Polymer Surfaces: Properties and Characterization*

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II. Brief Outline of Polymers and Polymer Additives.

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XI. Summary

Selected References:

1. A. W. Adamson, Physical Chemistry of Surfaces, 3rd ed., Wiley, 1976.

2. J. J. Bikerman, Physical Surfaces, Academic Press, 1970.

3. D. H. Kaelble, Physical Chemistry of Adhesion, Wiley, 1971.

4. J. T. Davies and E. K. Rideal, Interfacial Phenomena, Adacemic Press, 1963, 2nd edition.

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I. CONCEPT OF SURFACE AND INTERFACE

A. Surfaces

A surface is a discontinuity. A surface is defined wherever a phase terminates. The phase may terminate at a vacuum or at the surface of another phase. The surface formed where two phases meet is an interface. Five common interfaces are known: solid/gas, solid/liquid, solid/solid, liquid/gas, and liquid/liquid.

One often speaks of a free or ideal surface; i..e, the interface made by a solid or liquid with a vacuum. Such a surface can be represented by a surface energy - a measure of the unsatisfied bonding capacity of the surface (Figure 1).
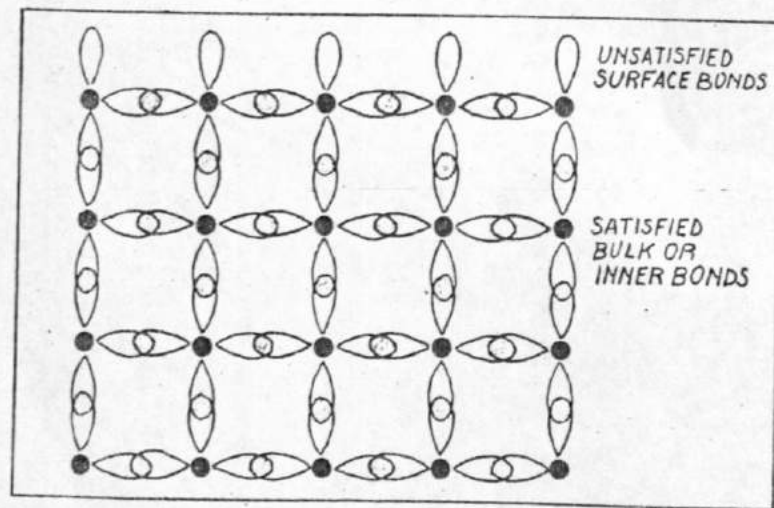

Figure 1. A schematic illustration of the unsatisfied
bonding capacity at a free surface

The surface energy may be due to unsatisfied primary bonds, as well as to secondary bonds. Using a metal as an example, we can approximate the solid surface energy from the heat of sublimation, if it is known. Such calculations are often in excellent agreement with experiment (1).

The surface energy due to secondary bond interactions can be calculated by using dipole-dipole and London dispersion potential expressions. (See References 2 and 3).

One often hears the term "surface tension" used in describing a surface. The surface atoms in any condensed phase are in an asymmetric force field, resulting in an attraction towards the bulk (Figure 2).
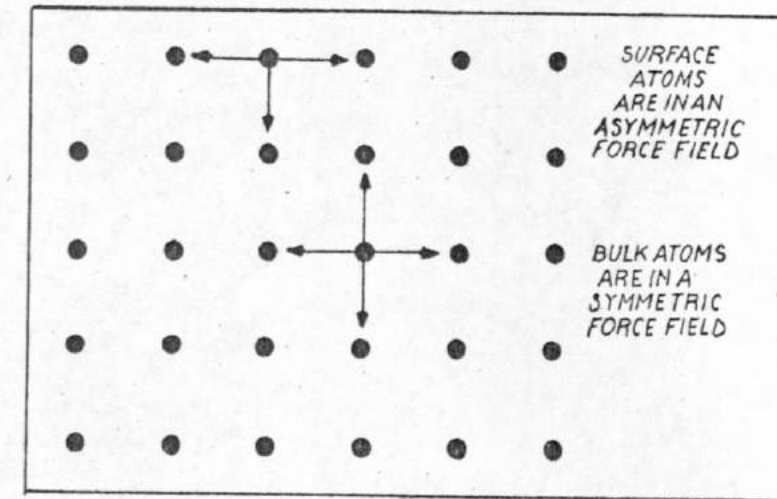

Figure 2. The asymmetric nature of the forces exerted
on surface atoms

In many condensed phases, particularly liquids, one can envision some of the surface atoms being displaced into the bulk, resulting in a surface deficient of atoms. The atom-depleted surface is then in "tension", a phenomenon called the surface tension. One of its manifestations is the tendency for the surface area to be reduced. Not all materials exhibit a surface tension. The nondeformability of many solids precludes the development of a surface tension, except at high temperatures. Thus solids may have a minimal or even zero surface tension. Under some conditions the surface may be in compression, or the surface tension is negative.

In the words of N. K. Adam (4):

"Hence every surface molecule is subject to a strong inward attraction, perpendicular to the surface. This inward attraction causes the surface to diminish in area, because the surface molecules are continually moving inwards more rapidly than others move outwards to take their places; the number of molecules in the surface is therefore continually diminishing, and the contraction of the surface continues until the maximum possible number of molecules are in the interior; i.e., until the surface is the smallest possible for a given volume, subject to the external conditions or forces acting on the drop".

Surface tension _is_ surface free energy. Work must be done to extend a liquid surface; i.e., molecules must be brought from the interior to the surface against the inward attractive forces. _Surface energy_ is a measure of the inward attractive force - the residual bonding capacity. _Surface tension_ incorporates _surface energy_ and _surface entropy_; i. e., the changes induced in the order or structure of the surface due to the existence of surface energy. Thus surface tension and surface free energy are equivalent, though the latter is certainly the preferred terminology. The units of surface tension are dynes/cm; units of surface free energy are ergs/cm^2, which are equivalent.

B. Interfaces

The free surface is a very important concept. It is often a good approximation to solid/gas or liquid/gas interfaces. However, one is often interested in interfaces, between condensed phases: solid/solid, solid/liquid, or liquid/liquid.

Consider the interface of Figure 3. γ_A represents the surface free energy of the free surface of phase A; and similarly for γ_B. The terms $\gamma_{A(B)}$ (the effect on A due to the presence of B) and $\gamma_{B(A)}$ (the effect on B due to the presence of A) serve to reduce the free energy at the interface. Thus we can say that the interfacial free energy, $\gamma_{AB} = \gamma_A - \gamma_{A(B)} + \gamma_B - \gamma_{B(A)}$. We will see later how these terms can be approximated.
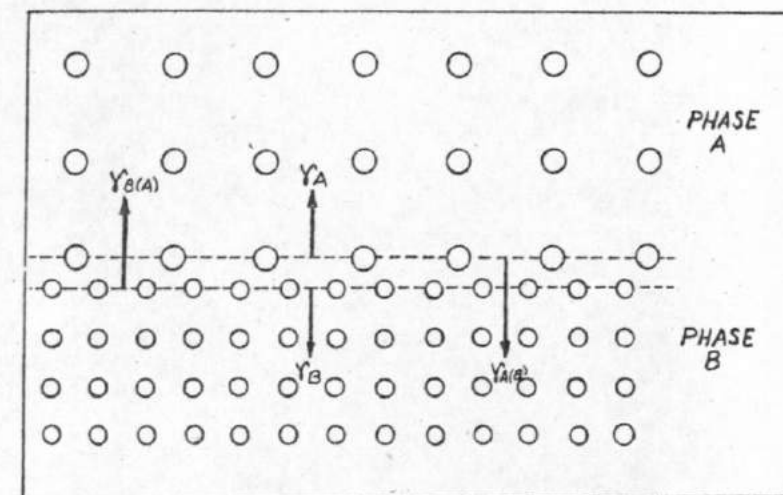
Figure 3. Hypothetical interface between two phases, A and B

The presence of B partially satisfies the unsatisfied bonding of A - and vice versa. The unsatisfied bonding capacity at the interface is known as the interfacial energy and γ_{AB} is known as the interfacial tension or interfacial free energy.
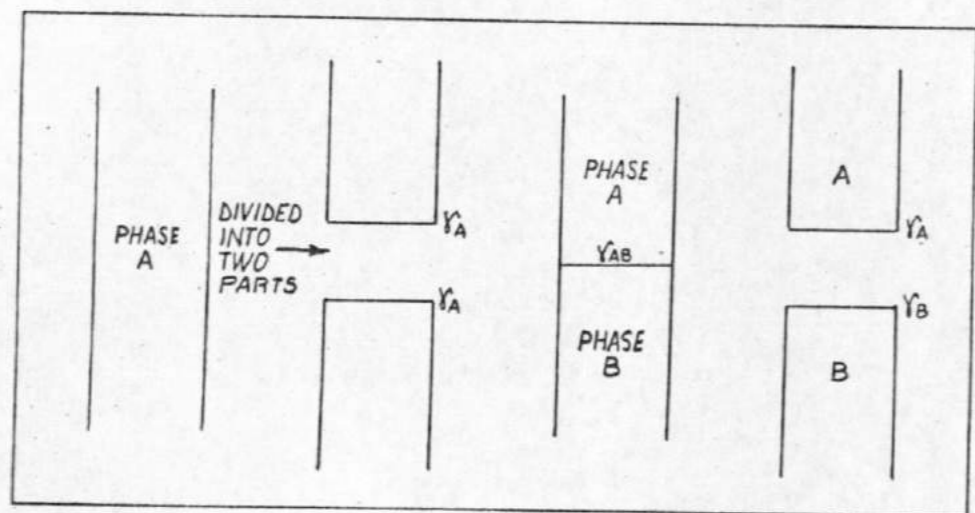
The _work of adhesion_ at an interface is a measure of the inter-phase bonding, and is defined as:

$$W_{AB} = (\gamma_A + \gamma_B) - \gamma_{AB} \tag{1}$$

or $W_{AB} = \gamma_{A(B)} + \gamma_{B(A)}$.

The _work of cohesion_ (W_c) of a single phase can be defined analagously by considering Figure 4.

It is clear that the interfacial tension between two identical phases in perfect registry must be zero; i.e., $\gamma_{AA} = 0$, and an interface does not exist.

$$\therefore W_c = 2\gamma_A \qquad (2) \qquad W_A = \gamma_A + \gamma_B - \gamma_{AB} \qquad (3)$$

Figure 4. Work of cohesion and adhesion

II. INTERFACE SEMANTICS AND THERMODYNAMICS

A. Gamma (γ)

The terms surface free energy, surface work, and surface stress are routinely used in the description of surfaces. Let us attempt to distinguish and understand these terms through a classical thermodynamic treatment (if you are a little rusty with your thermodynamics, a brief review is presented in the appendix.)

