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Keynote Lecture at the Conference on Separations
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Abstract

When contemplating or designing a separation process, every chemical engineer at once recognizes the thermodynamic boundary conditions that must be satisfied: when a mixture is continuously processed to yield at least partially purified products, energy and mass must be conserved and work must be done. In his daily tasks, a chemical engineer uses thermodynamic concepts as tacit, almost subconscious, knowledge. Thus, qualitative thermodynamics significantly informs process conception at its most fundamental level. However, quantitative design requires detailed knowledge of thermodynamic relations and physical chemistry. Most process engineers, concerned with flow sheets and economics, cannot easily command that detailed knowledge and therefore it is advantageous for them to maintain close contact with those specialists who do. Quantitative chemical thermodynamics provides an opportunity to evaluate possible separation processes not only because it may give support to the process engineer's bold imagination but also because, when coupled with molecular models, it can significantly reduce the experimental effort required to determine an optimum choice of process alternatives. Six examples are presented to indicate the application of thermodynamics for conventional and possible future separation processes.

Introduction

In one of his philosophical essays, Albert Einstein made a remarkable statement. He said

"Science is no more than the purification of daily thoughts".

In other words, science seeks to codify, to express in a general and efficient way, our oft-repeated observations of how nature behaves.

In a similar way, we might claim that

Thermodynamics is no more than the formal expression of that latent, tacit knowledge that is subconsciously ingrained in the mind of every chemical engineer.

Every chemical engineer knows instinctively that, barring unusual circumstances, heat flows from a higher to a lower temperature and that a component diffuses from a higher to a lower chemical potential. The first and second laws of thermodynamics are so deeply imbedded in us that whenever we design a heat exchanger or a separation process, we are, in effect, "doing" thermodynamics, even though we are not aware of doing so.

Therefore, when I was asked to lecture to separation engineers on thermodynamics, my expectation was that the audience would react like Le Bourgeois Gentilhomme in Molière's famous play where the gentilhomme is told the difference between poetry and prose and then says

"Good heavens! For more than 40 years I have been speaking prose without knowing it."

Separation engineers may not know much about formal thermodynamics, but they know thermodynamics in their bones.

Two short examples can quickly illustrate how every separations engineer unconsciously uses thermodynamics.

Suppose we want to separate carbon dioxide from a gaseous stream of natural gas using water as a selective solvent. Everyone knows that this will work but not very well. If water must be used, how can we make it work better? Simple: we add caustic. Acidic carbon dioxide will dissolve much better in water if we make the water alkaline because

I $CO_2 + H_2O \rightleftharpoons H^+ + HCO_3^-$ (weak)

II $H^+ + OH^- \rightleftharpoons H_2O$ (strong)

Anyone with a high-school course in chemistry knows Reactions I and II.

We are perhaps not aware of it but when, instinctively we say, "Add caustic", thermodynamically we are using the relation

$(-\Delta G^0)_I << (-\Delta G^0)_{II}$ where ΔG^0 is the standard Gibbs energy of reaction.

Another example: Suppose we want to separate chlorobenzene from a very dilute aqueous solution. At once we think of generating a vapor and we look at boiling points. Here they are

	Boiling point, °C
Water	100
Chlorobenzene	131.7

At first glance, evaporation does not look promising because water is more volatile than chlorobenzene; we want to evaporate the organic component, not the water. Yet we know instinctively that stripping out chlorobenzene will work well. We know that because we know that water and chlorobenzene do not "like" each other, and that, therefore, the volatility of chlorobenzene is far beyond what it would be if it formed an ideal solution with water.

We may not be aware of it, but thermodynamically, we use the relation

$\gamma^{\infty}_{CBz} >> 1$ where γ^{∞} = activity coefficient at infinite dilution.

In its informal, qualitative and subconscious form, thermodynamics lies at the very foundation of separation operations. But thermodynamics can do more than that. In its formal, quantitative form, thermodynamics can provide a powerful tool for conception and efficient development of separation processes. To illustrate, some examples are presented to show how quantitative thermodynamics can help the separations engineer. The initial examples refer to some well-known, more-or-less conventional processes but those given later are more speculative, directed toward potential future applications.

Separation of Air by Pressure-Swing Adsorption

While the cryogenic process for producing oxygen and nitrogen from air is now about 100 years old, an attractive alternate process has been receiving favorable attention during the last twenty years. Figure 1 shows the essentials: with the N_2-vent valves closed, air flows through a bed of solid zeolite adsorbent on the left side of the diagram; valves to and from the identical bed on the right are closed. Because of its quadrupole moment, nitrogen is preferentially adsorbed and therefore oxygen flows out at the top. When the left-side bed becomes saturated, valves to and from that bed are closed and those for the bed on the right side are opened. Air now flows through the bed on the right, again, nitrogen is adsorbed preferentially and oxygen flows out at the top. To regenerate the left-side bed, its valve to the N_2 vent is opened and nitrogen is pumped out, preparing the left bed for the next cycle. This process is called "pressure-swing" because the pressure for adsorption is higher than that used for desorption (bed regeneration).

To design this process at some known temperature, it is necessary to have adsorption equilibrium data for mixtures of nitrogen and oxygen as a function of composition and total pressure as shown, for example, in Figure 2 taken from the text of Ruthven (1984). The left side of Figure 2 shows adsorption isotherms for pure nitrogen and for pure oxygen while the right side shows results for mixtures; here α is the separation factor, X is the mole fraction of the (adsorbent-free) adsorbed phase and Y is the mole fraction in the vapor phase.

Much experimental effort was required to obtain the mixture results shown on the right side; to reduce that effort, it is helpful to use a molecular-thermodynamic model which can reliably predict equilibria for a mixture using only experimental adsorption data for the pure components. Several models have been proposed; a few are indicated in Figure 3 taken from a review by Sorial et al (1983). Predicted results from the vacancy solution model are shown by the dashed line; essentially identical results from three other models are shown by the continuous line which agrees very well with experiment. (IAST = Ideal Adsorbed Solution Theory.)

Figure 3 indicates how thermodynamics is useful for designing an optimum process for air separation by pressure-swing adsorption. Using only single-gas adsorption data over a range of temperature and pressure, the design engineer can determine at least some of the optimum conditions for the separation process without requiring extensive (and tedious) adsorption data for oxygen-nitrogen mixtures.

Separation by Pervaporation

Much attention has been given in recent years to separations based on membrane technology. One possible application of such technology is pervaporation as indicated in Figure 4: a liquid mixture flows over the top of the membrane; a reduced pressure on the bottom side of the membrane produces a vapor. Using a properly-chosen selective membrane, different components in the liquid mixture have different permeabilities in the membrane. Therefore, the composition of the liquid sorbed at interface b is not the same as that at interface a. To a reasonable approximation, the liquid mixture sorbed at a is in equilibrium with the bulk liquid and the liquid mixture sorbed at b is in equilibrium with the vapor.

For process design, we require phase equilibria at interfaces a and b. The necessary experimental effort can be much reduced by using some well-known concepts in molecular thermodynamics.

At the temperature of interest, the necessary experimental data include a membrane sorption isotherm for each pure component in the liquid mixture; and vapor-liquid equilibria for the (membrane-free) liquid mixture as a function of composition.

Data for each single-solute sorption isotherm are reduced using some model for the activity coefficient of the (volatile) liquid sorbed in the membrane. For these data, the vapor phase is pure volatile liquid and the condensed "fluid" phase is a binary mixture of the volatile liquid and the nonvolatile polymer that comprises the membrane. A typical activity-coefficient model might be UNIQUAC; data reduction yields the two binary parameters in UNIQUAC. These binary parameters reflect interactions between the volatile liquid and the membrane polymer.

Vapor-liquid equilibrium data for the membrane-free liquid mixture yield binary parameters reflecting interactions between any pair of unlike molecules in the membrane-free liquid mixture.

To predict the membrane composition at interface a, we now calculate liquid-liquid equilibria; using our activity coefficient model and the required binary parameters, we calculate activities for each component in the membrane-free mixture and in the sorbed membrane phase of interface a.

To predict the vapor-phase composition, we must first find the composition of the sorbed membrane at interface b using permeability data. (This composition is for $N+1$ components where N is the number of components in the liquid to be separated; the additional component is the membrane polymer.) Once we know the condensed-phase composition at b, we can find the composition of the equilibrium vapor using our activity-coefficient model. To describe vapor-phase properties at low pressures, we use ideal-gas relations; at advanced pressures, it may be necessary to include also equation-of-state nonideality corrections but, in practice, these are rarely needed.

Figure 5 shows experimental sorption data for five pure fluids at 60 °C. The lines show calculated results using the UNIQUAC equation with binary parameters obtained from the experimental data (Lichtenthaler and Cen 1995).

For water-ethanol mixtures, liquid-liquid equilibrium calculations were performed as indicated above and at the bottom of Figure 5; results are shown in Figure 6. The predicted lines show good agreement with experiment (Heintz and Stephan 1994).

As in the previous example concerning air separation, thermodynamics provides a tool for significantly reducing experimental effort. In this example, sorption data are required for pure components but not for mixtures.

Application of thermodynamics to separation processes is not limited to calculation of pertinent phase equilibria. In many cases, application of thermodynamics is through chemical equilibria, as illustrated in the next two examples.

Desulfurization of Gasified Coal

When coal is used to produce a gaseous fuel, some hydrogen sulfide is also often obtained because, frequently, coal contains small amounts of sulfur. When the gaseous fuel is subsequently burned to yield heat, sulfur dioxide--a pollutant--is obtained along with the usual products of combustion, water and carbon dioxide; these are vented to the atmosphere where sulfur dioxide can produce damaging acid rain. To prevent (or significantly reduce) sulfur-dioxide pollution, it is desirable to remove hydrogen sulfide from the gaseous fuel prior to combustion.

Figure 7 shows a process for separation of hydrogen sulfide developed by Fenouil and Lynn (1995). The fundamental idea is a classic one: contact gaseous hydrogen sulfide with solid calcium oxide to yield water and solid calcium sulfide. Calcium oxide, in turn, is obtained by decomposing calcium carbonate. But what do we do with the calcium sulfide? In the process of Fenouil and Scott, calcium sulfide is regenerated to calcium carbonate and a concentrated gaseous mixture containing hydrogen sulfide. That concentrated gaseous mixture is sent to a standard Claus plant where hydrogen sulfide is converted to solid elemental sulfur which can be used, for example, to make sulfuric acid.

