{A}} + \frac{\partial\mu^v_{\mathrm{An}}}{\partial x^v_{\mathrm{An}}}\,\mathrm{d}x^v_{\mathrm{An}} \qquad (18)$$

where $\bar{S}^v_{\mathrm{An}}$ and $\bar{V}^v_{\mathrm{An}}$ are the partial molar entropy and volume of $(\mathrm{A})^v_{\mathrm{n}}$ respectively, and both are functions of T, p^v_{A} and x^v_{An}. Of course, n^v_{An} will increase as the equilibrium vapor pressure increases from $p^v_{\mathrm{A}}(T, p^l)$ to $p^v_{\mathrm{A}}(T, p^l + \Delta p^l)$ at constant T. However, according to Eq. (18) at constant T

$$\begin{aligned}\Delta\mu^v_{\mathrm{An}} &= \mu^v_{\mathrm{An}}(T, p^v_{\mathrm{A}}(T, p^l + \Delta p^l), x^{v'}_{\mathrm{An}}) - \mu^v_{\mathrm{An}}(T, p^v_{\mathrm{A}}(T, p^l), x^v_{\mathrm{An}}) \\ &= \int_{p^v_{\mathrm{A}}(T, p^l)}^{p^v_{\mathrm{A}}(T, p^l+\Delta p^l)} V^v_{\mathrm{An}}\,\mathrm{d}p^v_{\mathrm{A}}\bigg|_{T, x^v_{\mathrm{An}}} + \int_{\mu^v_{\mathrm{An}}(T, p^v_{\mathrm{A}}(T, p^l), x^v_{\mathrm{An}})}^{\mu^v_{\mathrm{An}}(T, p^v_{\mathrm{A}}(T, p^l), x^{v'}_{\mathrm{An}}} \frac{\partial\mu^v_{\mathrm{An}}}{\partial x^v_{\mathrm{An}}}\,\mathrm{d}x^v_{\mathrm{An}}. \quad (19)\end{aligned}$$

Since equilibrium was maintained in the vapor and liquid phases of A as the pressure applied to the liquid increased from p^l to $p^l + \Delta p^l$, in Figure 3C and D, then $\Delta\mu^l_{\mathrm{An}}$ must equal $\Delta\mu^v_{\mathrm{An}}$ under all circumstances. Under the condition that T remained constant, it follows from Eqs (17) and (19) that

$$\begin{aligned}&\int_{p^l}^{p^l+\Delta p^l} \bar{V}^l_{\mathrm{An}}\,\mathrm{d}p^l + \mu^l_{\mathrm{An}}(T, p^l, x^{l'}_{\mathrm{An}}) - \mu^l_{\mathrm{An}}(T, p^l, x^l_{\mathrm{An}}) \\ &\quad = \int_{p^v_{\mathrm{A}}(T, p^l)}^{p^v_{\mathrm{A}}(T, p^l+\Delta p^l)} \bar{V}^v_{\mathrm{An}}\,\mathrm{d}p^v_{\mathrm{A}} + \mu^v_{\mathrm{An}}(T, p^v_{\mathrm{A}}(T, p^l), x^{v'}_{\mathrm{An}}) - \mu^v_{\mathrm{An}}(T, p^v_{\mathrm{A}}(T, p^l), x^v_{\mathrm{An}}). \\ &\qquad\qquad (20)\end{aligned}$$

If x^l_{An} is not affected by pressure applied to liquid A and if x^v_{An} is constant then Eq. (20) becomes

$$\left.\int_{p^l}^{p^l+\Delta p^l} \bar{V}^l_{\mathrm{An}}\,\mathrm{d}p^l\right|_{T,\,x^l_{\mathrm{An}}} = \int_{p^v_{\mathrm{A}}(T,\,p^l,\,x^v_{\mathrm{An}})}^{p^v_{\mathrm{A}}(T,\,p^l+\Delta p^l,\,x^v_{\mathrm{An}})} \bar{V}^v_{\mathrm{An}}\,\mathrm{d}p^v_{\mathrm{A}}. \tag{20a}$$

Liquid A in Hulett's column

Consider a closed system in a gravity field at constant T consisting of liquid A and vapor A composed of polymers $(\mathrm{A})_{\mathrm{j}}$ from $\mathrm{j} = 1$ to N, Figure 2B. Liquid A in Figure 2A is pure A, either pure monomer $(\mathrm{A})^l_1$ or a pure polymer $(\mathrm{A})^l_{\mathrm{n}}$, whereas liquid A and vapor A in Figure 2B are solutions of polymers. The mass of polymer $(\mathrm{A})_{\mathrm{j}}$ equals j times the mass of monomer $(\mathrm{A})_1$ in both the liquid and vapor phases. As illustrated in Figure 2B, the distribution of each $(\mathrm{A})_{\mathrm{j}}$ in the gravity field in both phases is governed, in part, by the same Boltzmann distribution law as in a pure monomer or pure polymer, namely,

$$N^v_{\mathrm{Aj}}(z)/N^v_{\mathrm{Aj}}(h) = \exp - \frac{m_{\mathrm{Aj}}g(z-h)}{kT} \tag{5h}$$

for $z > h$ and

$$N^l_{\mathrm{Aj}}(z)/N^l_{\mathrm{Aj}}(o) = \exp - \frac{m_{\mathrm{Aj}}gz}{kT} \tag{5i}$$

for $h > z > o$ in the right cylinder and for $2h + \Delta h^l_{\mathrm{A}} > z > o$ in the left cylinder. Furthermore, the distribution between the liquid and vapor phases of each polymer is governed by Boltzmann's law, namely,