The major thermodynamic quantity which characterizes a surface or an interface is the reversible work to create unit area of surface at constant, T, V, μ_i:

$\gamma \equiv$ specific surface work; i.e., the surface work per unit area.

This quantity is not equal to the surface free energy except under certain conditions. It is not surface stress. Perhaps 100 years before the development of the energy concept, the term surface tension was used to describe the contractile nature of surface films; i.e., their tendency to minimize surface area. This term became so entrenched in the literature that it is widely used today (just as electricity is even today the flow of positive charge). Thus γ is widely called the surface tension, though the meaning of those words may have little physical significance in many situations.

We will call the surface thermodynamic quantity "Gamma", γ, with the understanding that it is some quantity characterizing the thermodynamic behavior of an interface.

The γ of a newly created surface is defined as:

$\gamma \equiv dw/dA$; i.e.,

the specific surface work to form dA new surface. The creation of a new area of surface, dA, may cause a flow of dN molecules to or from the surface region, which leads to a surface excess (or deficiency) of component i :

$$\Gamma_i \equiv dN_i/dA \equiv \text{surface excess of component } i. \tag{4}$$

Recall that (See Appendix)

$$\left. \begin{aligned} \mu_i &= \left(\frac{\partial F}{\partial N_i} \right) T, V, N_j, A \\[4pt] \mu_i &= \left(\frac{\partial G}{\partial N_i} \right) T, P, N_j, A \\[4pt] \mu_i &= \left(\frac{\partial E}{\partial N_i} \right) S, V, N_j, A \end{aligned} \right\} \tag{5}$$

Note that we are using F for Helmholtz Free Energy to avoid confusion with A, the surface area.

We will now develop expressions for surface energy, Gibbs surface free energy, and Helmholtz surface free energy - as considerable confusion exists between these terms.

$$\left. \begin{aligned} (dE)_V &= TdS + \gamma dA + \Sigma \mu_i \, \Gamma_i \, dA \\[4pt] (dF)_{T, V} &= \gamma dA + \Sigma \mu_i \, \Gamma_i dA \\[4pt] (dG)_{T, P} &= \gamma dA + \Sigma \mu_i \, \Gamma_i dA \end{aligned} \right\} \tag{6}$$

noting that $dN_i = \Gamma_i dA$

$$\left(\frac{dF}{dA} \right)_{T, V} \equiv f_s = \gamma + \Sigma \mu_i \Gamma_i \equiv \text{specific surface Helmholtz free energy} \tag{7}$$

$$\left(\frac{dG}{dA} \right)_{T, P} \equiv g_s = \gamma + \Sigma \mu_i \Gamma_i \equiv \text{specific surface Gibbs free energy} \tag{8}$$

$$\left(\frac{dE}{dA} \right)_{S, V} \equiv e_s = \gamma + \Sigma \mu_i \Gamma_i \equiv \text{specific surface energy} \tag{9}$$

At constant T, P, S, V, and if $\Gamma_i = 0$, $\gamma = f_s = g_s = e_s$, but only under these conditions.

The process of forming a new surface can be split into several parts:

1. The phase must be cleaved to expose the new surface;
2. Atoms in the surface plane rearrange to assume their equilibrium positions;

3. In a multicomponent system, part 2 may also be combined with the migration of component atoms to or from the interface, Γ_i; i.e., the development of surface excesses or deficiencies.

In a liquid, parts 1 and 2 occur simultaneously. In a solid, part 2 may occur very slowly or not at all.

In a 1 component system, $\Gamma_i = 0$ unless there is such a restructuring around the interface so as to significantly change the density of the phase near the surface.

Therefore, at constant density in a single component system,

$$\gamma = f_s = g_s \tag{11}$$

or γ is both the Gibbs Free Energy and the Helmholtz Free Energy. Thus γ can be called the specific surface FREE ENERGY.

At constant S (no restructuring), γ will also be the surface energy, e_s.

Therefore, in the general case,

$$(g_s)_{T, P} = (f_s)_{T, V} = (e_s)_{S, V} \neq \gamma \tag{12}$$

We will use a term, γ, thermodynamic property of an interface - it is not in general g_s, f_s, or e_s, though it may be equal to one, both, or all three of these quantities under certain conditions. We will call this quantity GAMMA, or the specific surface work. It is commonly called the "surface tension".

Gamma is the work necessary to form or create unit area of new surface. Surface stress is the work necessary to stretch an existing surface. In a liquid this cannot be done without causing more atoms to join the surface; i.e., creating new surface. Hence in liquids the surface stress is gamma (the reversible work to form new surface); i.e., surface tension. In a solid this is not necessarily so.

The lack of mobility of atoms in a solid means we can stretch it without causing bulk atoms to join the surface planes. Thus we may stretch or compress the surface of a solid without changing the number of atoms in the surface, only their distances of separation. This produces a surface stress.

B. Adsorption

Adsorption is a concentration of some species in the interfacial zone, resulting in a decrease in the interfacial free energy. Adsorption can often be mechanistically treated in terms of the residual or unsatisfied bonding capacity at the interface. The adsorbed material takes up some of the residual bonding capacity, resulting in a decreased surface energy.

The classical thermodynamic treatment of adsorption is that proposed by Gibbs and Guggenheim (see Ref. 5).

Let us now consider the interfacial region between two phases, α and β (Figure 5). The interface can vary from a few $\overset{\circ}{A}$ to thousands of $\overset{\circ}{A}$. α
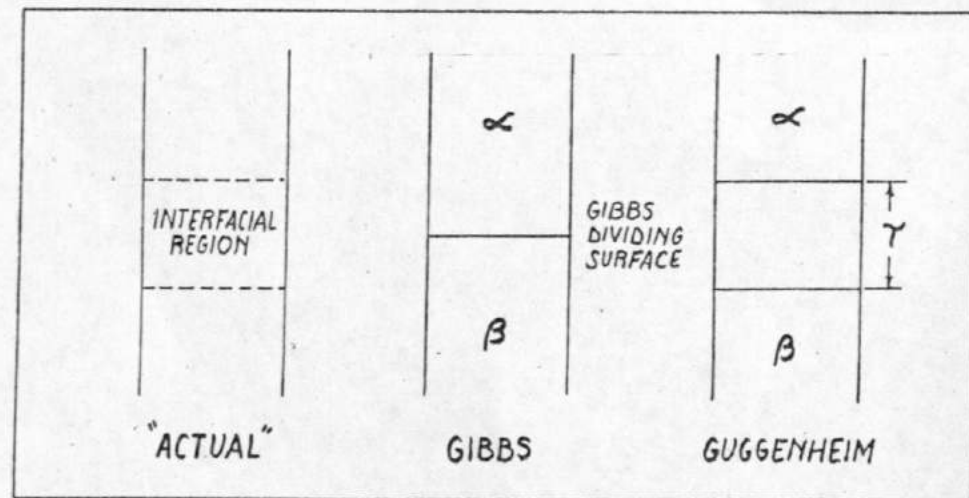

Figure 5. Gibbs, Guggenheim, and "actual" interfaces between condensed phases

and β will each have its characteristic bulk properties. The place where the properties begin to deviate from the bulk values is the boundary of the interfacial region. We can treat such a system in two ways. The first, due to Gibbs, is to assume α and β are homogeneous up to some dividing surface. The second, due to Guggenheim, treats the interfacial region as a homogeneous phase, σ. Both treatments lead to similar results. The Gibbs approach is often more useful in obtaining thermodynamic data.

1. Gibbs Approach

$$dE = TdS - PdV + \Sigma\mu_i dN_i + \gamma dA$$

$$dE^\alpha = TdS^\alpha - P^\alpha dV^\alpha + \Sigma\mu_i \ dN_i{}^\alpha$$

$$dE^\beta = TdS^\beta - P^\beta dV^\beta + \Sigma\mu_i dN_i{}^\beta$$

$dE - dE^\alpha - dE^\beta \equiv dE^S$, or the change in E associated with the interface (dividing surface); i.e., an excess energy due to the presence of the surface.

$$
\left.
\begin{aligned}
dS^S &= dS - dS^\alpha - dS^\beta \\
dN_i{}^S &= dN_i - dN_i{}^\alpha - dN_i{}^\beta \\
dE^S &= dE - dE^\alpha - dE^\beta \text{ or} \\
dE^S &= TdS^S + \gamma dA + \Sigma\mu_i \ d \ N_i{}^S
\end{aligned}
\right\}
\tag{13}
$$

E^S is an extensive state quantity as is E, thus the mathematical properties of such a variable allow us to say (just as in the Gibbs-Duhem derivation - see Appendix):

$$E^S = TS^S + \gamma A + \Sigma\mu_i N_i{}^S$$

$$dE^S = TdS^S + S^S dT + \gamma dA + Ad\gamma + \Sigma\mu_i dN_i{}^S + \Sigma N_i{}^S d\mu_i$$

equating with (13), we see

$$A d\gamma + S^S dT + \Sigma N_i{}^S d\mu_i = 0 \quad \text{or}$$

$$A d\gamma = -S^S dT - \Sigma N_i{}^S d\mu_i, \quad \text{dividing by A,}$$

$$d\gamma = \frac{-S^S}{A} dT - \Sigma \frac{N_i{}^S}{A} d\mu_i$$

$$\boxed{N_i{}^S/A \equiv \Gamma_i \equiv \text{surface excess of component i}} \tag{14}$$

$$\boxed{\therefore (d\gamma)_T = - \Sigma_i \Gamma_i d\mu_i} \tag{15}$$

(15) is the Gibbs Adsorption Equation, the third fundamental equation of surface chemistry (see Ref. 5), which relates a surface excess (or deficiency) of components with the change in surface free energy. Note the similarity of (15) with the Gibbs-Duhem (eq. 26 in the Appendix).

The Gibbs Adsorption Equation is in essence the Gibbs-Duhem equation applied to a system containing an interface.

2. Guggenheim Approach

Let the interfacial region be a phase, σ, of area A and length τ, with its own thermodynamic properties: V^σ, S^σ, E^σ, $N_i{}^\sigma$, G^σ, etc.