Figure 7 shows a stream containing 10^4 ppm H_2S; following the sulfur-removing step, this H_2S concentration is to decline by a factor of at least 20, preferably a factor of 100, to 10^2 ppm. A key question in process design is to determine the optimum temperature of the sulfur-removal step.

Thermodynamics can provide an answer to this key question by considering equilibria of the pertinent chemical reactions, as indicated in Figure 8. The reaction of primary interest is Reaction III but, because the solid reactant supplied to the process is not calcium oxide but calcium carbonate, it is necessary first to consider Reactions I and II which, together, comprise Reaction III. We then see that the desired product (CaS) is produced by two independent reactions, Reactions I and III.

Thermodynamic data are available for all necessary standard Gibbs energies and enthalpies of formation; these give the chemical equilibrium constants and their dependence on temperature. (The lower part of Figure 8 gives the chemical steps for conversion of CaS to $CaCO_3$; while these are not required for calculating the optimum temperature of the sulfur-removing step, they indicate how $CaCO_3$ is regenerated.)

For 35 bars and for two fixed concentrations of carbon dioxide and water in the equilibrium mixture, Figure 9 shows the effect of temperature on the equilibrium mole fraction of hydrogen sulfide leaving the sulfur-removal step. Because the enthalpy of reaction for Reaction I is positive while that for Reaction III is negative, Figure 9 shows that the optimum temperature is near 900 °C; near that temperature, the reduction in hydrogen-sulfide concentration is a factor of about 100, as desired.

This example illustrates how conventional chemical thermodynamics can provide valuable guidance toward optimizing a large-scale, commercially feasible process.

Removal of Antimony Ions from Dilute Aqueous Solution

Heavy metals are potentially dangerous pollutants; even small concentrations can pose a serious threat to health. Electrochemistry provides one method for removing a heavy-metal ion from water. In this example we consider a dilute solution of antimony (Sb) in strongly acidic water. We use electrochemistry to precipite antimony as a pure metal; the solubility of metallic (not ionic) antimony is essentially zero.

Figure 10 shows the essential ideas, given by Trainham and Newman (1977). Aqueous feed, containing Sb ions, enters at the left. The overwhelming majority of the entering flow goes up through a porous electrode; only a very small amount (a slip stream) goes down and is recycled. The porous electrode and its porous counter-electrode are connected to a variable voltage source; the porous electrode is also connected to a reference electrode A taken here as a standard calomel electrode.

The quantity ΔV_k is defined as shown; it can be set as desired by changing the variable voltage source. This quantity ΔV_k, in turn, is related to the equilibrium concentrations of the various ionic species and compounds that antimony may have in aqueous solution.

Figure 11 indicated the most likely ionic species and compounds, including highly poisonous, volatile SbH_3.

The equilibrium concentration of each ionic species or compound can be calculated from the Nernst equation corresponding to a particular value of ΔV_k which can be set by tuning the variable voltage source. In the Nernst equation, the concentration of chloride ion refers to that in the reference electrode and the concentration of hydrogen ion is determined by the pH of the aqueous solution. The density of the solvent (water) is in the equations to maintain consistency of units; here, concentrations are given in molarity while standard-state potentials refer to solutions whose concentrations are in molality.

Figure 12 shows equilibrium concentrations (mg/liter) for four soluble species; concentrations for Sb_2O_3 and SbO_2^- are not shown because they are too small. The equilibrium concentrations are given as a function of the cathode potential (see Figure 10) for a highly acidic solution (pH = 0). Also shown is the total concentration of soluble antimony species. The scale factor on the ordinate (10^{14}) indicates that the total concentration of soluble species is extremely small, probably below the limit of detection using the most sensitive analytical instruments now available; essentially all of the soluble antimony has been precipitated on the porous electrode as metallic antimony in the upper part of the electrochemical reactor in Figure 10.

The calculations outlined here refer to an idealized situation that neglects effects of mass transfer and electrode kinetics. Nevertheless, this example indicates the power of chemical thermodynamics to suggest a promising separation process and to provide an estimate of the optimum voltage for separation of soluble antimony from a dilute acidic aqueous solution. The calculations also show that a highly negative voltage must be avoided to prevent significant formation of poisonous volatile SbH_3.

Following these four examples concerning the applicability of thermodynamics to conception and design of separations that pertain to current technology, we now turn attention to two final examples that may become important in future technology.

Separations Based on Hydrogels

A typical textbook on elementary chemistry tells us that there are three states of matter: solids, liquids and gases. These texts neglect another state of matter, viz cross-linked polymers whose properties are intermediate between those of solids and liquids. This intermediate state--a gel--has elastic properties similar to those of "weak" solids but also has some mixing properties similar to those of liquids.

When a gel is in a liquid medium, it can swell; i.e., similar to a sponge, it can sorb a large amount of liquid. When the gel is hydrophilic, it is called a hydrogel. Some hydrogels can sorb 100 or even 1000 grams of water per gram of dry gel, depending on conditions. The ability to sorb water depends on temperature; further, if the polymer constituting the gel consists, in part, of weak-electrolyte (e.g., carboxyl or amino) groups, this ability also depends on pH. In some cases, the swelling properties can exhibit a discontinuity, in effect, a change in phase, similar to melting or vaporization, as shown schematically in Figure 13.

We cannot here go into details but merely state that we now have good quantitative understanding of the thermodynamics of gel swelling, including discontinuous gel swelling and collapse (phase transition); a recent review by Maurer (1995) provides the essential equations and references. When a hydrogel is immersed in water, the change in Gibbs energy comprises contributions from mixing the gel's polymer strands with water, from elastic forces which prevent the gel from expanding indefinitely and, for weak polyelectrolytes, from Donnan equilibria. The latter arise because, while the mobile ions can flow in and out of the gel, the fixed charges on the polymer cannot; e.g., if the polymer has a negative charge, the fixed anions cannot enter the outside aqueous phase but the mobile positive ions (typically H^+) are free to enter or leave the gel phase.

Thermodynamic analysis can be used to calculate the coordinates of the phase transition when a collapsed gel is in equilibrium with a swollen gel. For a nonelectrolyte gel in water, the compositions of the two gels are obtained from a combination of two theories: an expression for the activity of water in a polymer solution and from an expression for the elastic Helmholtz energy of the gel. As shown in Figure 14, when a function z is defined and plotted against gel composition, a van der Waals loop may be obtained, depending on the temperature. The equilibrium compositions are obtained at that temperature where z = 0 and where the area below the dotted line is equal to that above the dotted line.

Reversible gel swelling and collapse may be useful for separation operations. A suggestion toward that end was made by Cussler et al (1989) who proposed a continuous process for separating valuable proteins from undesired whey in an aqueous solution of defatted soybeans, shown in Figure 15. The extent of crosslinking in the gel is such that proteins (molecular weight 10^4 or more) cannot enter the gel while smaller solutes (whey) can do so. The process in Figure 15 consists of six steps; when the gel is cool, it rejects proteins but is able to absorb water with small solutes; when the swollen gel is heated, it collapses, thereby ejecting the previously imbibed solution of small solutes. The gel is then cooled for the next cycle.

An advantage of this proposed process is low energy requirements but there are significant problems, especially solids handling and slow rates of swelling and collapse. Cussler's process is not likely to become a commercial success but it illustrates possible applications of gels for separation operations. Development of possible applications will be facilitated by calculations based on recent advances in the thermodynamics of systems containing gels and multicomponent solutions.

Crystallization of Proteins

Chemical engineers have for many years been interested in the production of crystals from aqueous solution. Traditionally, that interest has been directed primarily at salts and organic solids of moderate molecular weight, although recently attention has also been given to crystallization of polymers. At present, interest in crystallization of proteins is limited to biochemists who need protein crystals for x-ray diffraction studies to determine protein structure. Today, crystalline proteins are of little concern to chemical industry but, with rapid advances in the agricultural, bio and medical sciences, such concern may become important in the not-too-distant future.

It is very difficult to produce protein crystals; indeed, the biochemist who first succeeded in crystallizing a polymer was awarded a Nobel prize for that achievement. There exists a large literature recording extensive experimental efforts by biochemists toward defining the necessary conditions to precipitate a protein crystal from solution. At present, crystallization of proteins is primarily an empirical art.

Can thermodynamics tell us something useful for reducing the experimental effort required to define the necessary conditions? Yes, it can. Recent studies have shown that, for a given protein, there is a relationship between favorable conditions for crystallization and the second osmotic virial coefficient of that protein in a given solvent. A typical solvent is water at a fixed pH with one or more solutes (e.g., salts, alcohols, polymers).

The second osmotic virial coefficient B reflects the forces of attraction and repulsion between two protein molecules in dilute solution. It is related to the osmotic pressure π by

$$\frac{\pi}{RT} = c\left[\frac{1}{M} + B\,c + - - - \right]$$

where c is the (mass) concentration of the protein and M is its molecular weight. If $B > 0$, we have a good solvent, one where the protein molecules "like" the solvent better than themselves. If $B < 0$, the solvent is not good because protein molecules now "like" each other better than the solvent. When $B = 0$, we have a theta solvent where protein molecules show no preference between the solvent and themselves.

In a good solvent, proteins have no "wish" to precipitate whereas in a poor solvent, they prefer "to be by themselves", i.e., to separate from the solvent.

At higher concentrations, near the solubility limit, crystals can form only if the protein molecules can approach each other with just the "right" orientation. In other words, at higher concentrations, crystals will be obtained only if the protein molecules are moderately "unhappy" in the solvent; if they are "too unhappy", they will agglomerate to form an amorphous precipitate. In thermodynamic language, crystals are most likely to form if the osmotic second virial coefficient is slightly, but not excessively, negative, as illustrated in Figures 16 and 17.

Second osmotic virial coefficients B can be measured by low-angle laser-light measurements. Figure 16 shows results for bovine serum albumin in four solvents; for each straight line, B is given by the line's slope. At concentrations in excess of those used to find B, crystallization was not possible in solvents I, I and IV but was successful in solvent III. Figure 17 shows similar results for lysozyme.