$$N^v_{\mathrm{Aj}}(h)/N^l_{\mathrm{Aj}}(h) = \exp - \frac{\Delta\bar{H}^{vl}_{\mathrm{Aj}}(h) - p^v_{\mathrm{A}}(h)\,\Delta\bar{V}^{vl}_{\mathrm{Aj}}(h)}{RT} \tag{5j}$$

at $z = h$; and at $z = 2h + \Delta h^l_{\mathrm{A}}$

$$\begin{aligned} &N^v_{\mathrm{Aj}}(2h + \Delta h^l_{\mathrm{A}})/N^l_{\mathrm{Aj}}(2h + \Delta h^l_{\mathrm{A}}) \\ &\quad = \exp - \frac{\Delta\bar{H}^{vl}_{\mathrm{Aj}}(2h + \Delta h^l_{\mathrm{A}}) - p^v_{\mathrm{A}}(2h + \Delta h^l_{\mathrm{A}})\,\Delta\bar{V}^{vl}_{\mathrm{Aj}}(2h + \Delta h^l_{\mathrm{A}})}{RT} \end{aligned} \tag{5k}$$

where the molar enthalpies for evaporation and the increase in molar volumes during evaporation pertain to their respective values at h and at $2h + \Delta h^l_{\mathrm{A}}$.

The number of every vapor polymer is less at $z > h$ than at h so that $\sum_{\mathrm{j}} N^v_{\mathrm{Aj}}(z) < \sum_{\mathrm{j}} N^v_{\mathrm{Aj}}(h)$ and $p^v_{\mathrm{A}}(z) = \sum_{\mathrm{j}} p^v_{\mathrm{Aj}}(z) < \sum_{\mathrm{j}} p^v_{\mathrm{Aj}}(h) = p^v_{\mathrm{A}}(h)$. Moreover, the number of a massive polymer decreases more with z than does the number of a light polymer. The mole fraction of any polymer $(A)^v_n$ at any $z > h$ is

$$x^v_{An}(z) = \frac{N^v_{An}(z)}{\sum_j N^v_{Aj}(z)}. \tag{21}$$

Likewise, the number of every liquid polymer is less at $z > o$ than at o so that $\sum_j N^l_{Aj}(z) < \sum_j N^l_{Aj}(o)$. The mole fraction of polymer $(A)^l_n$ is

$$x^l_{An}(z) = \frac{N^l_{An}(z)}{\sum_j N^l_{Aj}(z)}. \tag{22}$$

Thus, the mole fraction of a large polymer is reduced at $z > h$ and is least at $2h + \Delta h^l_A$. The mole fraction of the monomer or a small polymer is increased at $z > h$ and is least at h.

On the other hand, chemical equilibria are tending to maintain the mole fraction of every polymer independent of z. At every z polymer $(A)^l_n$ is in equilibrium with its reaction products,

$$(A)^l_n \rightleftharpoons (A)^l_{n-m} + (A)^l_m.$$

The energy states of the reactant and the products differ so that the distribution between reactant and products is given by the Boltzmann distribution. In the liquid phase, this is at constant T

$$\frac{N^l_{An}(T, p^l_A, z)}{N^l_{A(n-m)}(T, p^l_A, z) N^l_{Am}(T, p^l_A, z)} = \exp - \frac{\Delta \bar{H}^l_{A(n,n-m+m)} - p^l_A \Delta \bar{V}^l_{A(n,n-m+m)}}{RT} \tag{5l}$$

where $\Delta \bar{H}^l_A$ is the change of molar enthalpy and $\Delta \bar{V}^l_A$ is the molar volume increase for the reaction. Equation (5*l*) is also the equilibrium constant for the reaction, since

$$k^l_n = \frac{[(A)^l_n]}{[(A)^l_{n-m}][(A)^l_m]}.$$

Similarly, in the vapor phase at every z, polymer $(A)^v_n$ is in equilibrium with its reaction products $(A)^v_{n-m}$ and $(A)^v_m$ and the distribution between these polymers is at constant T

$$\frac{N^v_{An}(T, p^v_A, z)}{N^v_{A(n-m)}(T, p^v_A, z) N^v_{Am}(T, p^v_A, z)} = \exp - \frac{\Delta \bar{H}^v_{A(n,n-m+m)} - p^v_A \Delta \bar{V}^v_{A(n,n-m+m)}}{RT} \tag{5m}$$

where $\Delta \bar{H}^v_A$ is the change of molar enthalpy and $\Delta \bar{V}^v_A$ is the molar volume increase for the reaction. Equation (5*m*) is also the equilibrium constant for the reaction in the vapor phase, k^v_{An}. The enthalpy change for the reaction is the same in the liquid and vapor phases. The change of pressure-volume work for the reaction is the same in both phases so that $p^l_{\mathrm{A}}\Delta \bar{V}^l_{\mathrm{A}} = p^v_{\mathrm{A}}\Delta \bar{V}^v_{\mathrm{A}}$. Thus, the right sides of Eqs (5*l*) and (5*m*) are the same so that the distribution of polymer $(\mathrm{A})_{\mathrm{n}}$ with respect to $(\mathrm{A})_{\mathrm{n-m}}$ and $(\mathrm{A})_{\mathrm{m}}$ is the same in both phases at every $z > h$. Moreover, at every z the law of mass action and the equilibrium between $(\mathrm{A})_{\mathrm{n}}$ and $(\mathrm{A})_{\mathrm{n-m}}$ and $(\mathrm{A})_{\mathrm{m}}$ will tend to maintain the mole fraction of each polymer independent of z, whereas gravity tends to make each mole fraction dependent upon z. In any case, the mole fractions are the same in the liquid and vapor phases at every $z > h$.