Now the interfacial terms are inherent properties of the inter-phase and do not have to be defined as differences attributed to a hypothetical surface plane.

$$\therefore \quad dE^\sigma = TdS^\sigma + \gamma dA - PdV^\sigma + \Sigma\mu_i dN_i{}^\sigma$$

as before

$$E^\sigma = TS^\sigma + \gamma A - PV^\sigma + \Sigma\mu_i N_i{}^\sigma$$

$$\therefore \quad dE^\sigma = TdS^\sigma + S^\sigma dT + \gamma dA + A d\gamma - PdV^\sigma - V^\sigma dP$$

$$+ \Sigma\mu_i dV_i{}^\sigma + \Sigma N_i{}^\sigma d\mu_i \quad \text{or}$$

$$A d\gamma = -S^\sigma dT + V^\sigma dP - \Sigma N_i{}^\sigma d\mu_i$$

or, per unit area

$$\boxed{(d\gamma)_{T,P} = - \Sigma_i \Gamma_i{}^\sigma d\mu_i} \tag{16}$$

where

$$\Gamma_i{}^\sigma \equiv N_i{}^\sigma/A$$

For a 2-component (binary system:

$$d\gamma = - \Gamma_1{}^\sigma d\mu_1 - \Gamma_2{}^\sigma d\mu_2$$

We also know from the Gibbs-Duhem equation:

$$N_1 d\mu_1 + N_2 d\mu_2 = 0 \quad \text{or}$$

$$d\mu_1 = - N_2/N_1 d\mu_2$$

$$\therefore \quad d\gamma = - \left(\Gamma_2{}^\sigma - \frac{N_2}{N_1} \Gamma_1{}^\sigma \right) d\mu_2 \tag{17}$$

If $\Gamma_i > 0$; i.e., $N_i{}^S > 0$, i is concentrated in the surface zone and we call this adsorption.

If $\Gamma_i < 0$, $N_i{}^S < 0$, or there is a deficiency of i in surface zone and we call it negative adsorption.

III. CONTACT ANGLE AND WETTABILITY

Another basic expression necessary for an understanding of polymer surface phenomena is the Young-Dupree or contact angle equation. Consider a drop of liquid on a solid substrate. Consider the tangent to the drop surface at the region of S, L, V equilibrium (Figure 6) where the interfacial
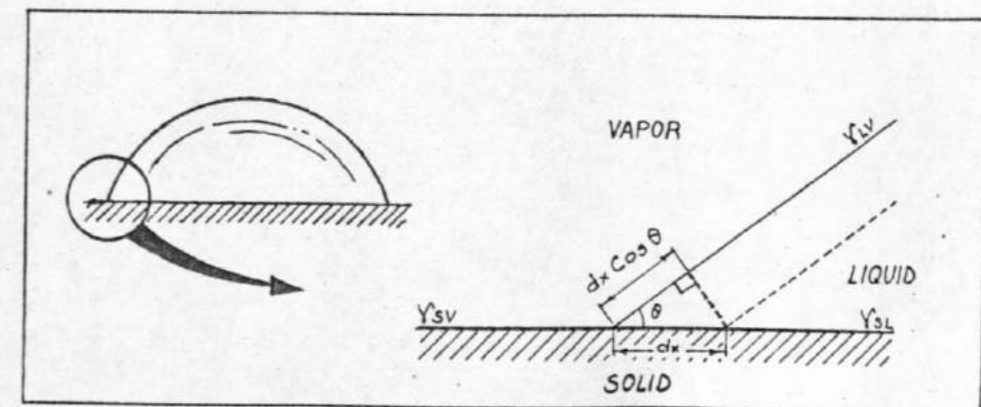

Figure 6. The Contact Angle

energies are represented by
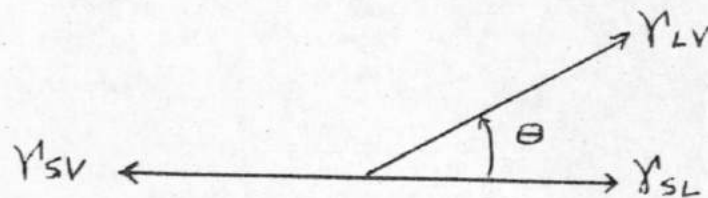
γ_{SV} (solid-vapor),

γ_{SL} (solid-liquid), and

γ_{LV} (liquid-vapor).

Let there be a small displacement, dx. Then $(dG)_{T,P,n} = \gamma_{SV}dx - \gamma_{SL}dx - \gamma_{LV}dx \cos \theta$; at equilibrium dG = 0, or

$$\boxed{\gamma_{SV} = \gamma_{SL} + \gamma_{LV} \cos \theta} \qquad (18)$$

This is the contact angle or wettability equation and is Adamson's fourth basic equation of surface chemistry (5). It can also be obtained by considering γ as a surface tension and performing a static force balance:

If the contact angle is 0, we say the liquid is completely spreading, or completely wets the substrate. The contact angle is a very useful inverse measure of wettability.

It is important to note the following standard symbols

$\gamma_S^0 \equiv$ surface tension of a solid phase in contact with vacuum; i.e., a free surface

$\gamma_{SV} \equiv$ surface tension of a solid phase in equilibrium with a vapor, V

γ_L^0, γ_{LV} are defined similarly for a liquid phase

A vapor adsorbed on the L or S surface will serve to reduce γ, therefore

$\gamma_{SV} \leq \gamma_S^0$

$\gamma_{LV} \leq \gamma_L^0$

In the case of the contact angle equation (18), the vapor component usually arises from the vapor of the liquid drop.

The spreading pressure, π, is a measure of the tendency of a vapor to adsorb and spread on a solid or liquid:

$$\gamma_S^0 - \gamma_{SV} \equiv \pi_S$$
$$\gamma_L^0 - \gamma_{LV} \equiv \pi_L \qquad (19)$$

If V refers to the liquid vapor, $\pi_L = 0$.

The contact angle expression can be expanded in terms of the spreading pressure relations such that

$$\cos \theta = \frac{(\gamma_S^0 - \pi_S) - \gamma_{SL}}{\gamma_{LV}} = \frac{\gamma_{SV} - \gamma_{SL}}{\gamma_{LV}} \qquad (20)$$

assuming $\pi_L = 0$.

The work of adhesion equation (1) can be recast as

$$W_{SL} = \gamma_{LV} + (\gamma_{SV} - \gamma_{SL}) \gamma_{LV}/\gamma_{LV}$$

and then combined with the cos θ expression to give:

$$W_{SL} = \gamma_{LV} (1 + \cos \theta). \qquad (21)$$

If $\theta = 0$, $W_{SL} = 2\gamma_{LV} = W_{LL}$, or the work of separating L from S (work of adhesion) is the same as the work required to separate the liquid from itself (work of cohesion). Thus the adsorped vapor film on the solid is behaving as if it were a liquid.

If $\theta > 0$, then the adsorbed film is different from the liquid, which is expected due to structuring, entropy effects, etc.

Spreading occurs when $W_{SL} \geq 2\gamma_{LV}$ or $W_{SL} \geq W_{LL}$. A liquid will spread over a solid when the interactions between liquid and solid are greater than those between liquid and itself.

<u>Critical Surface Tension</u>, γ_C:

Zisman[10] and his group have perhaps done more than any other laboratory to characterize the surface properties of polymers, by the use of the contact angle. Extensive studies of the contact angle of a variety of liquids on clean, low energy polymer surfaces revealed a linear relation between $\cos\theta$ and γ_L (figure 7) for a homologous series of organic liquids.
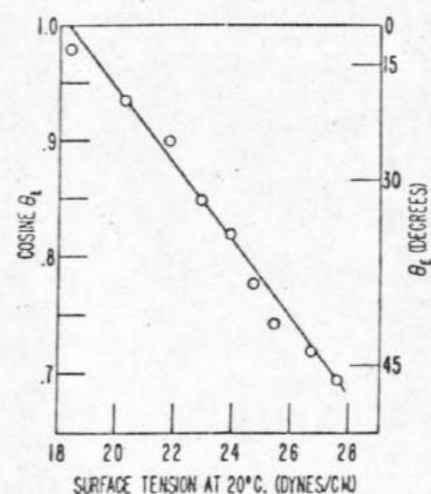

Figure 7. Wettability of polytetrafluoroethylene by the n-alkanes
(from Reference 10, p. 13)

The intersection of the line with $\cos\theta = 1$ occurred at a certain value of γ_L, which Zisman called the critical surface tension for wetting, γ_C, for that particular series of liquids. Even for non-homologous liquids, the points fell on a straight line or within a fairly narrow band. (Figures 8 and 9)
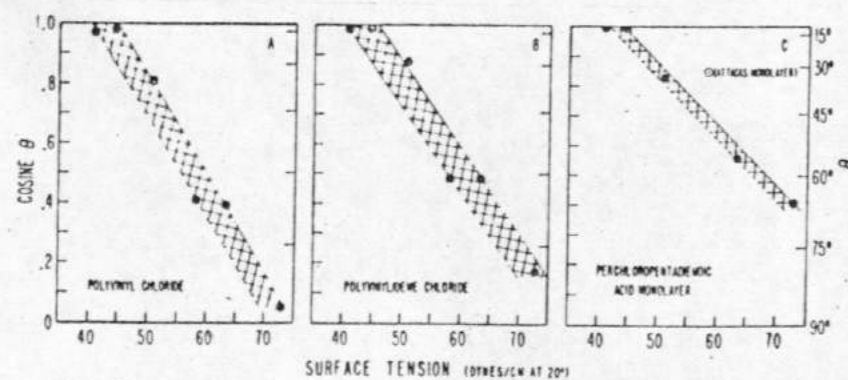

Figure 8. Wettability by various liquids on surface of:

A. Poly(vinyl chloride)
B. Poly(vinylidene chloride)
C. Close-packed monolayer of perchloropentadienoic acid
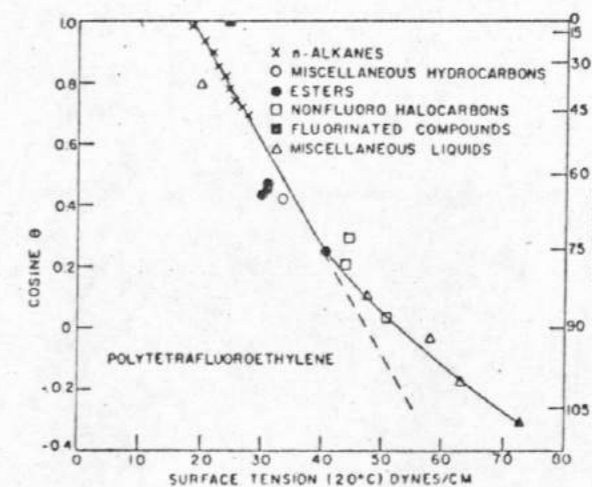
(From Reference 10, p. 14)

Figure 9. Wettability of polytetrafluoroethylene by various
liquids
(From Reference 10, p. 14)

The γ_C values derived from such plots correlate very well with the chemical nature of the polymer surface. This is evident from Tables I and II.