George and Wilson (1994) measured B for a variety of dilute proteins in a variety of solvents; for a given protein, they then consulted the biochemical literature to determine which of the solvents they studied did or did not produce crystals at higher protein concentrations. Results are shown in Figure 18 where the number of successes is plotted against B; here, success means that crystals were obtained. Figure 18 indicates that, when B is in a small negative range, success is likely. When B is outside that range, success is not likely.

This example illustrates how thermodynamics can reduce experimental effort for conceiving a protein-crystallization procedure. It shows that thermodynamic data for dilute protein solutions can be used to screen solvents, that is, to determine a priori whether or not a given solvent is or is not a good candidate for precipitating a given protein in a concentrated solution.

Conclusion

All of the examples presented here have a common purpose: to provide guidance toward optimizing a separation process and to provide computational methods for minimizing experimental effort.

Thermodynamics is an inevitable, unavoidable part of separation science because, essentially, thermodynamics provides the framework of what nature can do and wants to do under given conditions. Even in kinetically-controlled separation processes, thermodynamics plays an essential role because it tells us the driving force for bringing about a desired change. Thermodynamics is no more, but also no less, than the quantification of those phenomena in nature that make separations possible.

Thermodynamics is an unconscious part of our daily existence. When we hang up a wet towel to dry, we do so because the fugacity of water in the towel is larger than that in the air and when we draw air into our lungs, we do so because the fugacity of oxygen in air is larger than that in our blood.

As chemical engineers, we cannot--and indeed we do not--think about a separation process without also--unconsciously--thinking about thermodynamics; instinctively, from our earliest experience, we necessarily restrict any conceivable separation process to be consistent with the first and second laws of thermodynamics.

While our ability to design separation processes is effortlessly informed by our qualitative, existential knowledge of thermodynamics, that ability can be much enhanced by utilizing our quantitative, scientific understanding of thermodynamics. That understanding, however, demands appreciable effort because it requires familiarity with a large body of knowledge in classical, statistical and molecular thermodynamics.

For many practical chemical engineers concerned primarily with flow sheets and economics, it is not reasonable to expect familiarity with that large body of knowledge, and fortunately, it is not necessary. However, it is both reasonable and necessary that there be intensive dialogue between those who work with quantitative thermodynamics and those who conceive and design separation processes. Such dialogue tells the thermodynamicist where the important problems are and provides the separation-process engineer with the quantitative information that he needs to support or constrain his flights of imagination.

Acknowledgment

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TWO-BED PRESSURE-SWING ADSORPTION (PSA) SYSTEM FOR AIR SEPARATION

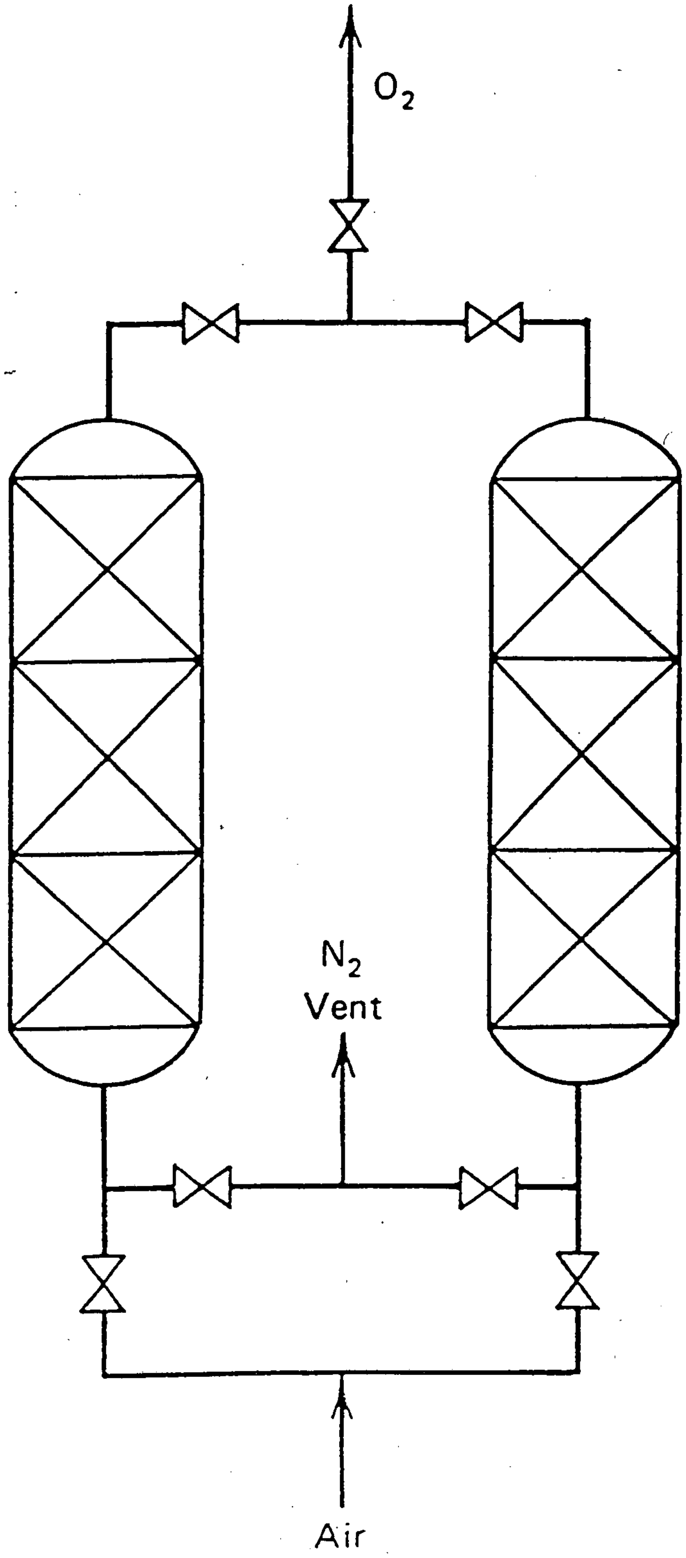


Figure 1

EQUILIBRIUM DATA FOR SORPTION OF O_2, N_2, AND O_2-N_2 MIXTURES ON ZEOLITE 5A SHOWING (a) SINGLE-COMPONENT ISOTHERMS AND (b) SEPARATION FACTOR, TOTAL ADSORBED-PHASE CONCENTRATION AND X-Y DIAGRAM

(FROM RUTHVEN, 1984)

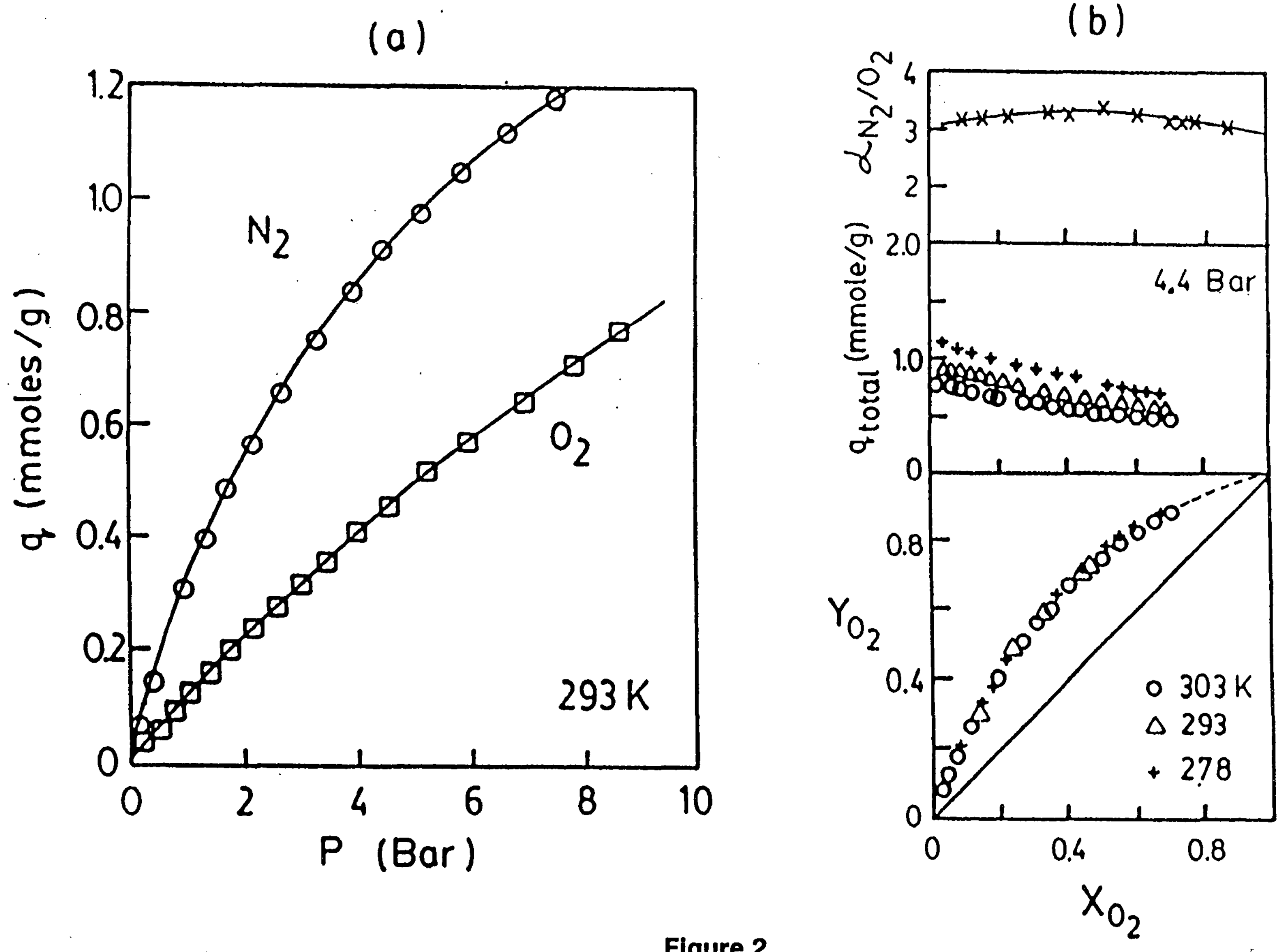


Figure 2

COMPARISON OF FOUR MODEL PREDICTIONS WITH EXPERIMENTAL EQUILIBRIA FOR O_2/N_2 ON LAPORTE 5A MOLECULAR SIEVE PELLETS AT 5 °C AND 4.4 BAR