Every polymer $(\mathrm{A})_{\mathrm{j}}$ in Figure 2B from h to $2h + \Delta h^l_{\mathrm{A}}$ increases in gravitational energy in both the vapor and liquid phases an amount $jm_{A_1}g(h + \Delta h^l_{\mathrm{A}})$. Δh^l_{A} is the distension of liquid A and of polymer $(\mathrm{A})^l_{\mathrm{j}}$ due to the increase in weight of a unit column of liquid A from h to $2h + \Delta h^l_{\mathrm{A}}$, namely $\int_h^{2h+\Delta h^l_{\mathrm{A}}} \rho^l_{\mathrm{A}}(z)\,\mathrm{d}z$. The product of this distension and this tension is pressure-volume work performed by each polymer $(\mathrm{A})^l_{\mathrm{j}}$ in liquid A, and this work is exactly equal to $jm_{\mathrm{A}_1}g(h + \Delta h^l_{\mathrm{A}})$. Whatever the combined effects of the chemical equilibria between polymers and the gravitational field on the distributions of polymers in liquid A and vapor A, their distributions are identical at any $z > h$. Thus, $x^v_{\mathrm{Aj}}(h) = x^l_{\mathrm{Aj}}(h)$ and $x^v_{\mathrm{Aj}}(2h + \Delta h^l_{\mathrm{A}}) = x^l_{\mathrm{Aj}}(2h + \Delta h^l_{\mathrm{A}})$. This ensures that the vapor pressures of liquid A equals the vapor pressures of vapor A at any z and $z = 2h + \Delta h^l_{\mathrm{A}}$ for every $(\mathrm{A})_{\mathrm{j}}$.

If pure liquid A and pure vapor A in Figure 2A were pure $(\mathrm{A})^{lo}_{\mathrm{j}}$ and $(\mathrm{A})^{vo}_{\mathrm{j}}$, respectively, then for every $(\mathrm{A})_{\mathrm{j}}$ in Figures 2A and 2B, the increase in its gravitational energy is the same in both liquid and vapor phases. This increase in gravitational energy at the surfaces of the columns on the left in both figures equals the pressure-volume work performed by polymer $(\mathrm{A})^l_{\mathrm{j}}$ at these surfaces. In these thought experiments of Figures 2A and 2B, several features of the liquid and vapor are interrelated: 1) the distributions of $(\mathrm{A})_{\mathrm{j}}$ with z in a gravity field; 2) the chemical equilibria between the polymers; 3) the increasing tension and distension of liquid A; and 4) the increasing pressure-volume work by each $(\mathrm{A})^{\mathrm{l}}_{\mathrm{j}}$. There is not one effect without the other. There may be still another effect if $\Delta \bar{V}^l_{\mathrm{A(n,n-m+m)}}$ in Eq. (5*l*) and $\Delta \bar{V}^v_{\mathrm{A(n,n-m+m)}}$ in Eq. (5*m*) are not zero. In this case, the equilibrium constant for any polymer will affect its mole fraction $x^l_{\mathrm{An}}(z)$ and the mole fractions of its reaction products. Pressure may also affect the partial molar enthalpy $\Delta \bar{H}^{vl}_{\mathrm{Aj}}$ and the partial molar volume expansion $\Delta \bar{V}^{vl}_{\mathrm{Aj}}$ in Eqs (5*j*) and (5*k*) so that the distribution of $(\mathrm{A})^l_{\mathrm{j}}$ between the liquid and vapor phases may differ at h and $2h + \Delta h^l_{\mathrm{A}}$ for liquid A in Figure 2B and differ at h and $2h + \Delta h^{lo}_{\mathrm{A}}$ for pure liquid $(\mathrm{A})^{lo}_{\mathrm{j}}$ in Figure 2A. Nevertheless, in all cases, $x^{lo}_{\mathrm{Aj}}(h) = x^{vo}_{\mathrm{Aj}}(h)$ and $x^{lo}_{\mathrm{Aj}}(2h + \Delta h^{lo}_{\mathrm{A}}) = x^{vo}_{\mathrm{Aj}}(2h + \Delta h^{lo}_{\mathrm{A}})$ in Figure 2A and $x^l_{\mathrm{Aj}}(h) = x^v_{\mathrm{Aj}}(h)$ and $x^l_{\mathrm{Aj}}(2h + \Delta h^l_{\mathrm{A}}) = x^v_{\mathrm{Aj}}(2h + \Delta h^l_{\mathrm{A}})$ in Figure 2B.

Osmotic pressure of polymer $(\mathrm{A})^l_{\mathrm{n}}$ in liquid A and its partial molar quantities

The chemical potential of $(\mathrm{A})^l_{\mathrm{n}}$ in liquid A is less than the chemical potential of pure liquid $(\mathrm{A})^{l\mathrm{o}}_{\mathrm{n}}$ at the same T and p^l. However, if the pressure applied to pure liquid $(\mathrm{A})^{l\mathrm{o}}_{\mathrm{n}}$ is lowered to $p^l - \pi_{\mathrm{An}}$, then its chemical potential at T becomes equal to the chemical potential of $(\mathrm{A})^l_{\mathrm{n}}$ in liquid A at T and p^l, i.e.,

$$\mu^l_{\mathrm{An}}(T, p^l, x^l_{\mathrm{An}}) = \mu^{l\mathrm{o}}_{\mathrm{An}}(T, p^l - \pi_{\mathrm{An}}). \tag{23}$$

Likewise, the chemical potential of $(\mathrm{A})^l_{\mathrm{n}}$ can be increased by increasing the pressure applied to liquid A from p^l to $p^l + \pi'_{\mathrm{An}}$; so again the chemical potentials of $(\mathrm{A})^l_{\mathrm{n}}$ and $(\mathrm{A})^{l\mathrm{o}}_{\mathrm{n}}$ are equal, i.e.,

$$\mu^l_{\mathrm{An}}(T, p^l + \pi'_{\mathrm{An}}, x^{l'}_{\mathrm{An}}) = \mu^{l\mathrm{o}}_{\mathrm{An}}(T, p^l). \tag{24}$$