Table I

Critical Surface Tensions of Low-Energy Surfaces (Ref. 10, p. 21)

Surface Constitution	γ_c, Dynes/Cm. at 20°
A. Fluorocarbon Surfaces	
$-CF_3$	6
$-CF_2H$	15
$-CF_3$ and $-CF_2-$	17
$-CF_2-$	18
$-CH_2-CF_3$	20
$-CF_2-CFH-$	22
$-CF_2-CH_2-$	25
$-CFH-CH_2-$	28
B. Hydrocarbon Surfaces	
$-CH_3$ (crystal)	22
$-CH_3$ (monolayer)	24
$-CH_2-$	31
$-CH_2-$ and $-CH-$	33
$-CH-$ (phenyl ring edge)	35
C. Chlorocarbon Surfaces	
$-CClH-CH_2-$	39
$-CCl_2-CH_2-$	40
$=CCl_2$	43
D. Nitrated Hydrocarbon Surfaces	
$-CH_2ONO_2$ (crystal) [110]	40
$-C(NO_2)_3$ (monolayer)	42
$-CH_2NHNO_2$ (crystal)	44
$-CH_2ONO_2$ (crystal) [101]	45

Table II

Critical Surface Tensions of Various Polymeric Solids (Ref. 10, p. 20)

Polymeric Solid	γ_c, Dynes/Cm. at 20°C.
Polymethacrylic ester of ϕ'-octanol	10.6
Polyhexafluoropropylene	16.2
Polytetrafluoroethylene	18.5
Polytrifluoroethylene	22
Poly(vinylidene fluoride)	25
Poly(vinyl fluoride)	28
Polyethylene	31
Polytrifluorochloroethylene	31
Polystyrene	33
Poly(vinyl alcohol)	37
Poly(methyl methacrylate)	39
Poly(vinyl chloride)	39
Poly(vinylidene chloride)	40
Poly(ethylene terephthalate)	43
Poly(hexamethylene adipamide)	46

The critical surface tension, γ_C, is a "...useful empirical parameter whose relative values act as one would expect of $\gamma_S o$, the specific surface free energies of the solid." (Reference 10, p. 14) The correlation between γ_C and $\gamma_S o$ is often extremely good (see Reference 9).

IV. CHEMICAL AND STRUCTURAL NATURE OF POLYMER SURFACES

Zisman's γ_C--surface composition relationships utilize the "...usually reasonable assumption that the surface composition of the solid polymer was the same as that of the horizontally oriented polymer molecule." (Reference 10, p. 15) However, many of these polymers are crystalline and different faces of a single crystal or a lamella will have different surface energies. Hoffman [11] estimates that the lateral surface energy is about 10 ergs/cm^2 and the fold surface energy is 57 ± 5 ergs/cm^2, for polyethylene. Keller[12] believes that a significantly higher value is more accurate. The energy of a "typical" polyethylene surface is probably some average of the two, possibly close to Zisman's[10] γ_C value of 31 ergs/cm^2. Hoffman[11] also gives data for polychlorotrifluoroethylene, where the lateral energy is 4 ergs/cm^2 and the fold surface energy is 40 ergs/cm^2; Zisman's γ_C for this polymer is also 31. Thus the γ_C value does not necessarily shed light on the energies of the crystallites.

Polymer single crystals are microscopic and have not been grown in large enough sizes to allow one to use contact angle techniques for surface energy determination. Because of their lamellar nature, however,

single crystals can be allowed to deposit from dilute solution to form an aggregate with the C-axis fairly well oriented perpendicular to the aggregate surface. Schornhorn and Ryan[13] have studied the wettability properties of polyethylene single crystal aggregates by contact angle measurements. The aggregates were highly crystalline. Their value for the surface of polyethylene single crystal aggregates is 53.6 dynes/cm^2. As the surface of an aggregate must be almost completely composed of fold surfaces, their results are in excellent agreement with Hoffman's[11] value of 57 ± 5. It is thus clear that the surface energy of a crystalline polymer is not only a function of its chemical nature but is also a function of how the molecules are oriented.

The surface energy is also a function of density, i.e., the number of surface groups per unit area. Thus a crystalline surface would be expected to have a higher surface energy than an amorphous one, due to density considerations alone. In fact, Roe has shown[19] that γ_C is proportional to the 4th power of the amorphous density for polyethylene. Schonhorn has proposed[17] that one must distinguish between γ_S^a (amorphous), γ_S^{ac} (amorphous-crystalline), and γ^c (crystalline) in the previously derived equation. He concludes[17] that, for apolar polymers, $\gamma_S^a = \gamma_C = \gamma_{LV}$ where γ_{LV} is the surface tension of the liquid polymer melt, but that γ_S^{ac} and γ_S^c may be quite different. Schonhorn goes on to prove this point (with Ryan) by measuring the wettability of polymer single crystals.[13] This can be due to a change in surface density as well as to particular bond orientations and/or strains.

His conclusion that $\gamma_S^a = \gamma_C = \gamma_{LV}$ essentially says that the surface region of typical polymers is an amorphous, liquid-like zone, with little or no crystallinity--in agreement with Lee et al.[15]

Polymers are usually cast or molded against low-energy surfaces which tend to reduce sticking. As the polymers crystallize, the low molecular weight or impurity species are rejected from the growing crystal.[14] A polymer crystal thus tends to be surrounded by uncrystallized material, which is probably why γ_C and other surface properties are not particularly sensitive to crystallinity or bulk density.[13,15-17] If the polymer is cast against a high energy substrate, which can furnish many heterogeneous nucleation sites, its surface properties are different from those of conventionally formed polymers. This has been demonstrated by Schonhorn in several papers.[16] He studied the surface properties of both crystal-

line and non-crystallizable polymer surfaces prepared by melting on both high energy (gold) and low energy (nitrogen gas) substrates. γ could be made to double by casting on gold. Similar results have now been obtained for polytetrafluorethylene [20] and perfluorinated ethylene-propylene (FEP) and copolymer (21).

In summary, it is quite clear that the surface tension of a polymer depends on:

1. the chemical nature of the surface, i.e., the types of chemical bonds and atoms present on the surface (see Table III and Reference 10).

2. the density of the surface, which is a measure of the number of chemical bonds or atom groupings on the surface (see References 13, 16, 17).

3. the crystallinity and orientation of the surface, with specific reference to epitaxy and crystallite orientations (see References 11, 13).

References 15 and 17 discuss these concepts in some detail.

Interfacial Hierarchies

The theme of this section is taken from a figure in an article by Eirich[36] (Figure 10).
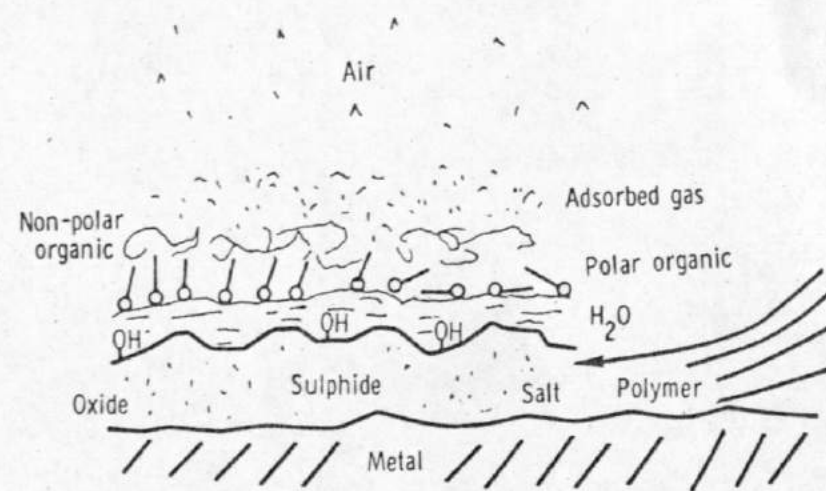

Figure 10. "Hierarchy" of spontaneously adsorbed layers on a metal surface (from Ref. 36, p. 351)

A high energy metal surface in contact with normal atmospheres is covered with a series of layers, each serving to reduce the surface free energy of the surface. The inner layers may consist of primary bonds, such as an oxide or sulphide on a metal, followed by strong polar bonds, such as water or OH^- adsorption. The hierarchy continues until the final surface is a relatively low surface energy non-polar organic. The hierarchy of Figure 10 naturally assumes that all the species illustrated are present in sufficient concentration. To "coat" or interface convert a surface is in the words of Eirich[36], to "....establish a different hierarchy of adsorbed layers which has to compete with, and stand up against, the natural order."

A relatively low energy polymer surface will have a much less complex hierarchy as it starts as a polar or non-polar organic surface. However, the polymer surface can have structural or morphological variations, particularly in the case of semi-crystalline polymers. One could postulate the structures presented in Figure 11.
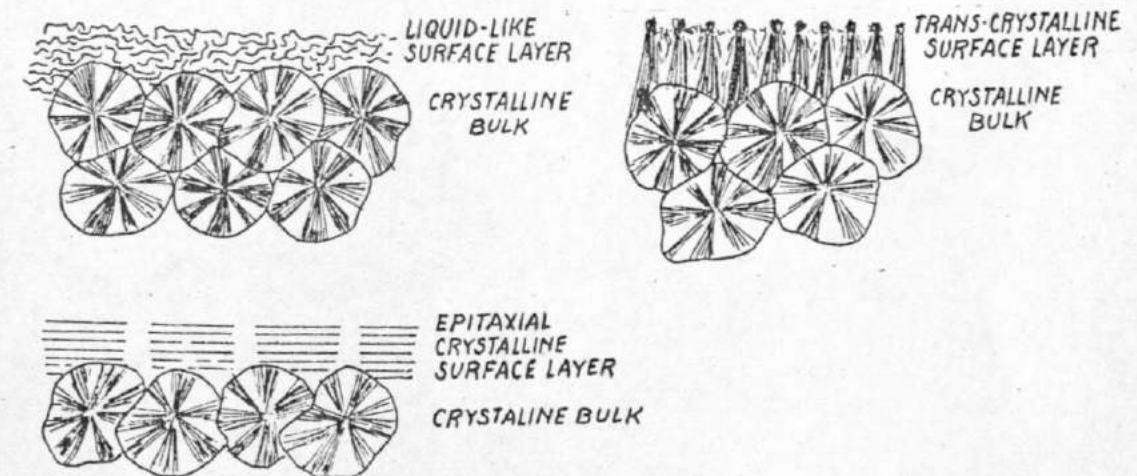

Figure 11. Some possible interfacial hierarchies for crystalline polymers

In addition to variations in surface structure due to simple casting on various mold surfaces, processing methods such as spinning, extrusion, injection molding, etc. will lead to various surface structures, which must be expected to influence the surface properties. These concepts have been discussed by Peterlin.[37]

Commercial polymer surfaces may also contain mold-release agents as well as plasticizers and perhaps other additives. Polymer surfaces may also be chemically different from their bulk--surface oxidation, hydroxylation, or carboxylation can occur under certain process conditions.

