

Elastomers in the Hot Sour Gas Environment

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It can be shown that elastomers have a more predictable swelling response in high-pressure supercritical gases than previously believed. This paper reviews environment interactions, emphasizing thermodynamic considerations and other concepts to develop a more consistent elastomer/gas interaction rationale.

"The Future is Gas," C₁ chemistry is being rediscovered as a result of a potentially vast supply of domestic natural gas-methane (CH₄). The production conditions are rigorous:

- Primary environment dictated by high heat and pressure.
- Secondary (sour) environment created by varying percentages of hydrogen sulfide (H₂S) and carbon dioxide (CO₂), two totally dissimilar gases.

The inevitable presence of water often create hydrates (crystalline CH₄ - H₂O structures) in gas production, unless methanol is injected to serve as an "antifreeze." The acidic production environment, created by reactions between water, CO₂ and H₂S, have to be

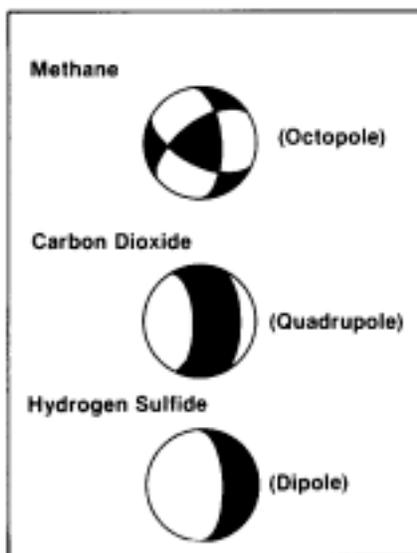


Fig. 1 — Electric charge distribution.

inhibited (neutralized) with bases to prevent corrosion of metal components.

Water, CO₂ and H₂S create aqueous and nonaqueous electrolytes - substances capable of conducting electricity. The existence of electrolytes indicates Lewis acid - base concepts will dictate elastomer/filler/gas responses not previously well defined.

Lewis Acid-Base Definitions. A critical survey of Lewis' definitions is covered by Jensen in his book, "The Lewis Acid - Base Concepts - An Over view"(1). For our purpose, we will be content to summarize Lewis concepts by quoting Jensen:

"An acid is a species that employs an empty orbital in initiating a reaction" (electron-pair acceptor-EPA);

"A base is a species that employs a

doubly occupied orbital in initiating a reaction" (electron-pair donor-EPD);

Neutralization is a coordinate (heterogenic) bond formation between the acid and the base:



"All degrees of electron donation are possible, ranging from nearly zero in the case of weak (but specific) intermolecular attractions, and idealized ion associations, to complete transfer of one or more electrons (redox)."

The energy changes accompanying these exchanges are difficult to quantify. Guttman(2) has developed actual donor numbers (DN) and acceptor numbers (AN).

Methane, carbon dioxide and hydrogen are so dissimilar, one might consider only mixing them together as a capricious trick. Considering the gases first, in a molecular thermodynamic sense, Fig. 1 illustrates the electric charge distribution on the gas molecule. They may be simplistically summarized as follows:

<i>Methane</i> (CH ₄):	Octopole - a uniform charge distribution creating a <i>nonpolar</i> molecule.
<i>Carbon dioxide</i> (CO ₂)	Quadrupole - strong negative charges at both ends, categorized as a Lewis acid or electron-pair acceptor (EPA agent), or an electrophile.
<i>Hydrogen sulfide</i> (H ₂ S)	Dipole-created by the 90° bond angle, categorized as a Lewis base or electron pair donor (EPD agent), or a nucleophile.

Table I — Physical Properties — Gases

	CH ₄	CO ₂	H ₂ S
Critical temperature-T _c (°K)	190.1	304.2	373.6
Critical pressure-P _c (MPa)	4.64	7.38	9.01
Critical volume-V _c (dm ³ /kg)	6.153	2.137	2.867
Critical density-P _c (kg/dm ³)	0.163	0.468	0.349

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Gas Properties. Table I indicates typical production will normally be at temperatures with the gases in their "supercritical state." Defining this statement, consider the following definitions:

Critical temperature T_c : Temperature above which gas cannot be liquefied no matter how high the pressure.