If $\Delta p^l = \pi'_{\mathrm{An}}$ in Eq. (17) and $\Delta p^l = \pi_{\mathrm{An}}$ in Eq. (6) and if Eqs (6) and (17) are summed, then with Eqs (23) and (24), the left side is zero so that at constant T

$$\int_{p^l}^{p^l + \pi'_{\mathrm{An}}} \bar{V}^l_{\mathrm{An}}\, \mathrm{d}p^l \bigg|_{T, n^l_{\mathrm{j}}} + [\mu^l_{\mathrm{An}}(T, p^l, x^{l'}_{\mathrm{An}}) - \mu^l_{\mathrm{An}}(T, p^l, x^l_{\mathrm{An}})]_{n_{\mathrm{j}} \neq n_{\mathrm{n}}}$$
$$= \int_{p^l - \pi_{\mathrm{An}}}^{p^l} \bar{V}^{l\mathrm{o}}_{\mathrm{An}}\, \mathrm{d}p^l \bigg|_{T}. \tag{25}$$

Subtracting Eq. (23) from Eq. (24),

$$\mu^l_{\mathrm{An}}(T, p^l + \pi'_{\mathrm{An}}, x^{l'}_{\mathrm{An}}) - \mu^l_{\mathrm{An}}(T, p^l, x^l_{\mathrm{An}}) = \mu^{l\mathrm{o}}_{\mathrm{An}}(T, p^l) - \mu^{l\mathrm{o}}_{\mathrm{An}}(T, p^l - \pi_{\mathrm{An}}). \tag{26}$$

Equations (25) and (26) state that increasing the pressure applied to the solution from p^l to $p^l + \pi'_{\mathrm{An}}$ is exactly the same as increasing the pressure applied to pure liquid $(\mathrm{A})^{l\mathrm{o}}_{\mathrm{n}}$ from $p^l - \pi_{\mathrm{An}}$ to p^l at constant T. π'_{An} is the osmotic pressure of species $(\mathrm{A})^l_{\mathrm{n}}$ in solution A at T and $p^l + \pi'_{\mathrm{An}}$ when its mole fraction is $x^{l'}_{\mathrm{An}}$ whereas π_{An} is the osmotic pressure of species $(\mathrm{A})^l_{\mathrm{n}}$ in solution A at T, p^l, x^l_{An}. If the mole fraction of $(\mathrm{A})^l_{\mathrm{n}}$ is not altered by pressure, then $\pi'_{\mathrm{An}} = \pi_{\mathrm{An}}$ and the second term on the left side of Eq. (25) is zero.

The osmotic pressure of polymer $(\mathrm{A})^l_{\mathrm{n}}$ in liquid A is depicted by the height $(h' - h)$ in the Hulett column, Figure 4. The semi-permeable membranes separating both the liquid and the vapor phases of A from pure $(\mathrm{A})^0_{\mathrm{n}}$ are permeable to polymer $(\mathrm{A})_{\mathrm{n}}$ and to no other polymer $(\mathrm{A})_{\mathrm{j} \neq \mathrm{n}}$ in A. Clearly, Figure 4 is a metastable representation of the thermodynamic equilibrium between polymer $(\mathrm{A})_{\mathrm{n}}$ in liquid A and pure polymer $(\mathrm{A})^0_{\mathrm{n}}$. Even if pure $(\mathrm{A})^{l\mathrm{o}}_{\mathrm{n}}$ could be produced and placed in the two cylinders on the right, it would not remain as such for long since it would soon react to form other polymers and become like liquid A in the left cylinder. Nevertheless, it is instructive to consider the thermodynamic, osmotic and vapor pressure equilibria between $(\mathrm{A})^l_{\mathrm{n}}$ in liquid A and pure $(\mathrm{A})^{l\mathrm{o}}_{\mathrm{n}}$.