Even in the case of non-crystalline polymers, one can expect some orientation influence of casting substrates and processing conditions.

It is, therefore, apparent that a polymer interface can be a complex hierarchy of structures and even molecular types--varying from the bulk material through the solid polymer interfacial zone to the actual outer surface, which may contain adsorbed water, polar and non-polar organics, and gases.

V. INTERFACE CONVERSION PROCESSES

Polymer surfaces can be modified by a variety of methods for a multiplicity of applications. The processes range from mechanical and thermal treatments, chemically-induced modifications, activated gas processes, and radiation-induced changes. Applications range from pretreatments for adhesive bonding and the binding of coupling agents, treatments to enhance dye receptivity and printability, and even treatments to render polymers biologically compatible or biochemically active.

Rauhut briefly reviews and cites many of the surface treatments which have been tried with polyethylene (22). The general topic of polymer surface reactions is covered in an excellent review by Angier (38).

We will be concerned with intentional surface reactions and interface conversions, as opposed to weatherability, surface degradation, etc. Furthermore, we will largely ignore mechanical and physical surface changes, such as mechanical abrasion, surface crystallinity, or solvent swelling, in this section.

Interface conversion processes for polymers can be divided into three general areas.

      1. "Standard" Chemical Reactions
      2. UV, Electron, and Gamma Radiation Reactions
      3. Excited Gas or Plasma Reactions

A. "Standard" Chemical Processes

If the polymer surface contains relatively reactive organic functional groups, a wide variety of classical organic reactions are generally available with which to couple or bond other molecules. Hydroxyls, amines, and carboxylic acid groups can generally be coupled to in a straight-forward manner.

One often would like to initiate free radicals on the polymer surface, which can then be used to graft copolymerize a vinyl monomer. This can

readily be done with -OH containing surface by the use of ceric salts, which complex with the alcohol and then decompose to form a free radical (39,40). This approach is widely used for the graph copolymerization of cellulose and polyvinyl alcohol and should also be suitable for many protein materials.

Many of the polymers of interest, however, are relatively inert and not amenable to classical functional group reactions. The most common surface treatment for such polymers is surface oxidation or peroxidation.

Chemical peroxidation (38) can often be attained by heating the polymer in the presence of high air or O_2 pressures. Polypropylene, for example, is peroxidized by heating for several hours at 60 - 120°C in 1-10 atm of oxygen or air. Amorphous polymer is usually much more easily oxidized than crystalline polymer. Usually the peroxidation can be restricted to the surface layer, with little or no change in the mechanical properties of the material. The perioxidized material can be grafted by contacting and heating with vinyl monomers. These processes have been used with polyethylene, polypropylene, polyamides, and polyesters (38). Some of the reactions which are believed to occur during thermal oxidation are listed in Table III.
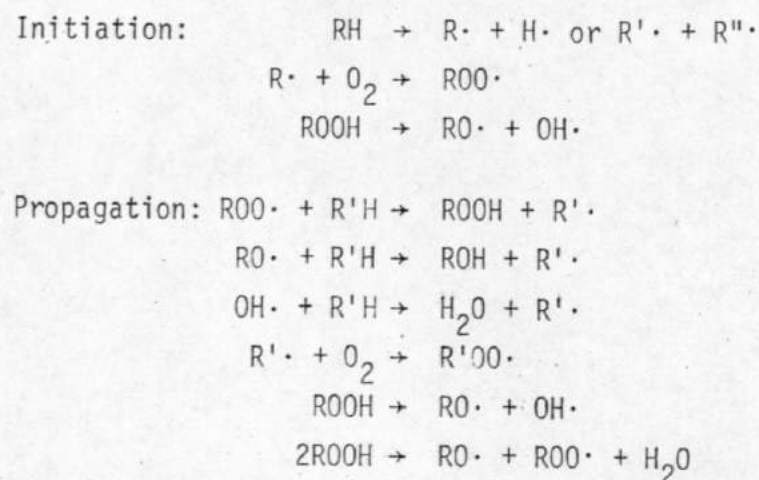
TABLE III.

OXIDATION OF POLYMERS

Initiation:
$$RH \rightarrow R\cdot + H\cdot \text{ or } R'\cdot + R''\cdot$$
$$R\cdot + O_2 \rightarrow ROO\cdot$$
$$ROOH \rightarrow RO\cdot + OH\cdot$$

Propagation:
$$ROO\cdot + R'H \rightarrow ROOH + R'\cdot$$
$$RO\cdot + R'H \rightarrow ROH + R'\cdot$$
$$OH\cdot + R'H \rightarrow H_2O + R'\cdot$$
$$R'\cdot + O_2 \rightarrow R'OO\cdot$$
$$ROOH \rightarrow RO\cdot + OH\cdot$$
$$2ROOH \rightarrow RO\cdot + ROO\cdot + H_2O$$

TABLE III (cont)

Termination: Decrease in number of participating species by:
  (1) Action of antioxidant
    (a) $HA + ROO\cdot \rightarrow ROOH + A\cdot$, where $A\cdot$ is inactive
    (b) heterolytic hydroperoxide decomposition
  (2) Disproportionation
  (3) Combination
  (4) Depletion of accessible material

(from Ref. 23, p. 258)

Ozone can be used to produce sites for graft copolymerization. The polymer can be treated in, say, 15% ozone in oxygen at 0.5 psi for 1 hour at room temperature (38). A polyethylene treated in this manner could be stored and graft copolymerized up to 184 hours after ozone treatment. A variety of polymers have been grafted via pretreatment with ozone.

Chromic Acid treatment is very effective for the surface oxidation of polyethylene (38,22). Other acid treatments are not as effective and may produce embrittlement. A variety of acids have been used as well as some base treatments (38,22). In fact, chromic acid treatment is as good or better than any other interface conversion process for optimizing adhesion to polyethylene (22,23).

Halogenation can be performed by exposure to chlorine vapor or solutions and to fluorine vapor (38). Many polymers and other organic compounds can be directly fluorinated by a process reported by Margrave and Lagow (41).

Other treatments include permanganate oxidation (22), ammonium peroxydisulfate (43), halosilanes (38), and alkali metal solutions (38). The latter are commonly used to pretreat fluorocarbon surfaces for adhesive bonding (42).

Practically all of these chemical treatments have been shown to improve adhesion. Many of the studies have not adequately characterized

the final surface, thus one does not know whether the result is due to new chemical groups or to the removal of weak boundary layers (the outer liquid-like region of polymer) by either dissolution or by cross-linking.

B. UV, Electron, and Gamma Radiation Processes (38,45-47)

High energy radiation interacts with matter by a variety of mechanisms. The result is often bond cleavage, ion generation, and free radical formation. Radiation-induced reaction mechanisms have been widely studied (45-47).

1. Ultraviolet

Ultraviolet radiation sources are usually mercury arcs or lamps which produce radiation of roughly 3-5 eV, energy of the order of organic chemical bonds. Thus it can be expected that UV quanta may break chemical bonds - perhaps selectively (48). Oster and coworkers have shown that UV radiation can induce cross-linking and grafting of polymers (49), particularly in the presence of sensitizers. Benzophenone, for example, is an excellent sensitizer for hydrogen abstraction and thus surface grafting (50) but a poor initiatior for polymerization - thus minimal homopolymer is formed by such a graft. A number of compounds are effective in sensitizing the UV-induced cross-linking of polyethylene (49); this process may be effective in strengthening weak boundary layers on polymer surfaces.

The penetration of UV radiation into bulk polymer is limited, thus UV effects are often confined to surface changes - either cross-linking or

grafting. The sensitized polymer may be directly irradiated in the presence of monomer.

It is believed that the reaction is one of hydrogen abstraction, which is greatly accelerated in the presence of suitable sensitizers.

The reactions can even be carried out with near ultraviolet radiation if a different sensitizer is used; for example, 2-methyl anthroquinone (51). This allows one to use even conventional "Black Light" UV sources.
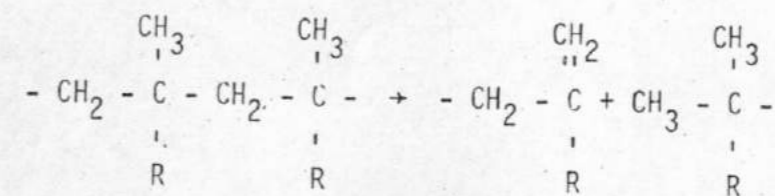
The ultraviolet radiation/sensitizer method appears to be a simple, effective method for the surface cross-linking and grafting of many polymers.

2. Ionizing Radiation

Beta and gamma rays are usually high energy radiations, with energies up to several hundred thousand times greater than normal chemical bonds. Thus these radiations are capable of extensive bond breakage and free radical formation. Most high energy radiation-induced changes are the result of secondary processes, involving the ions and excited molecules produced by the interaction of matter and radiation (46).

The sensitivity of a material to radiation-induced changes is often given in terms of the "G-value". The G-value is defined as the number of individual chemical events occurring per 100 eV of absorbed energy - usually the chemical event is free radical formation. $G(R\cdot)$ means the number of $R\cdot$ produced per 100 eV; $G(H_2)$ is the number of hydrogen molecules produced per 100 eV, etc. For most polymers, the radiation effects are dependent mainly on absorbed energy or dose rate, not on the nature of the radiation (47).

Radiation-chemical processes in polymers are generally classed into two types: degradation or cross-linking. Polymers containing no α-hydrogens tend to degrade when irradiated in vacuo:

$$- CH_2 - \underset{\underset{R}{|}}{\overset{\overset{CH_3}{|}}{C}} - CH_2 - \underset{\underset{R}{|}}{\overset{\overset{CH_3}{|}}{C}} - \rightarrow - CH_2 - \underset{\underset{R}{|}}{\overset{\overset{CH_2}{||}}{C}} + CH_3 - \underset{\underset{R}{|}}{\overset{\overset{CH_3}{|}}{C}} -$$

If each main chain carbon atom has one or more hydrogens, however, the tendency is for cross-linking to occur. This is probably strain or steric-related, in that the free radicals produced on a tetra-substituted carbon are sterically hindered in their recombination.

Table IV distinguishes cross-linking and degrading polymers. Burlant and Hoffman (47) have related the tendence to cross-link or degrade to the heat of polymerization (Table V), claiming that a high heat of polymer-ization (greater than 15 kcal/mole) characterizes a sterically unhindered system; i.e., one capable of recombining or cross-linking.