(SORIAL et al, 1983)

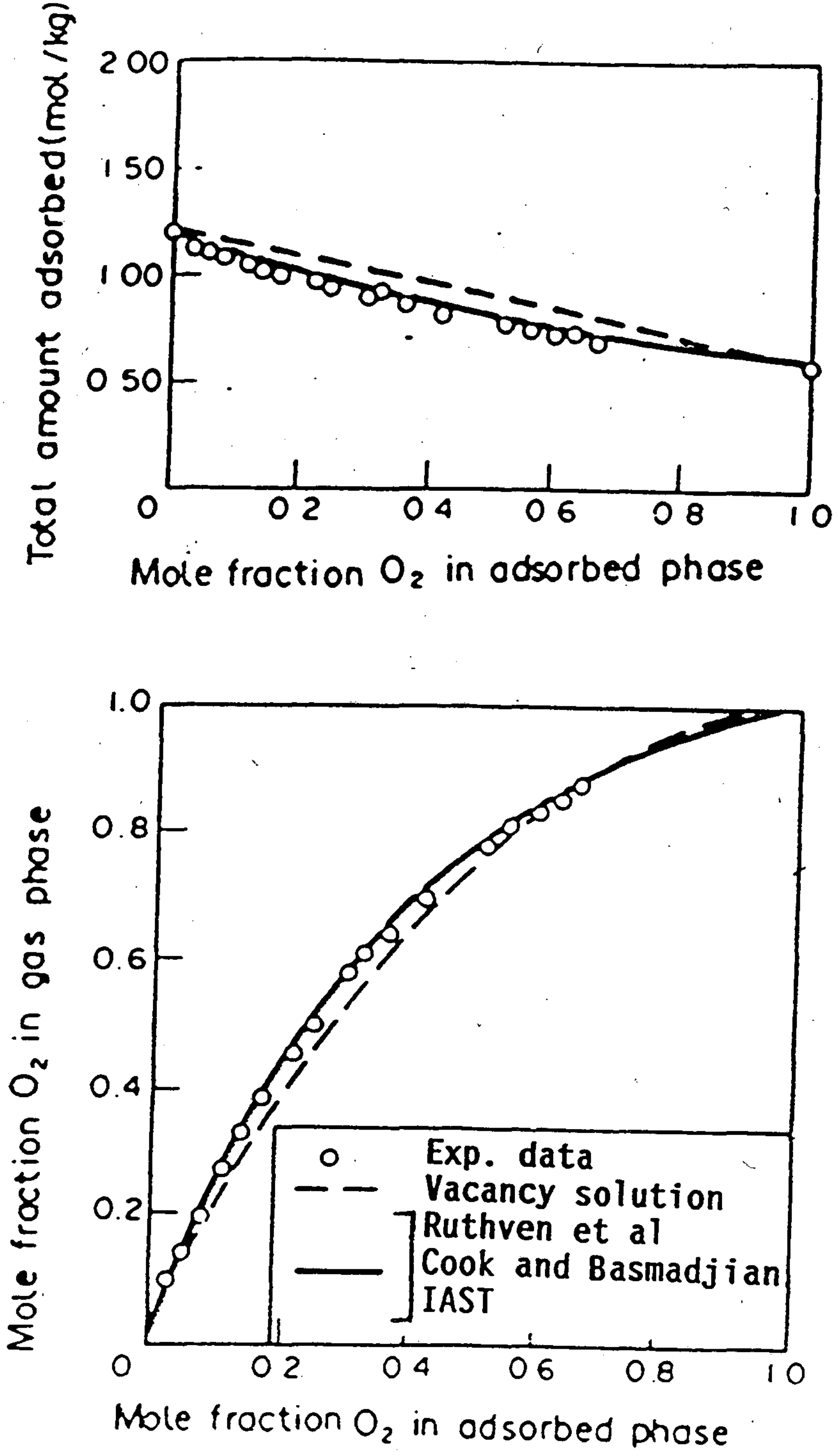
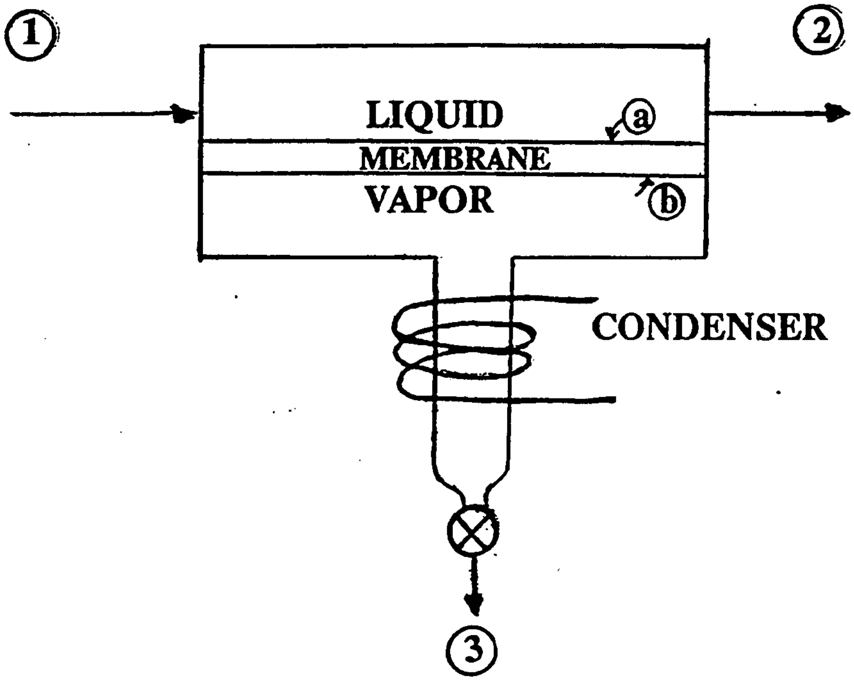


Figure 3

SEPARATION BY PERVAPORATION



①= LIQUID FEED
②= LIQUID RETENTATE
③= LIQUID PERMEATE

EQUILIBRIA AT MEMBRANE-FLUID INTERFACE

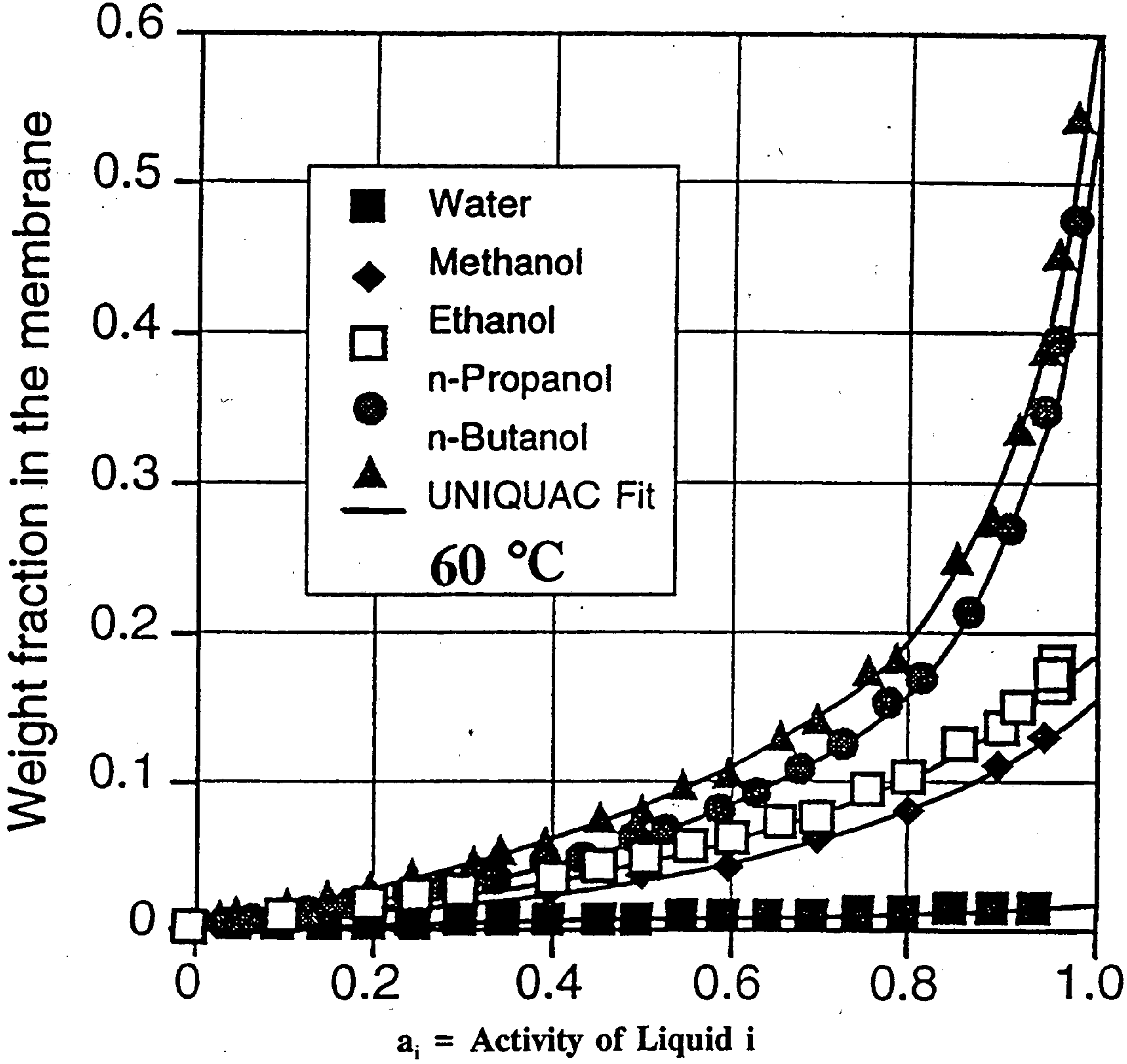
ⓐ= LIQUID-MEMBRANE
ⓑ= VAPOR-MEMBRANE (USUALLY AT LOW PRESSURE)

PROCESS CALCULATIONS FOR SEPARATION BY PERVAPORATION REQUIRE PHASE EQUILIBRIA AT a AND b.