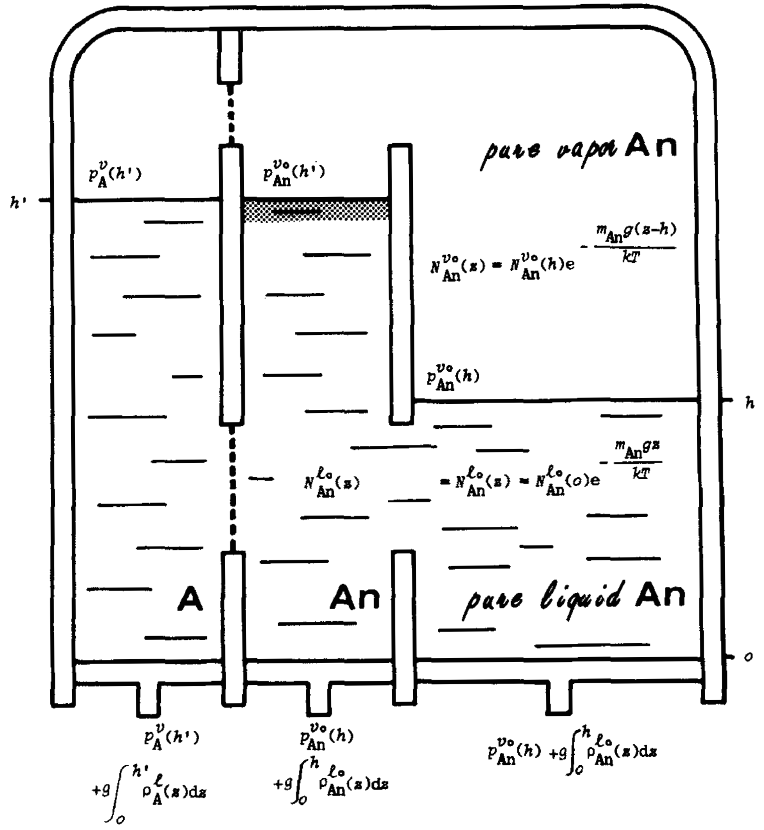

FIGURE 4 Pure liquid $(A)^{lo}_{n}$ in a Hulett column in equilibrium with its vapor $(A)^{vo}_{n}$ and with liquid polymer $(A)^{l}_{n}$ in liquid A. Liquid A and vapor A are solutions of polymers and are separated from pure liquid $(A)^{lo}_{n}$ and pure vapor $(A)^{vo}_{n}$ by rigid membranes permeable only to polymer $(A)_{n}$. The osmotic pressure of polymer $(A)_{n}$ in liquid A is the difference in pressures applied to liquid A in the left column and to pure liquid $(A)^{lo}_{n}$ in the middle column as the liquids $(A)^{l}_{n}$ and $(A)^{lo}_{n}$ have the same chemical potential at every z from o to h'.

The equilibrium height of the free surface of liquid A in the left cylinder is $(h' - h)$ above the surface of pure liquid $(A)^{lo}_{n}$ in the right cylinder. The middle cylinder contains pure liquid $(A)^{lo}_{n}$ with its surface supported by a matrix at the same height as the equilibrium height h' of liquid A in the left cylinder. Since the weight of pure liquid $(A)^{lo}_{n}$ in the middle cylinder from o to h is supported by the pressure applied by the piston below the liquid, the tension in pure liquid $(A)^{lo}_{n}$ at h' must be $g\int_{h}^{h'} \rho^{lo}_{An}(z)\,dz - p^{vo}_{An}(h')$. Moreover, the distributions of pure liquid $(A)^{lo}_{n}$ and pure vapor $(A)^{vo}_{n}$ in the middle and right cylinders at $z > h$ are the same relative to their respective concentrations at h so that their vapor pressures are also equal at $z = h'$. The liquid and vapor of

$(A)_n$ in the left cylinder are in osmotic equilibrium with the liquid and vapor of pure $(A)_n^0$ in the middle cylinder. It follows that: 1) the tension and distension of polymer $(A)_n^l$ between h to h', 2) the pressure-volume work performed by $(A)_n^l$, 3) the gravitational energy increase of polymer $(A)_n^l$, 4) the distribution of $(A)_n^l$ between h and h' and 5) the vapor pressure of $(A)_n^l$ at h' must all be exactly the same as for pure liquid $(A)_n^{lo}$ in the middle cylinder between h and h'.

The mole fraction of polymer $(A)_n^l$ in liquid A may have changed from h to h' due to the combined effects of: 1) its mass relative to the mass of other polymers tending to change $x_{An}^l(z)$, 2) the effect of the redistribution of polymers so as to keep the ratio $[(A)_n^l]/[(A)_{n-m}^l][(A)_m^l]$ equal to its equilibrium constant, and 3) the effect of tension on its equilibrium constant. Any change in the mole fraction of $(A)_n^l$ from h to h' would change its chemical potential at h' relative to its chemical potential at h, i.e., if $x_{An}^l(h') \neq x_{An}^l(h)$, then $\mu_{An}^l(T, p_A^l, x_{An}^l(h')) \neq \mu_{An}^l(T, p_A^l, x_{An}^l(h))$ at constant T and p_A^l. Nevertheless, the chemical potentials of $(A)_n$ in the left and middle columns of Figure 4 are the same at any z; and at $z = h'$, $\mu_{An}^l(T, p_A^v(h'), x_{An}^l(h')) = \mu_{An}^{lo}(T, p_{An}^{vo}(h'))$. Moreover, the change in chemical potential of polymer $(A)_n^l$ from h to h' due to the increase in its internal tension equals the change in chemical potential of pure polymer $(A)_n^{lo}$ from h *to* h' due to the increase in its tension, namely $g \int_h^{h'} \rho_{An}^{lo}(z)\,dz$.

The osmotic pressure of polymer $(A)_n^l$ in liquid A is the difference in the pressure applied to liquid A and the pressure applied to pure liquid $(A)_n^{lo}$ for which their chemical potentials are equal at constant T. In Figure 4, the pressure applied to liquid A at h' is $p_A^v(h') = \sum_j p_{Aj}^v(h')$ whereas the pressure applied to pure liquid $(A)_n^{lo}$ is $p_{An}^{vo}(h') - \int_h^{h'} \rho_{An}^{lo}(z)\,dz$. Thus,

$$\pi_{An}(h') = p_A^v(h') - p_{An}^{vo}(h') + \int_h^{h'} \rho_{An}^{lo}(z)\,dz. \tag{27}$$

On the other hand, at h in Figure 4, the pressure applied to liquid A is $p_A^v(h') + \int_h^{h'} \rho_A^l(z)\,dz$ as the pressure applied to pure liquid $(A)_n^{lo}$ is $p_{An}^{vo}(h)$; so that

$$\pi_{An}(h) = p_A^v(h') + \int_h^{h'} \rho_A^l(z)\,dz - p_{An}^{vo}(h). \tag{28}$$

It is worthwhile to repeat that the pressure-volume work performed on $(A)_n^l$ from h' to h is equal to the decrease in the gravitational energy of $(A)_n^l$ from h' to h, regardless of any change in $x_{An}^l(z)$ from h' to h in the left column of Figure 4. It is the combined effect of pressure change and change in mole fraction which changes the chemical potential of $(A)_n^l$ from h' to h. Thus, the increase in pressure and change in mole fraction from h' to h renders the chemical potential of $(A)_n^l$ at h equal to the chemical potential of $(A)_n^{lo}$ at h.