TABLE IV*
Cross-linking versus Degradation in Irradiated Polymers

Group I Cross-linking polymers	Group II Degrading polymers
Polymethylene (polyethylene)	
—CH₂—CH₂—CH₂—CH₂—	
Polypropylene	Polyisobutylene
—CH₂—CH—CH₂—CH—	CH₃ CH₃
CH₃ CH₃	—CH₂—C—CH₂—C—
	CH₃ CH₃
Polystyrene	Poly(α-methylstyrene)
—CH₂—CH—CH₂—CH—	CH₃ CH₃
C₆H₅ C₆H₅	—CH₂—C—CH₂—C—
	C₆H₅ C₆H₅
Polyacrylates	Polymethacrylates
—CH₂—CH—CH₂—CH—	CH₃ CH₃
COOR COOR	—CH₂—C—CH₂—C—
	COOR COOR
Polyacrylamide	Polymethacrylamide
—CH₂—CH—CH₂—CH—	CH₃ CH₃
CONH₂ CONH₂	—CH₂—C—CH₂—C—
	CONH₂ CONH₂
Poly(vinyl chloride)	Poly(vinylidene chloride)
—CH₂—CH—CH₂—CH—	Cl Cl
Cl Cl	—CH₂—C—CH₂—C—
	Cl Cl
Polyamides	Cellulose and derivatives
Polyesters	Polytetrafluoroethylene
Polyvinylpyrrolidone	Polytrifluorochloroethylene
Rubbers	
Polysiloxanes	
Poly(vinylalcohol)	
Polyacrolcine	

*from Ref.46, p. 353

TABLE V
Effects of Radiation on Polymers

Polymer	ΔH polymerization, Kcal/mol	Predominant effect, in vacuo
Poly-α-methylstyrene	9	degradation
Polymethyl methacrylate	13	degradation
Poly-α-methacrylonitrile	11–13	degradation
Polyisobutylene	13	degradation
Polymethacrylic acid	15.8	degradation
Polystyrene	17	crosslinking
Polybutadiene	17	crosslinking
SBR rubber	17–20	crosslinking
Polyisoprene	17.9	crosslinking
Polyacrylic acid	18.5	crosslinking
Polymethylacrylate	18.7	crosslinking
Polypropylene	>16.5	crosslinking
Polyethylene	22	crosslinking
Polyacrylonitrile	17.3	crosslinking

from Ref. 47, p. 106

Irradiation of all polymers leads to gas formation which can lead to internal stresses and cracks. Thus most polymers lost weight on irradiation in vacuo. Hydrocarbon polymers will produce mainly hydrogen, but methane and other hydrocarbon gases are also produced in small quantities.

Generally equal amounts of absorbed radiation energy produce equal changes in properties, irrespective of the type of radiation used. Mechanical properties are significantly altered only by relatively large radiation doses, generally ≥ 1 Megarad, for most polymers. Teflon, however, can be altered by a 50,000 rad dose. Polymers containing aromatic groups are usually very resistant to radiation damage, while elastomeric materials are usually very susceptible. Polyethylene generally requires a dose in excess of 5 megarads to be significantly cross-linked, and a dose greater than 8 megarads was necessary to affect gas permeability behavior (46).

Our discussion of the effects of ionizing radiation have assumed the process was occurring in vacuo. In the presence of air or oxygen, many other reactions and effects may occur.

The free radicals generated may react with oxygen to form peroxides, hydroperoxides, and diperoxide cross-links. Some Group I polymers (cross-

linking type) may degrade if irradiated in the presence of oxygen. Poly-propylene in air degrades oxidatively - even for low doses - but it cross links in vacuo (46). Polystyrene is very radiation resistant in vacuo, but oxidatively degrades in air.

Radiation can be used to produce reactive functional groups directly, on the polymer surface. Hydroxyls , carbonyls, and carboxyl groups are formed on most polymers by irradiation in air. Chlorine or bromine groups can be introduced by irradiating in the presence of halogen gases or solutions (46).

Graft co-polymers can be directly prepared on a polymer surface by a number of methods:

1. Mutual Irradiation - Monomer: The polymer substrate is in direct contact with the monomer to be grafted.

2. Trapped Free Radical: The polymer substrate is ir-radiated in vacuo and then contacted with the grafting monomer. The trapped free radicals then initiate grafting.

3. Peroxidation: The polymer is irradiated in the pre-sence of O_2 which leads to peroxide formation. The peroxides are then decomposed while in contact with the grafting monomer.

4. Mutual Irradiation - Polymer: The polymer substrate is in direct contact with the polymer or other mate-rial to be grafted.

These are advantages and disadvantages to each of these techniques. These are summarized in Table VI.

The grafting efficiency often depends on the relative G-value, par-ticularly for the mutual irradiation-monomer method. If G monomer < G polymer; i.e., many more free radicals are found on the polymer surface than in the monomer, a large number of polymer-monomer grafts are formed with little monomer homopolymerization. If G monomer > G polymer, one may get monomer polymerization with little or no surface grafting.

TABLE VI

Radiation Grafting Methods

Method	Advantages	Disadvantages
Mutual Irradiation - Monomer	Most efficient - free ra-dicals utilized as they form. Most widely used method.	Homopolymer forma-tion; grafted chains of high molecular weight; difficult to con-trol: inert envir-onment usually re-quired.
Trapped Free Radical	Very little homopolymer formation: "purest" graft copolymer.	Very inefficient: inert environment required.
Peroxidation	Ease of irradiation in air. No homopolymeriza-tion.	Oxidative degra-dation.
Mutual Irradiation - Polymer	Characteristics of grafted layer easily controllable.	Least used method; very inefficient.

Tables VII and VIII give the estimated G-values for radical formation for typical monomers and polymers. The footnote to Table VIII should be read and appreciated. G_R values are crude guidelines - and should never be taken as gospel, for many other processes may intervene and even dominate in the reactions.

TABLE VII*

Free Radical Yields of Monomers Derived from Radiation Polymerization Kinetics and from Scavenger Data

Monomer	Method	G_R
Butadiene	—	Presumably very low
Styrene	Kinetics and DPPH	0.69
Ethylene	Kinetics	≃4
Acrylonitrile	Kinetics	5.6
	DPPH	5.0
Methyl methacrylate	Kinetics	11.5
	DPPH	5.5-6
Methyl acrylate	DPPH	6.3
Vinyl acetate	Kinetics	12.0
	DPPH	9.6
Vinyl chloride	—	Presumably close to 10

*from Ref. 46, p. 605

TABLE VIII*

Expected Free Radical Yields of Polymers
Estimated from the G_R Values of Model Substances

Polymer	Model substance	Expected G_R
Polybutadiene	} Low-molecular-weight olefines	2–4
Polyisoprene		
Polystyrene	Isopropylbenzene, xylene	1.5–3.0
Polyethylene	Low-molecular-weight alkanes	6–8
Polyisobutylene	$G(P')$ (Section XI-4)	6–8
Poly(methyl methacrylate)	} Low-molecular-weight esters	6 or 12
Poly(vinyl acetate)		
Poly(methyl acrylate)		
Silicones	$G(-DPPH)=3.6$ in liquid siloxans	3.6 or 7.2
Cellulose	} Ethers and alcohols	10
Poly(vinyl alcohol)		
Poly(vinyl chloride)	} Low-molecular-weight alkyl chlorides	10–15
Poly(vinylidene chloride)		
Polyamides	}	Unknown, presumably high
Fluorinated polymers		

NOTE: The figures quoted in this table are only crude es-
timates and should not be considered as being defin-
itely established. They are believed to be useful,
however, in selecting a particular polymer-monomer
combination for grafting by the direct radiation
method.

from Ref. 46, p. 606

One can obtain the impression from the literature that virtually any-
thing can be grafted to everything - and this is to some degree true. With
all due respect for cross-linking, polymer degradation and monomer homo-
polymerization, high energy radiation-induced grafting is a rather non-
selective technique which permits interface conversions which could not
be carried out by other means, or could be only with great difficulty.

Chapiro shows many examples of how the grafting treatment can be
engineered to produce desired results (Figure 12). He also cites many
examples of successful grafts. Charlesby's book (45) and Angier's review
(38) are also excellent sources. Gilbert and Stannett's review (52) is
a very detailed and complete reference source on graft copolymerization
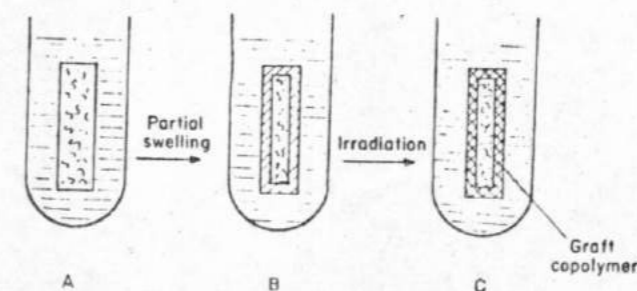with emphasis on textile fibers.

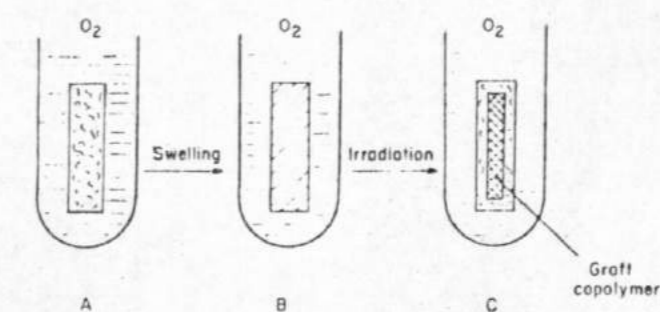Figure 12a. Controlled surface grafting by the partial-
swelling technique.

Figure 12b. "Embedded grafting" by selective inhibition
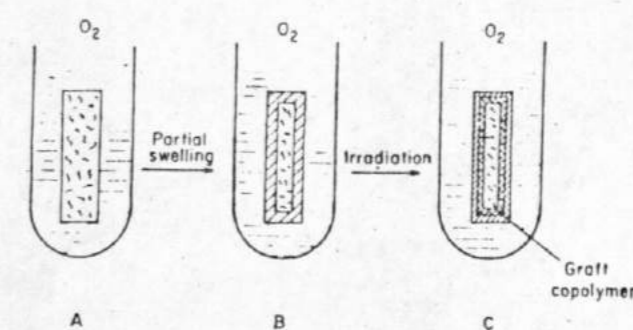in an outer zone.

Figure 12c. "Embedded grafting" combining partial swelling
and selective inhibition.