Critical pressure P_c : Lowest pressure at which gas will liquefy at its critical temperature.

Critical molar volume V_c : Volume of mole of gas at the critical temperature.

Fig. 2 is a carbon dioxide phase diagram illustrating the critical temperature, critical pressure, and triple point, and the supercritical fluid region. As would be expected, a three-gas mixture phase diagram would be far more complicated and probably does not exist. Understanding the partial pressure rule (refer to any physical chemistry text) does not make the gas predictions quite as daunting, however. Ender's highly original work should be referred to as key references.

The Supercritical State

This might be best understood by considering water (H_2O). Water is a liquid at room temperature because it is a very polar molecule. This is created by two conditions:

- A hydrogen atom attached to an oxygen atom develops the strongest of all intermolecular (as opposed to covalent) attractions. This leads to self-association of H_2O molecules creating a liquid state through an h-bond (formerly referred to as a hydrogen bond).

- Bond angle between HOH is about 109° , causing a net permanent dipole; this creates an additional intermolecular (dipole) attraction.

Heating water creates two events:

- The h-bond is both highly directional and distance sensitive - heat causes separation and bond strength diminishes ($2 \times \text{distance} = 1/64$ of original strength).

- Molecule now begins to rotate (heat is mobile energy of atoms) and rotation of the molecule creates a symmetrical field that averages out the electrical imbalance created by the permanent dipole.

The water is now a gas. The intermolecular attractive forces creating the liquid state have been cancelled. At $374.2^\circ C$, it is in the supercritical state.

Methanol is similar - adding one oxygen atom to methane (CH_4), a gas, now makes it a liquid, (CH_3OH). The same consequence of having both strong h-bonding and dipole attractions creates the liquid state at room temperature.

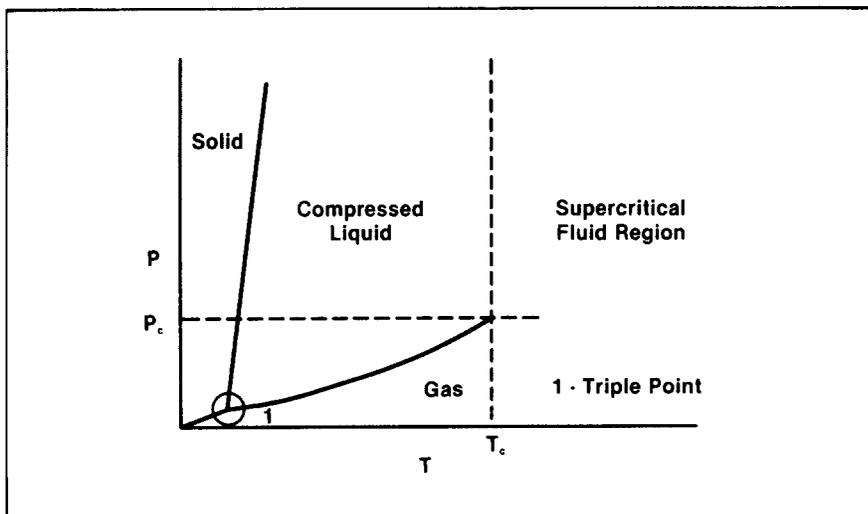


Fig. 2 — Schematic of gas phase diagram.

Methane is nonpolar because of symmetry. The high critical volume - V_c and low density (ρ) create minimal swelling even with EPDM elastomers at high pressures and temperatures(4).

Carbon dioxide has a small, permanent dipole with uneven charge distributions that are *not* cancelled by rotation in the critical state. It is capable of multiple types of associations with polar elastomers.

Hydrogen sulfide becomes nonpolar above its critical temperature, as evidenced by the high swelling of the nonpolar EPDM elastomer in Fig. 4.

For more detailed molecular descriptions of the gases, Refs. (5) and (6) are suggested.