Also, the decrease in pressure from h to h' renders the chemical potential of $(\mathrm{A})^{lo}_{\mathrm{n}}$ at h' equal to the chemical potential of $(\mathrm{A})^{l}_{\mathrm{n}}$ at h'. Since $\mu^{l}_{\mathrm{An}}(h) = \mu^{lo}_{\mathrm{An}}(h)$, it follows that

$$\mu^{l}_{\mathrm{An}}\left(T, p^{v}_{\mathrm{A}}(h') + \int_{h}^{h'} \rho^{l}_{\mathrm{A}}(z)\,\mathrm{d}z, x^{l}_{\mathrm{An}}(h)\right) = \mu^{lo}_{\mathrm{An}}(T, p^{vo}_{\mathrm{An}}(h)); \tag{29}$$

and since $\mu^{l}_{\mathrm{An}}(h') = \mu^{lo}_{\mathrm{An}}(h')$, it follows that

$$\mu^{l}_{\mathrm{An}}(T, p^{v}_{\mathrm{A}}(h'), x^{l}_{\mathrm{An}}(h')) = \mu^{lo}_{\mathrm{An}}\left(T, p^{vo}_{\mathrm{An}}(h') - \int_{h}^{h'} \rho^{lo}_{\mathrm{An}}(z)\,\mathrm{d}z\right). \tag{30}$$

If we let $p^{vo}_{\mathrm{An}}(h)$ in Eq. (29) equal p^{l}, then according to the definition of $\pi_{\mathrm{An}}(h)$, Eq. (28), Eq. (29) becomes

$$\mu^{l}_{\mathrm{An}}(T, p^{l} + \pi_{\mathrm{An}}(h), x^{l}_{\mathrm{An}}(h)) = \mu^{lo}_{\mathrm{An}}(T, p^{l}). \tag{31}$$

Likewise, if we let $p^{v}_{\mathrm{A}}(h')$ in Eq. (30) equal $p^{l'}$, then according to the definition of $\pi_{\mathrm{An}}(h')$, Eq. (27), Eq. (30) becomes

$$\mu^{l}_{\mathrm{An}}(T, p^{l'}, x^{l}_{\mathrm{An}}(h')) = \mu^{lo}_{\mathrm{An}}(T, p^{l'} - \pi_{\mathrm{An}}(h')). \tag{32}$$

The important conclusion to be drawn from this thought experiment is that whatever the mole fraction of polymer $(\mathrm{A})^{l}_{\mathrm{n}}$ may be, $x^{l}_{\mathrm{An}}(h)$ in Eq. (31) or $x^{l}_{\mathrm{An}}(h')$ in Eq. (32), its chemical potential always differs from the chemical potential of pure $(\mathrm{A})^{lo}_{\mathrm{n}}$ at the same T and applied pressure precisely as if it is internally subjected to an enhanced tension, $\pi_{\mathrm{An}}(h')$ at h' or $\pi_{\mathrm{An}}(h)$ at h. This statement may be generalized for any partial molar quantity $\bar{Z}^{l}_{\mathrm{An}}(h) = \bar{Z}^{lo}_{\mathrm{An}}(h)$ or $\bar{Z}^{l}_{\mathrm{An}}(h') = \bar{Z}^{lo}_{\mathrm{An}}(h')$ at any constant temperature T. Thus,

$$\bar{Z}^{l}_{\mathrm{An}}(T, p^{l} + \pi_{\mathrm{An}}(h), x^{l}_{\mathrm{An}}(h)) = \bar{Z}^{lo}_{\mathrm{An}}(T, p^{l}), \tag{33}$$

and

$$\bar{Z}^{l}_{\mathrm{An}}(T, p^{l'}, x^{l}_{\mathrm{An}}(h')) = \bar{Z}^{lo}_{\mathrm{An}}(T, p^{l'} - \pi_{\mathrm{An}}(h')). \tag{34}$$

$\bar{Z}^{l}_{\mathrm{An}}$ may be the partial molar volume of $(\mathrm{A})_{\mathrm{n}}$, its partial molar enthalpy of vaporization, etc.

Internal tension in polymer $(\mathrm{A})^{l}_{\mathrm{n}}$

The internal tension in polymer $(\mathrm{A})^{l}_{\mathrm{n}}$ in liquid A is designated τ_{An}.

Let us assume that liquid A consists of polymers of various sizes from 1 to N. The molar amount of liquid A must equal the sum of the moles of polymers of each size,

$$\sum_{\mathrm{j}} n^{l}_{\mathrm{Aj}} = n^{l}_{A1} + n^{l}_{\mathrm{A2}} + \cdots + n^{l}_{\mathrm{AN}}.$$

This number is necessarily less than M^l_A/MW_{A1}, where MW_{A1} is the molecular weight of monomer $(A)_1$ in liquid A. Obviously, when polymers form, there are fewer molecules in random motion in M^l_A than if M^l_A were all monomers. Since the kinetic energy in liquid A is partitioned equally between all $\sum_j n^l_{Aj}L$ centers of mass, the average kinetic energy of each center of mass will be the same without regard to its size.