(all from Ref. 46, pp. 616-7)

C. Excited Gas or Plasma Reactions

Interest in the use of activated gases or plasmas for interface conversion of polymers has grown greatly in recent years. Corona discharge treatments have been used for the past 20 years, largely to improve the printability of polyethylene and other materials. More recent work has centered on radiofrequency activation of various gases. A very recent review of electrical discharge treatment processes is available (24) as well as a symposium proceedings (64).

Plasma is often called the 4th state of matter, consisting of reactive mixtures of energetic ions and electrons. Bradley and Fales (24) distinguish three basic types of plasmas:

"(I) Thermal plasmas produced by atmospheric pressure arcs. It is characteristic of thermal arcs, whose temperatures lie between 5000° and 50,000°K, that the kinetic energies of its constituent gas molecules, ions and electrons are in equilibrium. A familiar example of a thermal plasma is the luminous gas of an arc welder.

(II) Cold plasmas produced by glow discharges. The neon sign is a typical example of a cold plasma in which the gaseous ions and neutral gas range from ambient temperature to a few hundred degrees, while the electrons (considered as a gas) have a "temperature" of the order of tens of thousands of degrees Kelvin (°K). Thermal equilibrium obviously does not exist in such plasmas.

(III) Between the extremes of types (I) and (II) lie hybrid plasmas, where numerous tiny thermal sparks are uniformly distributed throughout a large volume of nonionized gas, and the average temperature of the entire volume is low. This variant of the cold plasma is exemplified by corona and ozonizer-type discharges.

Our concern is with relatively low temperature plasmas, types II and III. Only corona discharge and radiofrequency-activation will be discussed.

1. Corona-Discharge Processes

Corona discharges are characterized by high voltages and low currents. When the electrode potential increases to a sufficiently high value, partial ionization of the surrounding gas may take place. This can occur at atmospheric pressure if one of the electrodes has sharp points or edges. The electrode gap is then partially ionized and may glow.

The gas in the gap thus consists of a number of activated gas species, ions, and electrons - all capable of reacting with a polymer placed in the gap.

The electrode-polymer film geometry is shown in Figure 13.
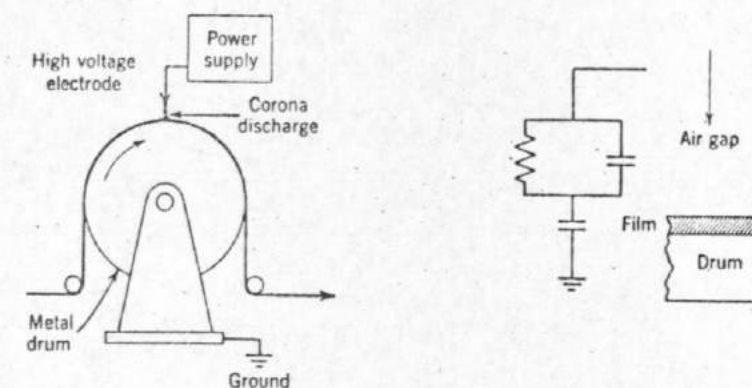

Figure 13. Apparatus for surface activation of plastic film by corona discharge with equivalent electrical circuit at right. (from Ref. 61, p. 162)

Commercial corona processes are generally carried out in air, thus the surface activation is largely the result of oxidation processes. The treatment obviously improves the wettability of hydrophobic polymer surfaces. The corona discharge can also be made to occur in the presence of other gases to produce inert activated species or reactive activated species (see next two sections).

Corona discharge (also called electrical discharge) treatment processes are widely used, mainly for the treatment of polyethylene film. A guide to corona film treatment is available (63).

2. Radiofrequency Activation of Inert Gases (CASING)

This method was pioneered by Hansen and Schonhorn (23,25) and is now generally called the CASING process (cross linking by activated species of inert gases). The polymer material is simply exposed to the activated inert gas environment for a short time. Generally radiofrequency activation (54) is used, ". . . but any of a number of other methods such as microwave excitation or corona discharge. . ." could be used (25). It is believed that hydrogen and fluorine abstraction occur, resulting in recombination processes which form a cross-linked surface layer. The unique aspects of

this method is that, contrary to practically all other interface conversion processes, the surface energy is essentially unchanged. One merely cross-links the existing material. No other species are added and there is minimal loss of material, generally H_2 (23). The result is that the weak boundary layer normally present on polymer surfaces is converted to a higher molecular weight, cross-linked zone. Hara and Schonhorn have schematically depicted the effect of CASING on amorphous and highly crystalline surface regions (21) (Figure 14). Zisman plots of control and CASING treated materials are essentially the same (21).
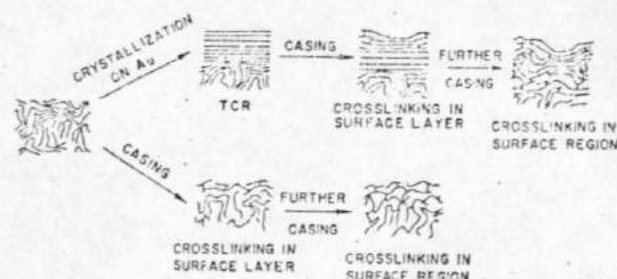

Figure 14. Schematic diagram depicting the effect of a variety of surface treatments on the surface morphology of FEP teflon. (from Ref. 21, p. 104)

Hansen (23) has summarized some of the possible reactions induced by RF-activated helium (Table IX).. Examples of what happens when activated helium interacts with polyethylene have also been documented (23) (Table X).
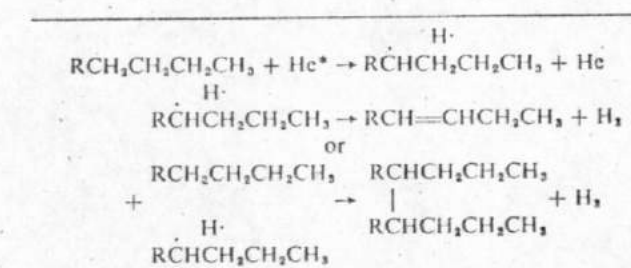
TABLE IX

FORMATION OF HIGHER-MOLECULAR-WEIGHT SPECIES WITH ACTIVATED HELIUM	POSSIBLE FREE RADICAL REACTIONS RESULTING FROM TREATMENT WITH ACTIVATED HELIUM
Excited Molecules	
$R_1H + He^* \rightarrow R_1H^* + He$	$He^* + RH \rightarrow R\cdot + H\cdot + He$
$R_1H^* + R_2H \rightarrow R_1R_2 + H_2$	$He^* + R_1R_2 \rightarrow R_1\cdot + R_2\cdot + He$
$R_1CH_2CH_2R_2^* \rightarrow R_1CH=CHR_2 + H_2$	$H\cdot + RH \rightarrow H_2 + R\cdot$
	$R\cdot + R_1\cdot \rightarrow RR_1$
Ion-Molecule Reactions	$R\cdot + R_2\cdot \rightarrow RR_2$
$He^+ + RH \rightarrow He + RH^+$	$R\cdot + R\cdot \rightarrow RR$
$CH_4^+ + CH_4 \rightarrow CH_5^+ + CH_3\cdot$	
$CH_3^+ + CH_4 \rightarrow C_2H_5^+ + H_2$	
$C_2H_5^+ + CH_4 \rightarrow C_3H_7^+ \rightarrow H_2$	

(from Ref. 23, p. 272)

TABLE X

Typical Reactions Occuring During the Treatment of Polyethylene with Activated Helium

$$RCH_2CH_2CH_2CH_3 + He^* \rightarrow R\overset{H\cdot}{\underset{}{C}}HCH_2CH_2CH_3 + He$$
$$R\overset{H\cdot}{\underset{}{C}}HCH_2CH_2CH_3 \rightarrow RCH=CHCH_2CH_3 + H_2$$
or
$$RCH_2CH_2CH_2CH_3 \quad RCHCH_2CH_2CH_3$$
$$+ \quad \rightarrow \quad | \quad + H_2$$
$$R\overset{H\cdot}{\underset{}{C}}HCH_2CH_2CH_3 \quad RCHCH_2CH_2CH_3$$

(from Ref. 23, p. 273)

It is interesting, and perhaps somewhat surprising, that the CASING method also results in increased printability. The increased adhesion-ability can be understood in terms of the improvement of the weak boundary layer properties, but it is difficult to understand how this can also lead to improved printing properties.

CASING has been studied on a wide variety of polymers (21-3, 25, 55-6). The most common inert gases used have been helium (25) and argon (24).

The surface cross-linking produced by a CASING treatment has many potential applications: adhesive bonding, printability, surface encapsulation, abrasion resistance, coefficient of friction modification, modification of diffusion and permeability characteristics, etc. (see References 24 and 25).

3. Radiofrequency Activation of Reactive Gases

Activated inert gases function largely as free radicals and hydrogen abstractors. The inert gas itself is not incorporated in the final polymer product. Oxygen, nitrogen, ammonia, nitrous oxide, water, carbon dioxide, carbon monoxide, and other gases can also be excited or activated. These species can react in the same manner as the inert gases, but they can also become directly involved in the reaction. Thus the treatment of polymer surfaces with activated reactive gases produces effects very similar to CASING as well as changing the chemical nature of the surface.

Atomic oxygen can be readily generated by passing oxygen through a radiofrequency coil (23, 54). Some of the reactions of atomic oxygen with polyethylene are given in Table XI.

TABLE XI
Reaction of Polyethylene with Atomic Oxygen

Rapid:	$RH + O \cdot \rightarrow R' \cdot + RO \cdot$ or $R \cdot + OH \cdot$
Rapid:	$R \cdot + O \cdot \rightarrow RO \cdot$
Slow:	$RH \rightarrow R \cdot + H \cdot$ or $R \cdot + R \cdot$
Rapid:	$R \cdot + O_2 \rightarrow ROO \cdot$
	$ROO \cdot + R'H \rightarrow ROOH + R' \cdot$
Slow:	$ROOH \rightarrow RO \cdot + OH$

from Ref. 23, p. 262

It is clear that the surface is highly oxidized; carboxyl, hydroxyl, and carboxylic acid groups may be generated, depending on the polymer and the reaction conditions. A large number of polymers have been treated with excited oxygen (55), including polypropylene (57) and polymethylsiloxane (58).

Amino groups have been incorporated onto a variety of polymer surfaces by the use of ammonia and hydrogen/nitrogen plasmas (59).

Plasmas of vinyl monomers can be used to directly deposit polymer coatings on a variety of substrates. This process is often called the Glofilm coating process (60).

Much of the work on reactive gas plasmas applied to polymer interface conversion is very new. Clearly, we can expect a large number of new developments and applications in the near future.