Three elastomers are under current consideration for use as sealing components. The rationale for their usage is briefly outlined:

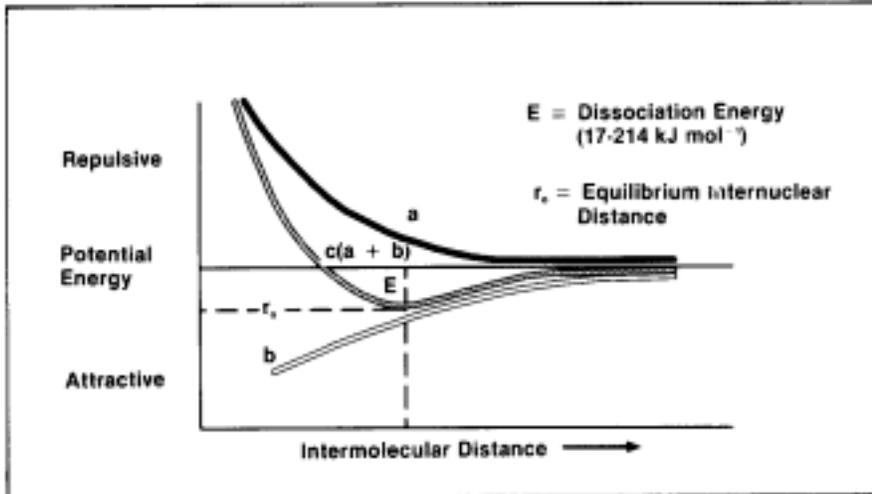


Fig. 3 — A schematic of intermolecular potential energy.

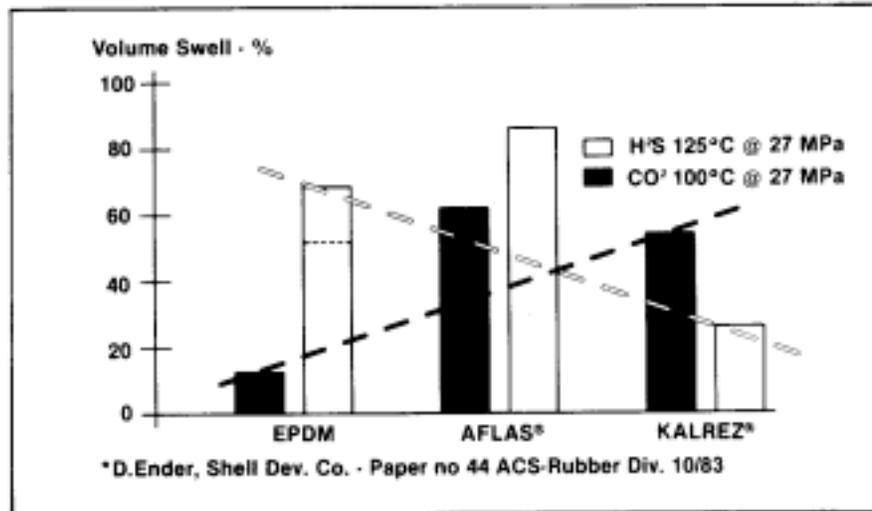


Fig. 4 — A schematic of gas-elastomer swelling.*

Ethylene-propylene terpolymers (EPDM). DOE sponsored investigations (7), with associated publicity, have created considerable interest. Although these polymers are not oil resistant, they undergo little interaction with methane, even at high pressures. The maximum gas density achieved by methane is relatively low; swell is density related.

Tetrafluoroethylene-propylene copolymers (Aflas*). A half-fluorinated elastomer, Aflas has greater heat resistance than EPDM. Oil resistance is imparted by the polar tetrafluoroethylene component. Although the hydrogen-fluorine ratio is about 1/1, these polymers have a minimal tendency for dehydrofluorination, due to heat or a basic (high pH) environment.

Tetrafluoroethylene - perfluorovinyl methylether (FFKM) (Kalrez*). A totally fluorinated elastomer, Kalrez has had good acceptance in sour crude service. It has the best overall heat and fluid resistance of any elastomer currently available. The difficulty in molding large sections, coupled with high cost, has limited sealing designs to those utilizing O-rings and V-rings.

Other Elastomers. Hydrofluorocarbon elastomers containing vinylidene fluoride (VF₂) monomers (Fluorel*, Viton*), have an inherent tendency to dehydrofluorinate, yielding hydrogen fluoride. The reaction is initiated by heat and basic environments. VF₂ or (1,1-difluoroethylene) is technically a geminal difluoride, and the fluorine is readily eliminated by a base. This is essentially the mechanism utilized to create the original cure-site to crosslink such fluoroelastomers.