As all polymers are internally reflected from the free surface of the liquid of volume V^l_A, their thermal pressure at the boundary will be $RT\sum_j n^l_{Aj}/V^l_A$. The internal tension between polymers of size n, τ_{An}, opposing that pressure will be (according to a principle explained in Ref. 2, pp. 260–263 and footnote 3) the thermal pressure from all polymers divided by the fraction of the liquid surface consisting of polymer $(A)^l_n$. Assuming that the surface fraction and volume fraction of polymer $(A)^l_n$ are the same and equal to $n^l_{An}\bar{V}^l_{An}/V^l_A$, then

$$\tau_{An} = \frac{RT(n^l_{A_1} + n^l_{A_2} + \cdots + n^l_{AN})}{n^l_{An}\bar{V}^l_{An}},$$

or

$$= \frac{RT}{x^l_{An}\bar{V}^l_{An}}. \tag{35}$$

Internal tension and osmotic pressure of liquid polymer $(A)^l_n$

If all molecules in liquid A were pure polymer $(A)^{lo}_n$, there would be $n^{lo}_{An} = M^l_A/MW_{An}$ moles in a volume V^{lo}_{An}. Then the internal tension, τ^0_{An}, in this polymer would be the tension opposing the total thermal force exerted by the polymer per unit of surface divided by the fraction of the unit area consisting of this polymer, namely 1. That is,

$$\tau^0_{An} = \frac{RTn^{lo}_{An}}{V^{lo}_{An}} \div \frac{n^{lo}_{An}\bar{V}^{lo}_{An}}{V^{lo}_{An}}$$

$$= \frac{RT}{\bar{V}^{lo}_{An}}. \tag{36}$$

This, of course, assumes that the pressure applied to the pure liquid polymer $(A)^{lo}_n$ is zero. The tension in polymer $(A)^l_n$ in liquid A, τ_{An}, exceeds the tension in pure polymer $(A)^{lo}_n$ by an amount

$$\tau_{An} - \tau^0_{An} = \frac{RT}{x^l_{An}\bar{V}^l_{An}} - \frac{RT}{\bar{V}^{lo}_{An}}. \tag{37}$$

If we define $\pi_{An} = (\tau_{An} - \tau^0_{An})$, then according to Eq. (34), $\bar{V}^l_{An}(T, p^l, x^l_{An}) = \bar{V}^{lo}_{A}(T, p^l - \pi_{An})$, and to Eq. (37), π_{An} becomes

$$\pi_{An} = RT\left(\frac{1}{x^l_{An}\,\bar{V}^{lo}_{An}(T, p^l - \pi_{An})} - \frac{1}{\bar{V}^{lo}_{An}(T, p^l)}\right) \tag{38}$$

When dimers, trimers, etc., form in liquid A, the chemical potential of the monomer in liquid A is less than the chemical potential of pure monomer $(A)^{lo}_1$ at the same T and p^l by an amount

$$\mu^l_{A1}(T, p^l, x^l_{A1}) - \mu^{lo}_{A1}(T, p^l) = \int_{p^l}^{p^l - \pi_{A1}} \bar{V}^{lo}_{A1}\, dp^l.$$

Similarly, the chemical potential of each polymer in liquid A is less than the chemical potential of its pure polymer at the same T and p^l. When polymers form, polymerization lowers the chemical potential of every polymer. Thus, polymerization lowers the free energy of the liquid A system.

The relative abundance of a polymer of size n in liquid A is determined by the strength of the bond between its n molecules relative to the strength of the bond between the molecules in polymers of other sizes. That is, in accord with the Boltzmann distribution, Eq. (5l), polymer $(A)^l_n$ will be more abundant to the extent that its internal molar energy is less than the internal molar energies of the polymers $(A)^l_{n-m}$ and $(A)^l_m$. Then the decrease in internal energy will be large when $(A)^l_n$ is formed from $(A)^l_{n-m}$ and $(A)^l_m$ so that $\Delta\bar{U}_{A(n-m+m,n)} \equiv \bar{U}_{An} - (\bar{U}_{A(n-m)} + \bar{U}_{Am}) \ll 0$, and the exponent in Eq. (5l) is positive and large. Although the molar energy of polymer $(A)^l_n$ may differ greatly from the combined molar energies of $(A)^l_{n-m}$ and $(A)^l_m$, the Gibbs molar free energy of $(A)^l_n$ equals the Gibbs molar free energies of $(A)^l_{n-m}$ and $(A)^l_m$ when in equilibrium, i.e., $\Delta\bar{G}^l_{A(n-m+M,n)} = 0$.

According to Eq. (35), the internal tension in polymer $(A)^l_n$ is determined by the moles of all polymers relative to the moles of polymer $(A)^l_n$. Thus, τ_{An} as well as π_{An} in Eq. (38) are large when the moles of polymer $(A)^l_n$ are few relative to the moles of monomer and other polymers of A; and according to Eq. (23), the chemical potential of polymer $(A)^l_n$ will be low relative to pure polymer $(A)^{lo}_n$ at the same T and p^l. If the molecules in liquid A are not more strongly coupled in polymer $(A)^l_n$ (i.e., higher bond energy and lower internal energy) than the polymers from which $(A)^l_n$ is formed, then the moles of polymer $(A)^l_n$ will be few in liquid A, and the chemical potential of liquid A will be diminished little by polymerization to $(A)^l_n$.

Tension applied to liquid A increases to the same extent the tension in the coupling force between polymer $(A)^l_n$ and thereby lowers its bond energy, increases its internal energy, lowers its chemical potential and its vapor pressure. Every polymer $(A)^l_j$ will be similarly affected so that the vapor pressure of each will be lowered in proportion to the tension applied to liquid

A, with no change in the mole fraction of any polymer within liquid A or in the vapor phase in equilibrium with liquid A. Likewise, the bond energy of the n molecules within polymer $(A)^l_n$ is lessened by tension between them and their internal energy is increased. We may presume that a tension applied to liquid A not only increases the tension in the coupling force for the n^l_{An} moles of polymer $(A)^l_n$ but also increases the tension in the coupling for the n molecules within $(A)^l_n$ and thereby increases the internal energy of the latter. Since we may also presume that the internal tension between the n^l_{An} moles of polymer $(A)^l_n$ in liquid A, τ_{An}, will also induce the same tension between the n molecules within each polymer $(A)^l_n$, then, as polymer $(A)^l_n$ becomes more abundant so that τ_{An} diminishes, this reduced tension will increase the bond energy and diminish the internal energy of the n molecules within $(A)^l_n$ and enhance the abundance of $(A)^l_n$. Only if the bonding between the n molecules of $(A)^l_n$ is strong and the internal energy is small relative to polymers of another size, will the number of $(A)^l_n$ increase to become the dominant polymer in liquid A. If the molecules in $(A)^l_n$ are only slightly more strongly bonded than between monomers of liquid A, liquid A will remain as monomers, and the tension between these molecules will be minimized.