Figure 4

PURE-COMPONENT SORPTION DATA AND CORRELATION FOR ABSORPTION IN A POLYETHER-BLOCK-AMIDE MEMBRANE

(FROM CEN & LICHTENTHALER, 1995)



FOR MULTICOMPONENT LIQUID MIXTURE:

a_i (IN LIQUID MIXTURE) = a_i (IN MEMBRANE)

↑ FROM UNIQUAC (MEMBRANE-FREE)

↑ FROM UNIQUAC WITH MEMBRANE AS ONE COMPONENT

Figure 5

PREDICTED AND MEASURED SORPTION EQUILIBRIA FOR WATER-ETHANOL MIXTURES IN A POLYVINYL ALCOHOL MEMBRANE AT 60 °C

(FROM HEINTZ & STEPHAN, 1994)

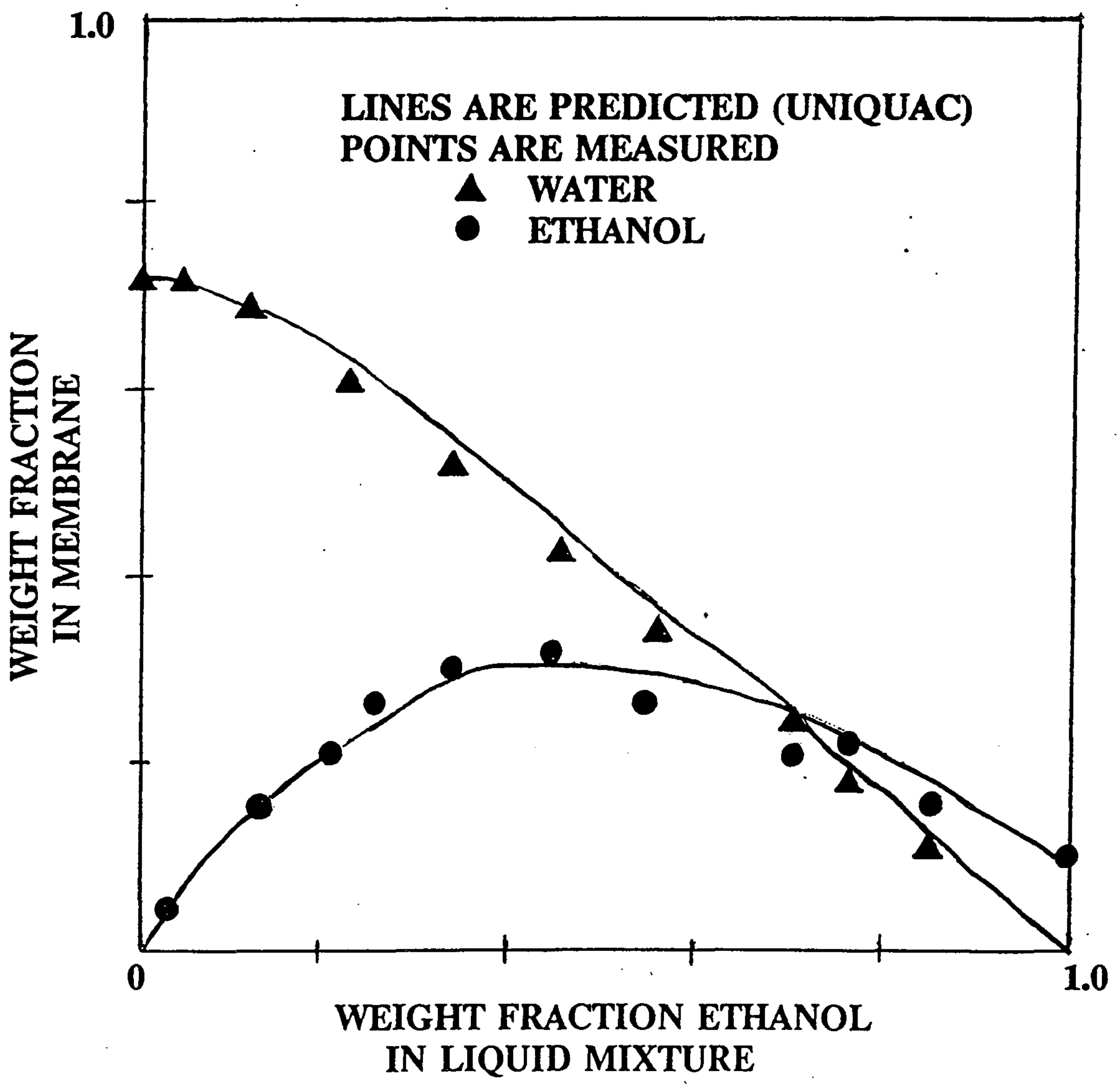
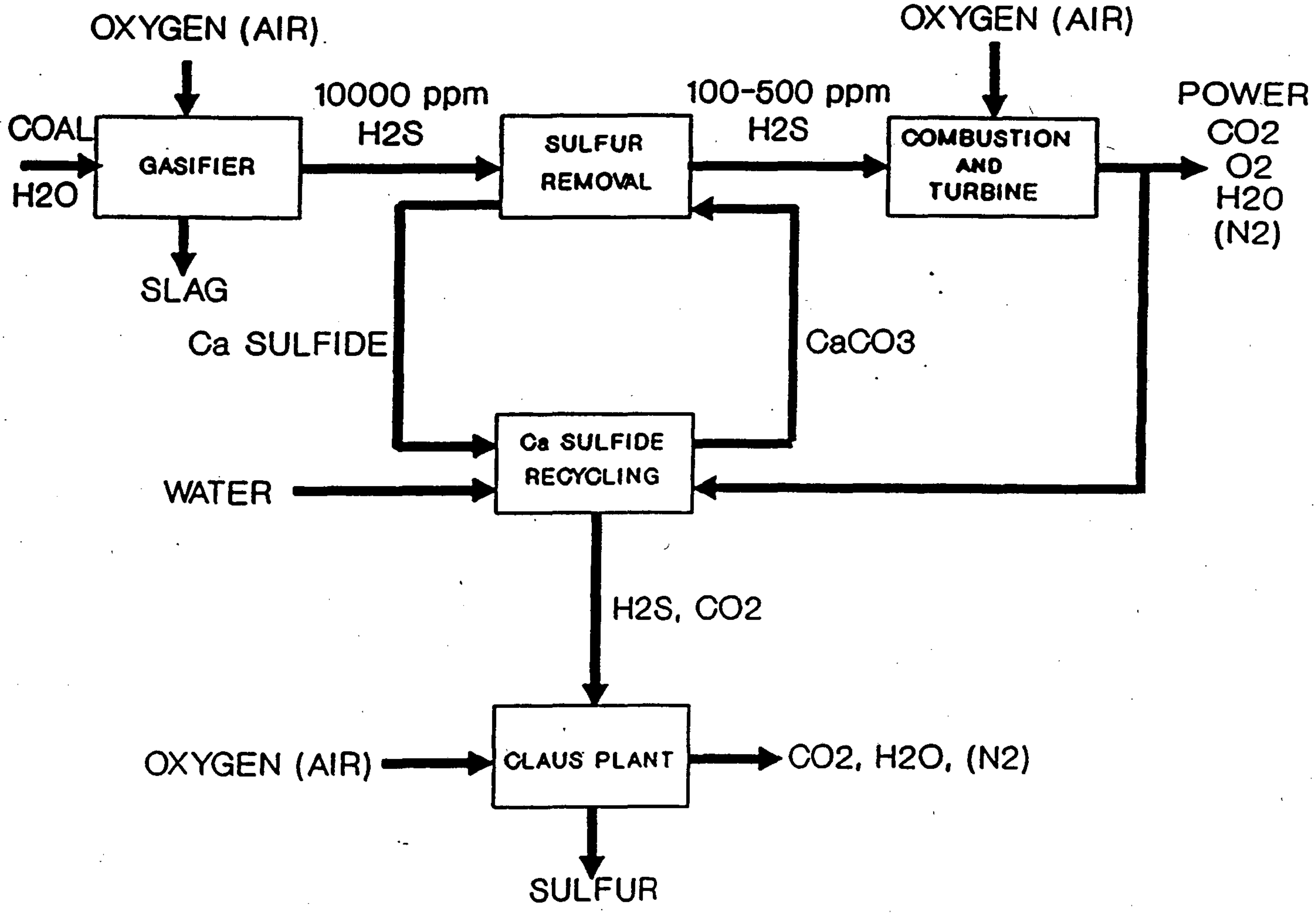


Figure 6

COAL GASIFICATION FOR POWER GENERATION. DESULFURIZATION

(FROM FENOUIL AND LYNN, 1994)



KEY QUESTION: WHAT IS THE OPTIMAL TEMPERATURE OF THE SULFUR-REMOVAL STEP ?