Hydrogenated nitrile (HNBR) is created by hydrogenating the butadiene double-bonds, developing a methylene-acrylonitrile copolymer. Preliminary short-term data appears encouraging but one should remember the reactivity of any monomer is unaffected by the size of a larger polymer.

Simply stated, well defined organic reactions are not obviated because the monomer is now a polymer. This concept was verified recently by Pfisterer, et al. (8) in their work on identifying the hydrogen sulfide mechanism of attack on a conventional butadiene - acrylonitrile (NBR) elastomer.

Goodson(9) has run IR spectroscopy on "hardened" conventional NBR packer elements returned from service. His data indicate the acrylonitrile (cyano) groups have undergone two separate reaction mechanisms:

- *Hydrolysis* in the presence of zinc bromide completion fluid, indicated by IR amide and carboxylic acid peaks.
- *Reduction* in the presence of hydrogen sulfide, indicated by IR primary amine peaks.

Solubility Parameter Concepts. Gas - elastomer interactions are best explained by integrating Lewis acid-base concepts with Hildebrand's "Theory of Regular Solutions" (10). This makes use of the solubility parameter concept δ , as developed by Hildebrand and Scott(11). It is simply defined as the square root of the energy of vaporization (E_v) per unit volume (V) of a liquid:

$$\Delta E_v = V\delta^2 \quad (2)$$

This equation defines the "cohesive energy density" (ced) and its square root as the "solubility parameters δ ". Thus,

$$\begin{aligned} \delta &= \left(\frac{\Delta E_v}{V} \right)^{0.5} \\ &= \left(\frac{\Delta H_v - RT}{V} \right)^{0.5} = (\text{ced})^{0.5} \end{aligned} \quad (3)$$

Equation(3) gives us the basic δ_d , or "dispersion force" value. The more complex modification as proposed by Burrell and later Hansen(12) for polar liquids does not appear relevant for gases under high pressure in a supercritical state for several reasons:

Supercritical gases at pressures of 100 MPa have a density approaching a liquid while maintaining the mobility of a gas.

Hirschfelder and Roseveare(13) developed an equation applicable to gases at high pressures based on the observation that, at high temperatures, the internal energy (ΔE_v) of a gas at a constant temperature is a linear function of its density, and that at sufficiently high temperatures the molecules behave like rigid, non-attractive spheres. This is a logical assumption on the basis of the Lennard - Jones molecular attraction-repulsion potential curves (Fig. 3).

Czubryt, et al.(14) comment that high pressure gas solubility parameters are functions of only this density, and are approximated by the linear relationship,

$$\delta_{\text{gas}} = \delta_{\text{liquid}} (\rho/\rho_{\text{liquid}}) \quad (4)$$

Earlier work by Giddings, et al.(15,16)

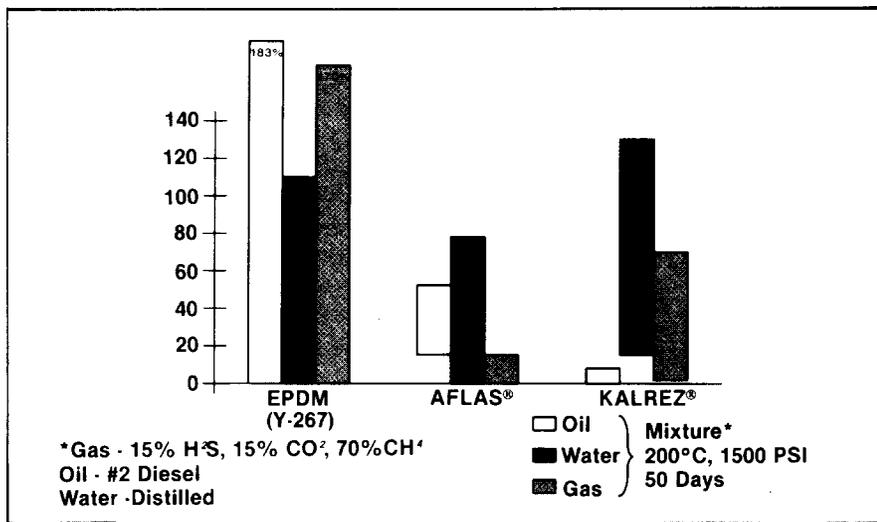


Fig. 5 — Oil/water/gas — elastomer swelling range.