Clearly, the partial molar quantities and colligative properties of polymer $(A)^l_n$ in liquid A are derived from the stronger attractive force between molecules within polymer $(A)^l_n$ compared with the attractive force between polymer $(A)^l_n$ and the other polymers of size 1 to N. Furthermore, these quantities and properties are likely to be strongly temperature dependent since clusters of size n will rapidly diminish and the number of clusters of smaller size will rapidly increase with increasing temperature.

McDougal[7] determined that the vapor of acetic acid consisted of 8.0% monomers and 92.0% dimers at 25°C when its vapor pressure was the equilibrium vapor pressure of liquid acetic acid, 15.5 mmHg. At 30°C, the equilibrium vapor pressure increased to 20.6 mmHg, and the vapor was 9.0% monomers and 91.0% dimers; that is, less dimerization at the higher temperature. Since the mole fraction of monomers was the same in liquid as in the vapor, then $x^l_{\text{ethenoic 1}} = 0.148$ at 25°C and $=0.165$ at 30°C.

CONCLUSIONS

When molecules of liquid A polymerize at T and applied pressure p^l, then each polymer $(A)^l_n$ becomes a separate species in liquid A. The chemical potential of $(A)^l_n$ is lower than the chemical potential of pure liquid polymer $(A)^{lo}_n$ at the same T and p^l by an amount

$$\mu^l_{An}(T, p^l, x^l_{An}) - \mu^{lo}_{An}(T, p^l) = \int_{p^l}^{p^l - \pi_{An}} \bar{V}^{lo}_{An}\, dp^l$$

where π_{An} is the osmotic pressure of polymer $(A)^l_n$ in liquid A, i.e. π_{An} is the difference in pressures applied to liquid A and pure liquid polymer $(A)^{lo}_n$ for which their chemical potentials are equal at the same T,

$$\mu^l_{An}(T, p^l, x^l_{An}) = \mu^{lo}_{An}(T, p^l - \pi_{An}).$$

Likewise, all partial molar quantities of liquid A are equal to the molar quantities of pure liquid polymer $(A)_n$ at the same T when the pressure applied to the latter is less than the pressure applied to the former by π_{An};

$$\bar{V}^l_{An}(T, p^l, x^l_{An}) = \bar{V}^{lo}_{An}(T, p^l - \pi_{An}),$$

$$\bar{S}^l_{An}(T, p^l, x^l_{An}) = \bar{S}^{lo}_{An}(T, p^l - \pi_{An}),$$

$$\Delta\bar{H}^l_{An}(T, p^l, x^l_{An}) = \Delta\bar{H}^{lo}_{An}(T, p^l - \pi_{An}),$$

etc.

When liquid A at T and p^l is in equilibrium with its vapor, the chemical potential of each polymer $(A)^l_n$ in the liquid must be equal to the chemical potential of that polymer in the vapor. Thus, the magnitude of $p^v_{An}(T, p^l)$ indicates the abundance of polymer $(A)^l_n$ in the vapor phase as well as in the liquid phase. The more liquid A is polymerized, the lower will be the pressure of its vapor for a given mass of liquid A per unit volume. The mole fraction of every polymer (A)n in the liquid phase must equal its mole fraction in the vapor phase when the two phases are in equilibrium, i.e., $x^l_{An} = x^v_{An}$ even as they are changed by changing the temperature or pressure applied to liquid A. We may conclude further that if the vapor consists of only one polymer, $(A)^v_n$ then only polymer $(A)^l_n$ will be found in the liquid phase. One important practical result follows from these conditions; namely, only monomers exist in pure liquid water. At every T from 0 to 100°C, there is sufficient water in the saturated vapor phase to account for the measured vapor pressure only if the water vapor is monomeric. Therefore, liquid water must also be monomeric; or if polymers exist at all in liquid water, their molar amount must be very small.

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References

1. H. T. Hammel, Hulett's enhanced solvent tension: An alternative to Lewis' diminished solvent activity. *Physics and Chemistry of Liquids*, **13**, 25–36 (1983).
2. H. T. Hammel, Solution solvent couples solute molecules and enhances their internal tension. *Physics and Chemistry of Liquids*, **13**, 255–268 (1984).

3. H. T. Hammel, Exact relationship between compressibility of solution and compressibilities of its pure constituents. *Physics and Chemistry of Liquids*, **14**, 171–179 (1985).
4. H. T. Hammel, Solubility and enhanced tension of solute in solution. *Physics and Chemistry of Liquids*, **15**, 185–202 (1985).
5. M. L. McGlashan, *Chemical Thermodynamics*, p. 75, Eq. (5.3.9). Academic Press, London (1979).
6. Ibid., p. 32, Eq. (2.7.13).
7. F. H. MacDougall, The molecular state of the vapor of acetic acid at low pressures at 25, 30, 35 and 40°C. *American Chemical Society Journal*, **58**, 2585–2591 (1936).
8. $\Delta h^{l_o}_{\mathrm{A}}/h$ is an intensive property of pure liquid A which depends on its compressibility and is independent of its other intensive properties such as $\rho^{l_o}_{\mathrm{A}}$, $\Delta\bar{H}^{vl_o}_{\mathrm{A}}$, $\bar{S}^{l_o}_{\mathrm{A}}$, $\bar{V}^{l_o}_{\mathrm{A}}$, $\mu^{l_o}_{\mathrm{A}}$, etc.