Figure 7

CHEMICAL REACTIONS

SULFUR-REMOVAL STEP

(I) $CaCO_3(s) + H_2S(g) \rightleftharpoons CaS(s) + H_2O(g) + CO_2(g)$
(II) $CaCO_3(s) \rightleftharpoons CaO(s) + CO_2(g)$

These two independent reactions can be combined to give:

(III) $CaO(s) + H_2S(g) \rightleftharpoons CaS(s) + H_2O(g)$

Reaction	ΔH, kJ/mol	K_{eq}(900°C)
I	+ 165	550
II	+ 100	1
III	- 65	550

RECYCLING CaS TO $CaCO_3$

$CaS(s) + H_2S(aq) \rightleftharpoons Ca(HS)_2(aq)$
$Ca(HS)_2(aq) + H_2O(l) + CO_2(g) \rightleftharpoons CaCO_3(s) + 2\ H_2S(g)$

Overall: $CaS(s) + CO_2(g) + H_2O(l) \rightleftharpoons CaCO_3(s) + H_2S(g)$

Figure 8

CALCULATION OF OPTIMUM TEMPERATURE FOR MINIMIZING PARTIAL PRESSURE OF H_2S

(FROM FENOUIL AND LYNN, 1994)

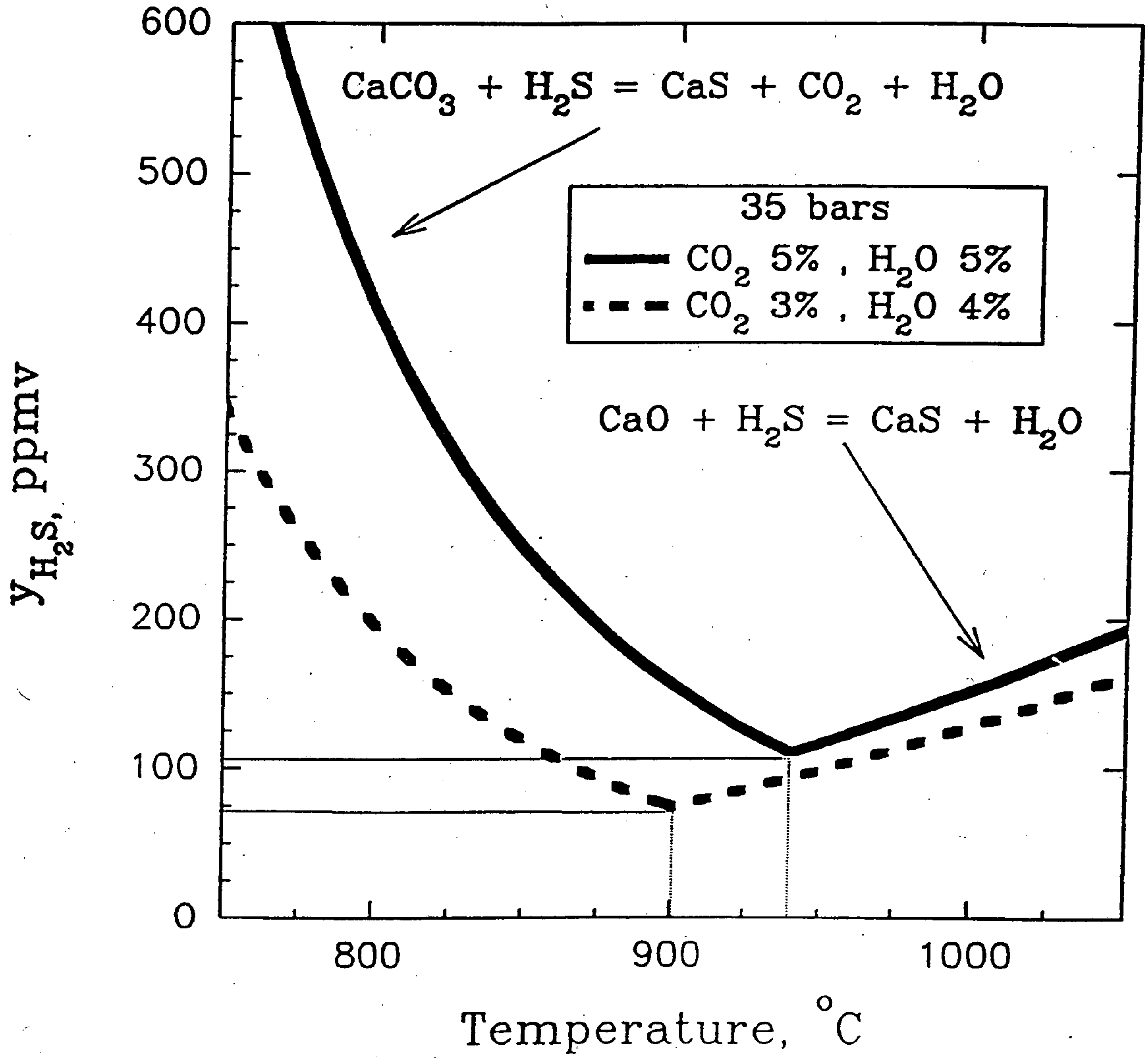
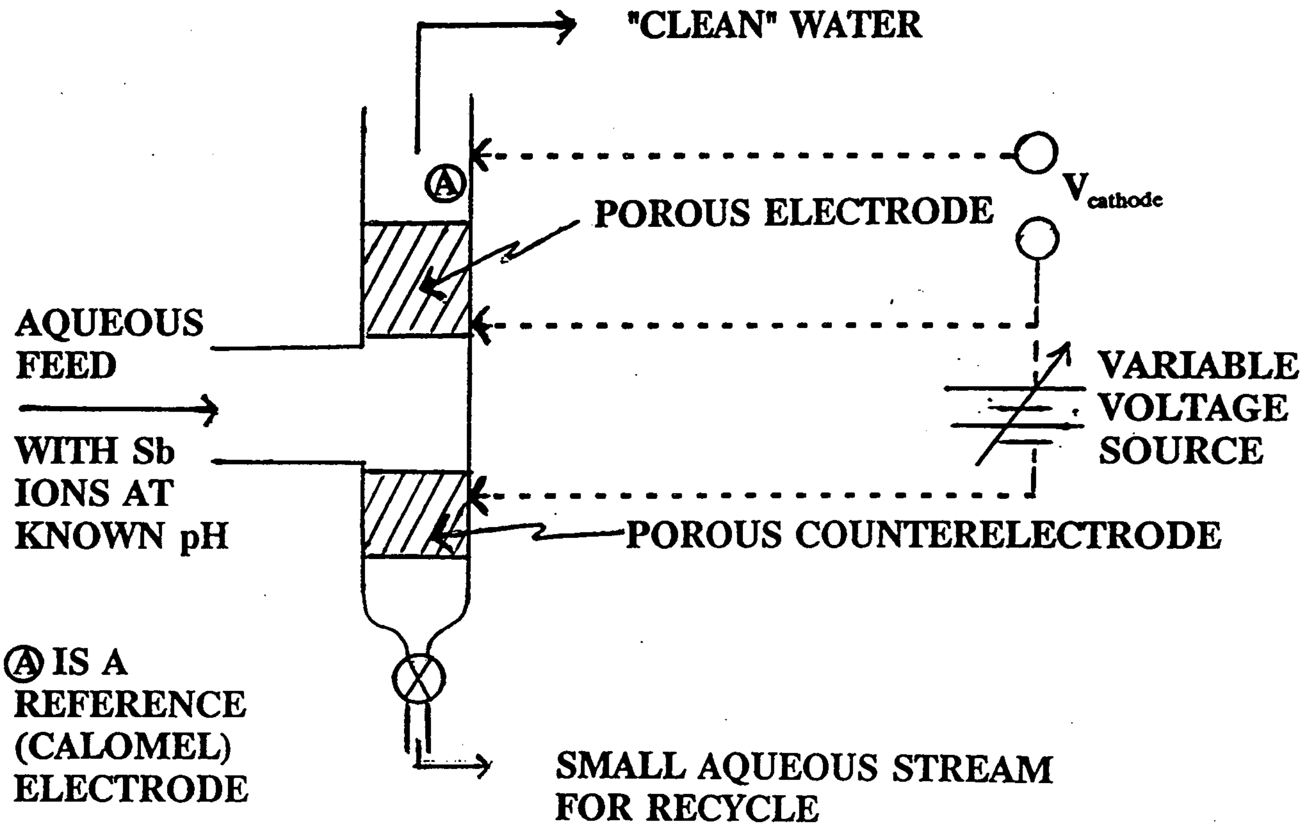


Figure 9

ELECTROCHEMICAL REMOVAL OF A HEAVY METAL ION (Sb) FROM AQUEOUS SOLUTION



$\Delta V_k = V_{cathode} - U_k^\theta + U_{calomel}^\theta$ CAN BE SET AS DESIRED

U_k^θ = STANDARD ELECTRODE POTENTIAL FOR REACTION k

$U_{calomel}^\theta$ = STANDARD ELECTRODE POTENTIAL FOR CALOMEL REACTION: $2e^- + Hg_2Cl_2 \rightarrow 2Hg + 2Cl^-$ IN SATURATED KCl SOLUTION

THESE POTENTIALS ARE THERMODYNAMIC CONSTANTS, KNOWN FOR MANY REACTIONS.

Figure 10

REMOVAL OF Sb ION FROM WATER

POSSIBLE SPECIES CONTAINING Sb ATOMS:

metallic Sb, SbH_3 (gas)
Sb_2O_3, SbO^+, $Sb(OH)_3$ $HSbO_2$, SbO_2^-

WE WANT TO PRODUCE metallic Sb (precipitate).
WE WANT TO AVOID POISONOUS SbH_3 (gas).

SIX REACTIONS IN AQUEOUS SOLUTION.

e.g.

$$Sb + 3H^+ + 3e^- \rightarrow SbH_3$$

$$Sb + H_2O \rightarrow SbO^+ + 2H^+ + 3e^-$$

THE CONCENTRATION OF EACH AQUEOUS SPECIES IS OBTAINED FROM ITS NERNST EQUATION.

e.g.

$$C_{SbH_3} = \frac{(C_{H^+})(C_{Cl^-})^3}{\rho_0^5} \exp\left[\frac{-3F}{RT}\Delta V_k\right]$$

F = FARADAY'S CONSTANT

$$C_{SbO^+} = \frac{\rho_0^6}{(C_{H^+})^2(C_{Cl^-})^3} \exp\left[\frac{3F}{RT}\Delta V_k\right]$$