suggests that by using reduced properties for density (ρ_r) [ratio of apparent density (ρ) to critical density (ρ_c)] the following equation roughly approximates solubility parameters of compressed gases at higher pressures:

$$\delta = 1.25 \rho_r^{2/3} (\rho/\rho_{\text{liquid}}) \quad (5)$$

Gas-Elastomer Interactions. Ender(3) verifies increasing gas density does increase the swelling effect on elastomers. This is not the complete story, however. Consider Fig. 4, developed from Ender's data. If solubility parameter δ was the entire story, one might simplistically rationalize the following based on elastomer chemical structures:

EPDM	nonfluorinated
Aflas*	half-fluorinated
	EPDM
Kalrez*	totally-fluorinated
	EPDM

Following through on this thinking, the swelling of Aflas should be about one half of EPDM or Kalrez. Fig. 4 illustrates the swelling Aflas is twice what might be anticipated. Jensen(17) gives us an insight as to the cause of this effect, quoting from his chapter:

"Quantifying these considerations is, however, more difficult as most species are to some extent amphoteric and their EPA and EPD properties tend to work in opposite directions as far as the sign and magnitude of the zeta potential are concerned. Perhaps the simplest approach to this problem would be to use an empirical linear correlation similar to that proposed by Koppel and Palm in 1971 to analyze the solvent dependency of various physico-chemical properties

equilibrium constant, a reaction enthalpy, an NMR shift, or, in our case, the zeta potential of a colloidal particle. Generally if the EPA-EPD character of the solvent is significant, it tends to swamp the last term."

Jensen(18) further suggests the anomalous swelling of Aflas is explained in the following manner:

"The equation of interest is No. 38:

$$\begin{array}{c}
 P \\
 \uparrow \\
 \text{Property of} \\
 \text{interest} \\
 \text{(swell)} \\
 \\
 \alpha \cdot \text{DN} \\
 \uparrow \\
 \text{Lewis} \\
 \text{basicity} \\
 \text{sensitivity}
 \end{array}
 =
 \begin{array}{c}
 P_0 \\
 \uparrow \\
 \text{Property in} \\
 \text{reference} \\
 \text{state} \\
 \\
 \beta \cdot \text{AN} \\
 \uparrow \\
 \text{Lewis} \\
 \text{acidity} \\
 \text{sensitivity}
 \end{array}
 +
 \begin{array}{c}
 \\
 \\
 \\
 \\
 \xi \cdot \delta_s \\
 \uparrow \\
 \text{Nonspecific} \\
 \text{sensitivity} \\
 \text{(solubility} \\
 \text{parameter)}
 \end{array}$$

α , β and ξ are determined by least squares multiple parameter regression analysis by measuring P in a variety of systems of known DN, AN and δ_s . The values can then be used to calculate P in other systems.

For your system:

$$P = P_0 + \alpha \cdot \text{DN} + \beta \cdot \text{AN} + \xi \cdot \delta_s \quad (38)$$

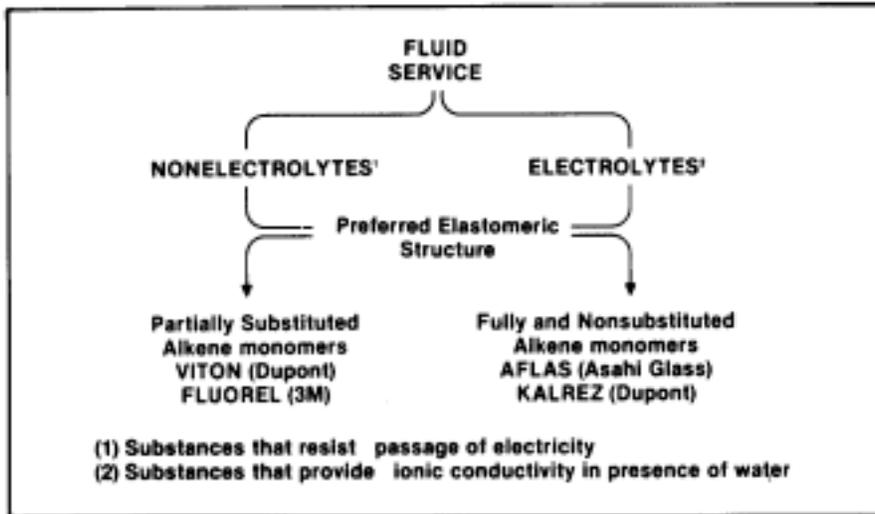


Fig. 6 — A flow chart for selecting the base elastomer for fluid service.