D. Comparison of Interface Conversion Processes

Complete comparisons of all the various conversion processes are not generally available. Rauhut's paper (22) is probably the most complete comparison available for polyethylene. Rauhut concludes that ". . . the most effective agent for oxidizing the polyethylene surface was chromic acid, particularly when applied at a temperature higher than that used previously (i.e., at 80°C for high density polyethylene)." (Ref. 22, p. 38) He further recommends chromic acid or radiation as surface pretreatments for molded polyethylene parts.

The CASING method was not evaluated by Rauhut. Hansen (23) did compare the CASING process with electron bombardment and chromic acid.

An 80°C chromic acid treatment was shown as effective in promoting adhesion as any other treatment available. It produces a highly wettable, highly oxidized surface. Yet CASING accomplishes the same thing with no change in wettability. "What is generally not appreciated is that glass cleaning solution, like activated helium, also results in crosslinking and strengthening of the weak boundary layer at the surface of the polymer." (Ref. 23, p. 281)

Although beyond the scope of this paper, it is important to at least mention the interface conversions which can be achieved by the silane and silyl peroxide adhesion promoters and coupling agents (65-71).

There are many questions yet to be answered, but it is clear that a number of successful interface conversion processes are available now which can be profitably utilized for a wide variety of applications.

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(5a) $\div$ dT $\Rightarrow$ $\dfrac{dE}{dT} = T\dfrac{dS}{dT} - P\dfrac{dV}{dT}$; $\left(\dfrac{\partial E}{\partial T}\right)_V = T\left(\dfrac{\partial S}{\partial T}\right)_V$

(5b) $\div$ dV $\Rightarrow$ $\dfrac{dE}{dV} = T\dfrac{dS}{dV} - P$; $\left(\dfrac{\partial E}{\partial V}\right)_T = T\left(\dfrac{\partial S}{\partial V}\right)_T - P$

A little more juggling can produce:

(5c) $\left(\dfrac{\partial S}{\partial V}\right)_T = \left(\dfrac{\partial P}{\partial T}\right)_V$; $\left(\dfrac{\partial S}{\partial P}\right)_T = -\left(\dfrac{\partial V}{\partial T}\right)_P$

A __state__ variable depends on the actual state of the system and not with how that state was derived, i.e., independent of __path__.

Examples are E, V, T, S, P.

Such variables are $\therefore$ exact differentials.

A __non-state__ variable depends on the path the system takes and is a non-exact differential.

Examples are Q and W.

An __intensive__ variable is independent of the mass of the system (P,T).

An __extensive__ variable is a function of mass (V, E, H, S, A, G).

An __extensive__ variable can be converted to __intensive__ by expressing it as a partial molar quantity, i.e., dividing by the number of moles or mass in the system:

(5d) $\overline{G}_i = \left(\dfrac{\partial G}{\partial n_i}\right)_{T,P,n_j}$

G is extensive
$\overline{G}$ is intensive

It is now convenient to introduce three new extensive state variables: H, A, and G.

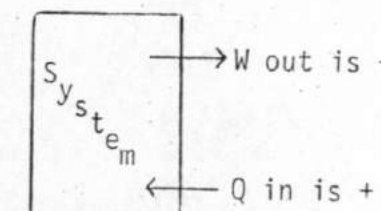__Review of Basic Thermodynamics:__

First Law - conservation of energy concept

(1) $\boxed{\Delta E = Q - W}$

$\Delta E \equiv$ change in internal energy

Q = heat

W = work, usually considered to be PdV work but can also include electrical, magnetic, gravitational work.

(2) In differential form: $dE = \delta Q - PdV$

Second Law - based on the irreversibility of spontaneous or natural processes

$S = \int_A^B \dfrac{dQ}{T}$ for a reversible process $= S_A - S_B$

$S \equiv$ entropy, a new state function

(3) $dS = \left(\dfrac{dQ}{T}\right)_{rev}$ $\left(dS_{system} + dS_{surroundings}\right)_{rev} = 0$

(4) $dS > \left(\dfrac{\delta Q}{T}\right)_{irrev}$ $\left(dS_{system} + dS_{surroundings}\right)_{irrev.} > 0$

A good discussion of "energy," "entropy," heat, work, and temperature is given by:

P. W. Bridgman, __Nature of Thermodynamics__, 1961, reprint of 1941 edn., Harper paperback.

Law I (2) + Law II (3) $\Rightarrow$

(5) $\boxed{dE = TdS - PdV}$

Maxwell's thermodynamic relations can be determined directly:

Open Systems:

Relations (1) through (16) apply to constant mass or closed systems. If we remove the constant mass condition, energy can be added to the system by adding more molecules. Such a system is called an open system.

Let μ_i be the energy contributed to the system by the addition of one molecule of type i.

Let dN_i be the number of i molecules added. Then an amount of energy, $\mu_i\, dN_i$, has been added to the system.

Thus, equations (12)-(14) can now be generalized:

(18a)
$$dE = TdS - PdV + \sum_i \mu_i\, dN_i$$

(18b) $\quad dH = TdS + VdP + \sum_i \mu_i\, dN_i$

(18c) $\quad dG = VdP - SdT + \sum_i \mu_i\, dN_i$

(18d) $\quad dA = -SdT - PdV + \sum_i \mu_i\, dN_i$

(18a) is sometimes called the Basic Equation of Modern Thermodynamics. Differentiating (18) with respect to N_i, holding everything else constant:

(19) $\quad \mu_i = \left(\frac{\partial E}{\partial N_i}\right)_{S,V,N_j} = \left(\frac{\partial A}{\partial N_i}\right)_{T,V,N_j} = \left(\frac{\partial H}{\partial N_i}\right)_{S,P,N_j} = \left(\frac{\partial G}{\partial N_i}\right)_{T,P,N_j}$

We have already noted that a system at constant T and P goes from a higher free energy state to one of lower free energy--or the system travels down a "free energy gradient." The analogy can be made with a potential difference--hence, the term "thermodynamic potential."

At constant T and P, the "potential" function is G.

At constant T and V, the "potential" function is A.

(20)
$$\mu_i \equiv \text{Chemical Potential} = \left(\frac{\partial G}{\partial n_i}\right)_{T,P,n_j}$$

(6) $\quad H \equiv$ heat content or enthalpy $\equiv E + PV$

(7) $\quad A \equiv$ Helmholtz Free Energy $\equiv E - TS$

(8) $\quad G \equiv$ Gibbs Free Energy $\equiv H - TS = E + PV - TS = A + PV$

In differential form, these become

(9) $\quad dH = dE + PdV + VdP$

(10) $\quad dA = dE - TdS - SdT$

(11) $\quad dG = dH - TdS - SdT$

(12) $\quad$ (9) & (5) $\Rightarrow dH = TdS + VdP$

(13) $\quad$ (10) & (5) $\Rightarrow dA = -SdT - PdV$

(14) $\quad$ (11) & (12) $\Rightarrow dG = VdP - SdT$

(15) $\quad$ From (13): $\left(\frac{\partial A}{\partial V}\right)_T = -P$; $\left(\frac{\partial A}{\partial T}\right)_V = -S$

(16) $\quad$ From (14): $\left(\frac{\partial G}{\partial P}\right)_T = V$; $\left(\frac{\partial G}{\partial T}\right)_P = -S$

Equations (1) through (16) are widely used in thermodynamics. These relations can be used to derive many additional expressions which are more useful in certain situations, particularly relations which are amenable to experimental verification.

Equilibrium:

A system is in thermodynamic equilibrium if there is no further tendency for its properties to change. One condition is that S is maximized (at constant E,V). Second condition is that E is minimized (at constant S,V). Equilibrium depends on both conditions, hence, it can be expressed as a minimum in A or G.

$(A)_{T,V}$ or $(G)_{T,P}$ is minimized at equilibrium.

(17) $\Rightarrow \left.\begin{array}{l} (dA)_{T,V} = 0 \\ (dG)_{T,P} = 0 \end{array}\right\}$ at equilibrium

N_i = number of molecules of type i

n_i = number of moles of i

Thus, μ_i as defined in (20) is $\overline{G}_i$ (defined in 5d).

The chemical potential is the free energy change due to a change in the number of moles of component i, assuming T, P, and all other components remain constant. Chemical potentials, therefore, are a measure of how the free energy of a system varies with composition.

In summary:

(18a) $dG = VdP - SdT + \sum_i \mu_i \, dn_i$

         $(dG)_{T,P} = \sum_i \mu_i \, dn_i$

At equilibrium

(21) $(dG)_{T,P} = 0 = \sum_i \mu_i dn_i$

Equilibrium exists between 2 phases, α and β, when:

(22) $\begin{cases} \text{Thermal:} \quad T^\alpha = T^\beta \\ \text{Mechanical:} \quad P^\alpha = P^\beta \\ \text{Chemical:} \quad \mu_i^{\,\alpha} = \mu_i^{\,\beta} \end{cases}$

Gibbs-Duhem Equation:

The condition for equilibrium, $\sum_i \mu_i \, dn_i = 0$, is in outward appearance similar to another thermo relation, the Gibbs-Duhem equation. This expression is really a restricted form of the Gibbs Adsorption Equation. Consider some extensive state variable, $x = f(T,P,N_i,N_j)$. As this is an exact differential we can say:

(23) $dx = \left(\frac{\partial x}{\partial T}\right)_{P,N_i,N_j} dT + \left(\frac{\partial x}{\partial P}\right)_{T,N_i,N_j} dP + \sum_i \left(\frac{\partial x}{\partial N_i}\right)_{T,P,N_j} dN_i$

(24) $(dx)_{T,P} = \sum_i \overline{X}_i \, dn_i$

The mathematical properties of the function permit us to write:

(24a) $X = \sum_i \overline{X}_i \, n_i$

Differentiating

(25) $dX = \sum_i \overline{X}_i \, dn_i + \sum_i n_i \, d\overline{X}_i$

Equating (24) and (25), we see that

$\sum_i n_i \, d\overline{X}_i = 0$

or when X = G

(26) $\boxed{\sum n_i \, d\mu_i = 0}$

Equation (26) is commonly called the Gibbs-Duhem Equation.

Summary

In general

$dE = q - w + \sum \mu_i \, dN_i$

where w = all forms of work

$= PdV - \underbrace{\sum \psi \, de}_{\substack{\text{electrical} \\ \text{work}}} - \underbrace{\sum m_i \, g \, L_i \, dN_i}_{\substack{\text{gravitational} \\ \text{work}}} - \underbrace{\sum \gamma \, dO}_{\substack{\text{surface} \\ \text{work}}}$

where γ = surface tension
    O = surface area

or at constant T,P and ignoring electrical and gravitational work

(27) $\boxed{(dG)_{T,P} = \sum \gamma \, dO + \sum \mu_i \, dN_i}$