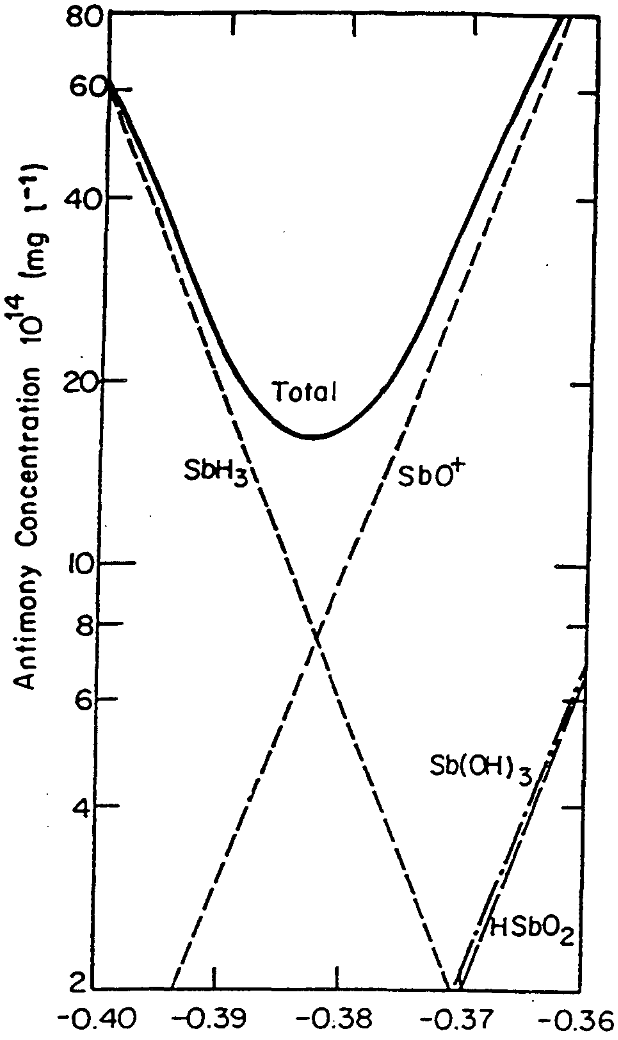
ρ_0 = SOLVENT DENSITY

Figure 11

REMOVAL OF ANTIMONY IONS FROM A HIGHLY ACIDIC AQUEOUS STREAM

EQUILIBRIUM ANTIMONY CONCENTRATION AS A FUNCTION OF ELECTRODE POTENTIAL RELATIVE TO A SATURATED CALOMEL ELECTRODE

(FROM TRAINHAM & NEWMAN, 1977)

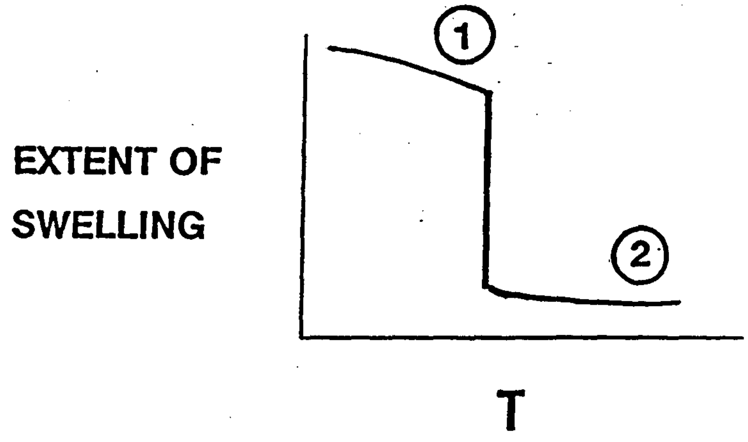


Cathode Potential, Volts
when C_{H^+} = 1 mole/liter

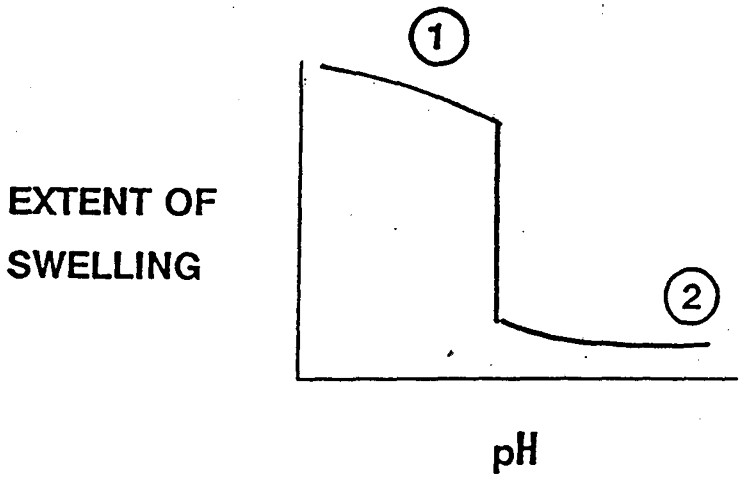
WHEN THE CATHODE POTENTIAL IS SET AT -0.382 VOLTS, THE EQUILIBRIUM EFFLUENT CONCENTRATION OF Sb IONS IS 17 · 10^{-14} mg/liter. REMOVAL OF ANTIMONY ION IS ESSENTIALLY TOTAL.

Figure 12

SWELLING PROPERTIES OF SOME GELS



TEMPERATURE-SENSITIVE GEL



POLYELECTROLYTE pH-SENSITIVE GEL

① SWOLLEN GEL

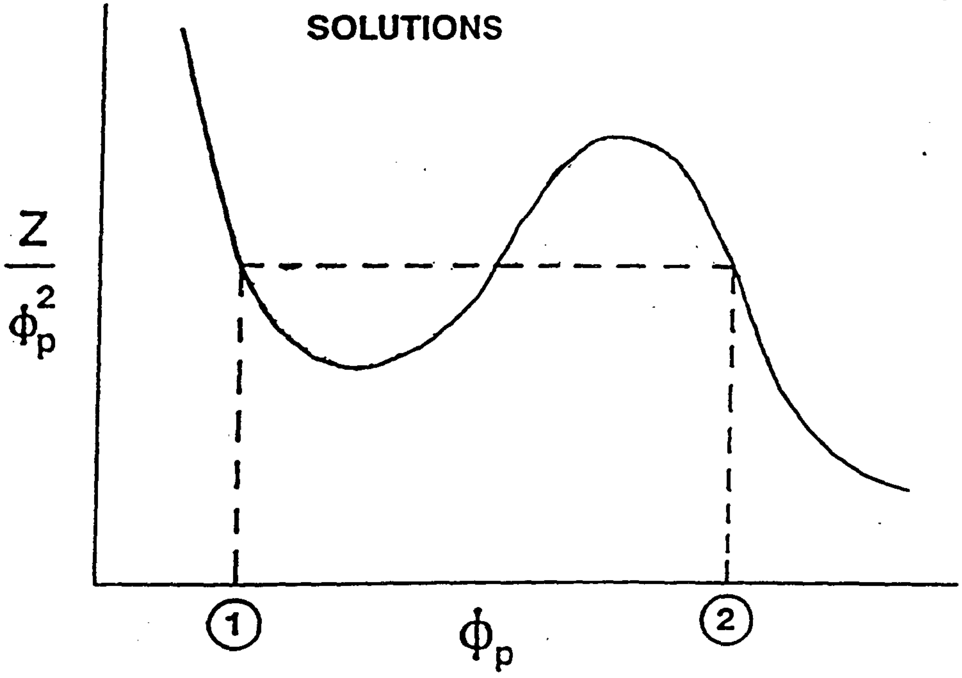
② COLLAPSED GEL

Figure 13

THERMODYNAMICS OF SWOLLEN-GEL/COLLAPSED-GEL EQUILIBRIA

AT THE DASHED HORIZONTAL LINE, $Z/\phi_p^2 = 0$

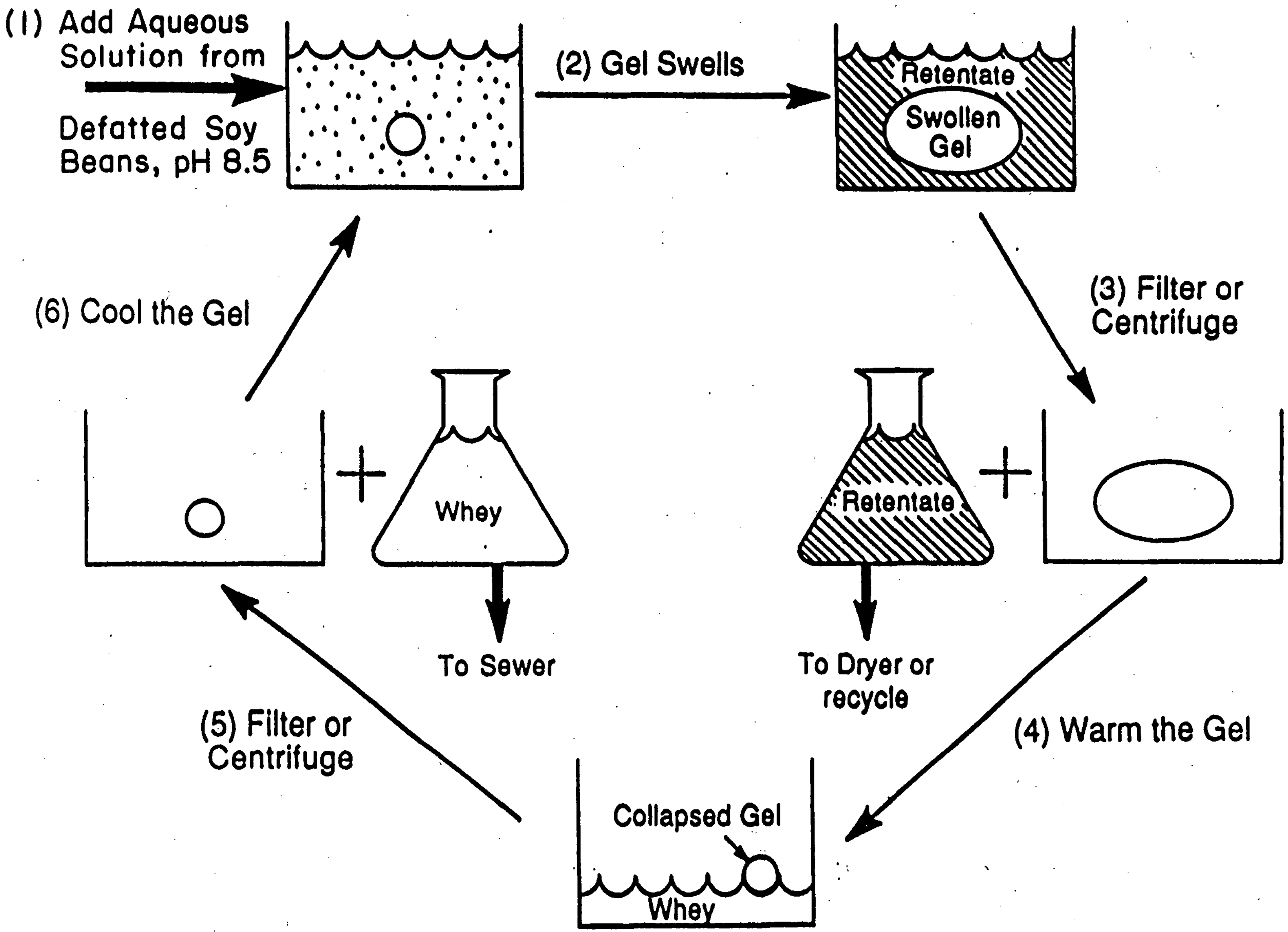
$$Z = \underbrace{\ln a_w}_{\text{FROM THEORY OF POLYMER SOLUTIONS}} + \underbrace{\frac{v_w}{RT}\left(\frac{\partial A}{\partial V}\right)_{T,X}}_{\text{FROM THEORY OF ELASTIC NETWORKS}}$$



ϕ_p = VOLUME FRACTION POLYMER IN GEL
① = COMPOSITION OF SWOLLEN GEL
② = COMPOSITION OF COLLAPSED GEL
a_w, v_w = ACTIVITY AND MOLAR VOLUME OF WATER
A, V = HELMHOLTZ ENERGY AND VOLUME OF GEL
X = OTHER VARIABLES (e.g. IONIC STRENGTH, pH ...)