P_0 = volume swell in air = 0
 P = volume swell for gas or liquid
 DN, AN, δ_d = characterize the gas or liquid
 α, β & ξ = characterize the polymer

For your gases (these are qualitative guesses):

δ_d - ($H_2S > CO_2$)
 DN - ($H_2S > CO_2$)
 AN - ($CO_2 > H_2S$)

For your polymers (these are qualitative guesses):

EPDM ($\alpha = \beta = 0$ re only ξ is operative, polymer is non-specific)
 Aflas (α and β large - and swamp ξ polymer is amphoteric)
 Kalrez ($\alpha = 0$, β large and swamps ξ , i.e., polymer is a Lewis base.)"

Elastomer Selection

The rigorous conditions of present and future gas production and their effect

on elastomers is summarized in Fig. 5, based on testing by Goodson(19). The varying swelling range indicated a sensitivity to both crosslink density and the crosslinking chemistry. The high swell in water indicates the presence of ionic compounds as described in a recent paper by Edwards(20). The logical elastomer for this service would be a fluoroelastomer polymerized from a combination of monomers that are:

- Non-substituted (hydrocarbon) alkenes - ethylene, propylene.
- Fully-substituted (perfluoro) alkenes - tetrafluoroethylene hexafluoropropylene, perfluoro (methylvinlether).

Fig. 6 is a "flow chart" to be referred to on fluoroelastomer selection.

Elastomeric Swelling Limits. There are two important considerations regarding ultimate swelling of elastomers in the sour gas environment:

- Swelling of the elastomer by any supercritical gas, a physical adsorption (as opposed to chemical adsorption) phenomena is essentially temperature independent(21).
- Swelling automatically becomes self-limiting due to the adsorption potential of the surface. This limits the

number of layers formed in a multilayer gas absorption to five or six(21). Fig. 7 illustrates this "multiplier" effect, using the "tangent-sphere models" described by Jensen(1).

In summary, although not specifically indicated in Ender's paper(3), the gas/elastomer swelling actually noted was rapidly leveling off. There would have been only minimal increases (and some decreases) at pressures of 100 MPa (15,000 psi) and greater.

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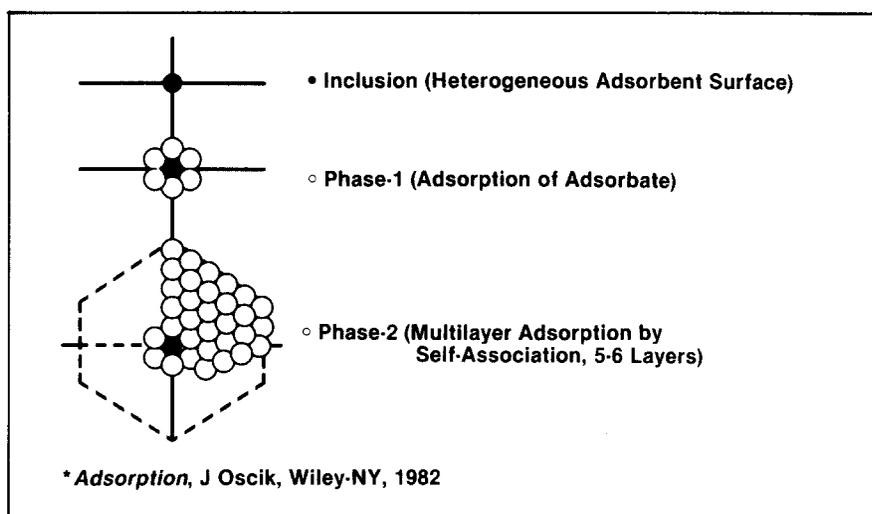


Fig. 7 — A schematic of adsorption phenomena initiation.

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