Figure 14

PURIFICATION AND CONCENTRATION OF PROTEIN EXTRACT FROM SOYBEANS (FROM CUSSLER)



IN STEP (2), GEL REJECTS SOLUTES WITH MOLECULAR WEIGHT OF (ABOUT) 10^4 OR MORE.

Figure 15

FOR CRYSTALLIZATION, WE WANT B SLIGHTLY NEGATIVE BUT NOT TOO NEGATIVE, LEST EXCESSIVELY "UNHAPPY" DISSOLVED PROTEINS FORM AN AMORPHOUS PRECIPITATE

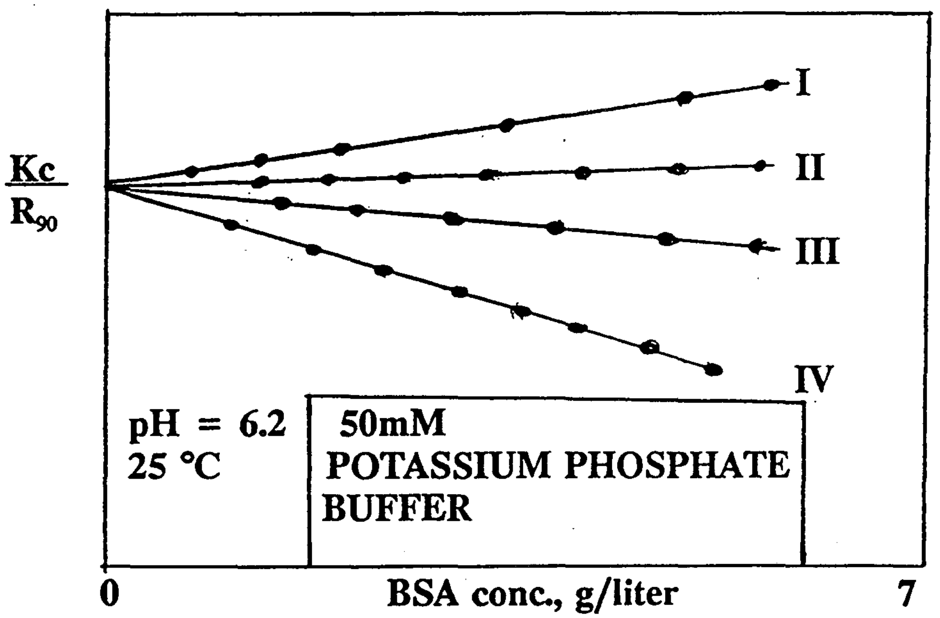
B IS MEASURED BY LOW-ANGLE LASER-LIGHT SCATTERING:

$$\frac{Kc}{R_{90}} = \frac{1}{M} + 2\,Bc$$

c = PROTEIN CONCENTRATION

M = MOLECULAR WEIGHT

K AND R_{90} ARE OBTAINED FROM SCATTERING DATA.

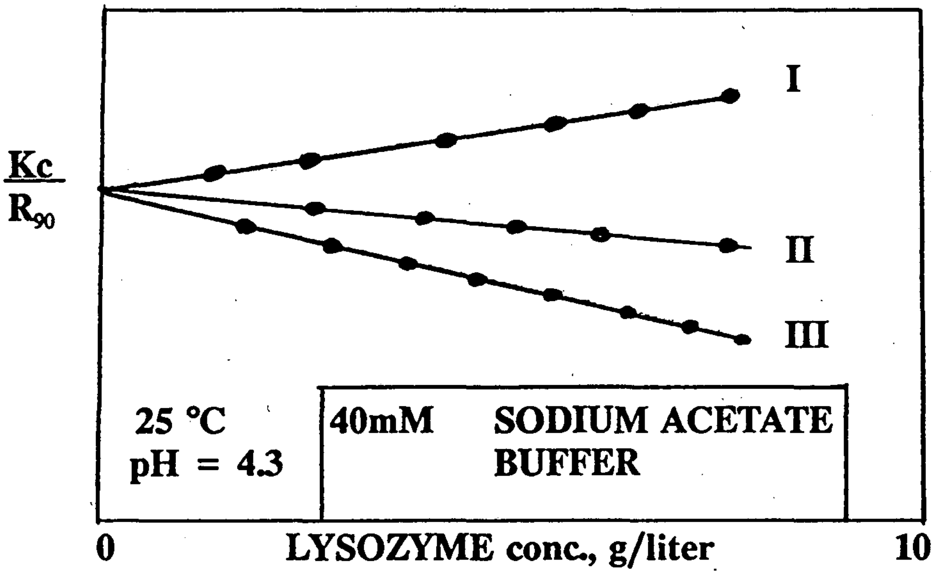


SOLUTION	VOLUME % SAT. $(NH_4)_2SO_4$
I	20
II	37
III	52
IV	60

GOOD CRYSTALLIZATION OBSERVED WHEN VOL% SAT. AMMONIUM SULFATE WAS 52. AT THAT CONDITION, $B = -0.2 \times 10^{-6}$ MOL-LITER/g^2

Figure 16

EXPERIMENTAL RESULTS FOR LYSOZYME



I NO PRECIPITATION OBSERVED IN BUFFERED WATER.
$B = +1.2 \times 10^{-6}$ MOL-LITER/g^2

II SOLVENT CHANGED TO 2 WT % AQUEOUS SODIUM CHLORIDE. CRYSTALS FORM
$B = -0.3 \times 10^{-6}$

III SOLVENT CHANGED TO 1.25 M AQUEOUS AMMONIUM SULFATE. AMORPHOUS PRECIPITATE FORMS.
$B = -0.9 \times 10^{-6}$

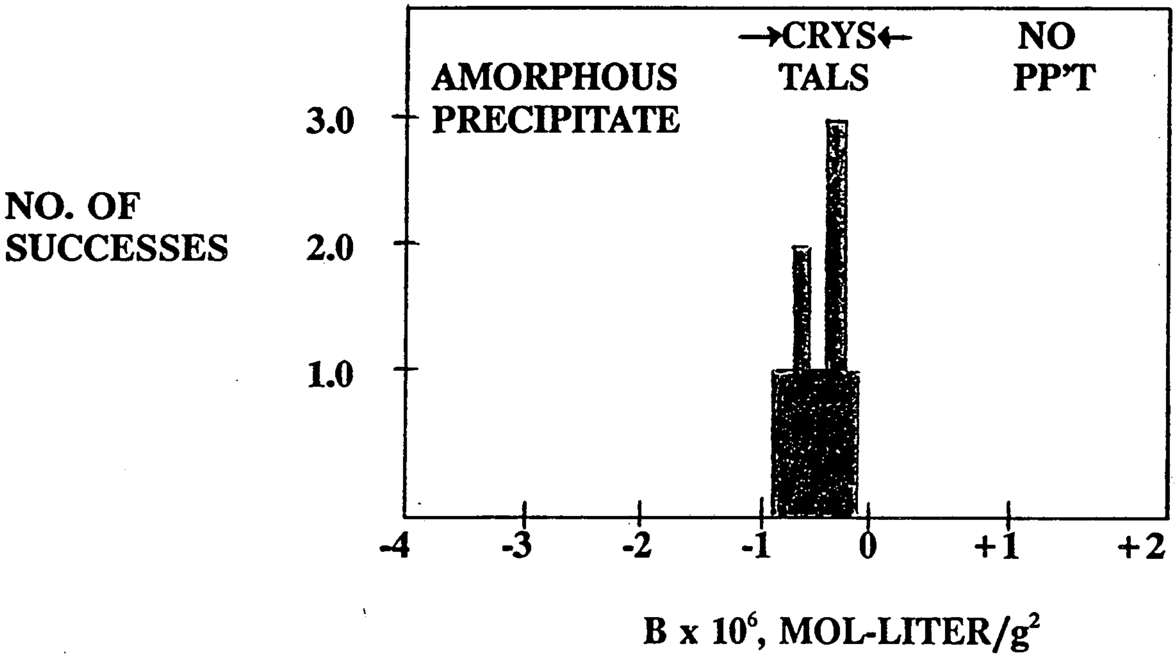
Figure 17

HISTOGRAM OF SUCCESSFUL CRYSTALLIZATIONS
(FROM A. GEORGE AND W. WILSON, 1994)

PROTEINS STUDIED

LYSOZYME, CANAVALIN, CONCANAVALIN, BSA, STMV, OVOSTATIN, RIBONUCLEASE, α-CHYMOTRYPSIN, OVALBUMIN

WITH A VARIETY OF SALTS, ADDED SOLVENTS AND pH



CONCLUSION: IF THE MEASURED B FOR A PROTEIN IN A GIVEN SOLVENT IS IN THE RANGE

$$-0.85 \leq B \leq -0.1 \quad \times 10^{-6} \text{ MOL-LITER/g}^2,$$

THERE IS A GOOD CHANCE THAT CRYSTALS WILL FORM.

Figure 18

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