

Unusual chemical thermodynamics*

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Abstract: Thermodynamics is truly a universal science, and its applications to phenomena outside the chemical laboratory or processing plant are many. Two are discussed here; the prediction of the high-temperature chemical equilibria and transport properties needed for the design of interplanetary probes, and the distribution of long-lived chemicals throughout the environment. Also, the possibilities of combining *ab initio* quantum calculations with activity coefficient models and equations of state to make predictions of vapor-liquid equilibria over large ranges of temperature and pressure is illustrated.

INTRODUCTION

I am pleased to have been invited to present the 1998 Rossini Lecture and honored to be included in this very distinguished lecture series. Previous lectures have presented a detailed retrospective of one area of research to which the lecturer has devoted a significant amount of time. I will depart from that model, and instead consider several topics in chemical thermodynamics that I have found interesting and unusual in my career in academia. The unifying theme is unusual applications of or to thermodynamics. As thermodynamics is truly a universal science there are many examples of applications of chemical thermodynamics to problems other than in the chemical industry. I will briefly discuss a contribution that thermodynamics has made to sending a space probe to the planet Jupiter and to estimating the distribution of long-lived chemicals in the environment. Finally, I will consider the possibilities of using quantum mechanics in applied engineering thermodynamics calculations.

THERMOPHYSICAL PROPERTIES CALCULATION FOR AN INTERPLANETARY PROBE

Almost 30 years ago, I was asked to assist in the computation of the transport properties that would be encountered on entry by an instrumented probe to the planet Jupiter as part of what would become the Galileo Project. Jupiter is known to have an atmosphere consisting mostly of hydrogen and helium. As a result of the high temperatures encountered within the entry shockwave ($T = 20\,000$ K or higher) and the very low critical temperatures of hydrogen and helium, thermodynamic calculations leads one to conclude that even at a high pressures encountered, the mixture is an ideal gas. This is because at these temperatures the kinetic energy of the particles is much higher than the interaction energies. Therefore, from readily available information on the structure and dissociation energy of hydrogen, and the electronic energy state of the atoms involved, one can use standard ideal gas statistical mechanics [1] to predict the concentrations of the various species as a function of temperature. An example of this is shown in Fig. 1 for one fixed mass density.

With these compositions, one can calculate the transport properties; Chapman–Enskog theory [2] without density corrections can be used since the gas is ideal. However, the collision cross-sections involved are complicated because of the variety of species involved, especially the charged species. A discussion of these cross sections would be long and not very interesting. Therefore, I will immediately

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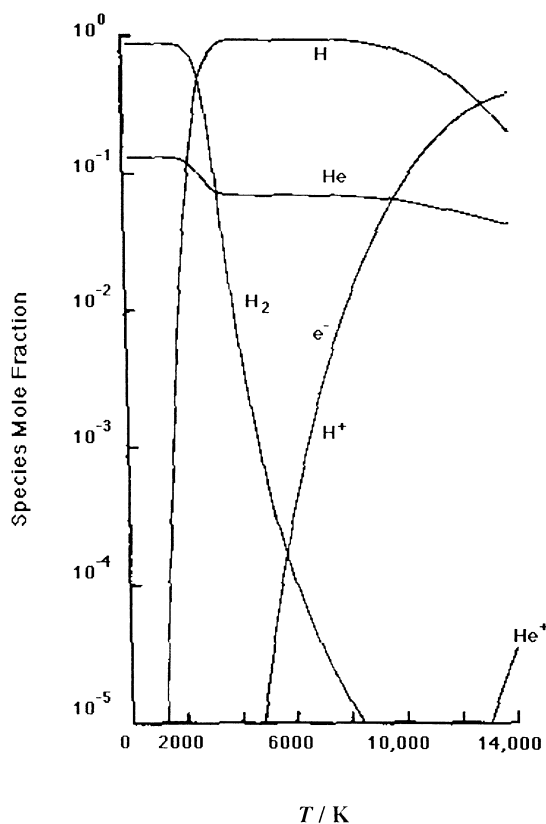


Fig. 1 Equilibrium at fixed densities of a helium + hydrogen mixture at mole fraction of helium = 0.11 as function of temperature.

jump to the results shown in Figs 2 and 3 for the viscosity and thermal conductivity, respectively. What should be noticed here is how these properties change as a function of temperature as a result of first the dissociation reaction and then the ionization reactions that occur. For comparison, the figures also show as dashed lines the large errors that result of extrapolating the measurable, lower-temperature thermal conductivity and viscosity with approximately the $T^{0.5}$ temperature dependence to the high temperatures of interest.

There are two lessons from this example. The first is the danger of simplistic extrapolations well beyond the range of available data. Here over some ranges in temperature the error would be almost one order of magnitude. Also, the complicated variations of the transport properties with density, resulting from the changes in composition due to the shifting chemical equilibria, would not have been predicted. The second lesson is that a good thermodynamic model is far better than simple extrapolation.

FATE OF CHEMICALS IN THE ENVIRONMENT

Next I will consider the problem of the distribution of long-lived organic chemicals in the environment. In contrast to the ideal gas example above, the environment consisting of air, water, soil, sediment and biota or living things, is a complex system to model. Given this complexity, and that any model will only be very approximate, it is sensible to begin by using only the simplest of models. One model that has had some success is the phase equilibrium model for long-lived chemicals pioneered by D. Mackay [3]. The assumption of the model is that a chemical that has a long half life in the environment, for example the pesticide DDT, polychlorinated biphenyls (or PCBs) and dioxin, will achieve a state of environmental phase equilibrium. This model will not be completely correct because of mass transport limitations, for example, the diffusion of chemicals into or out of undisturbed soil is

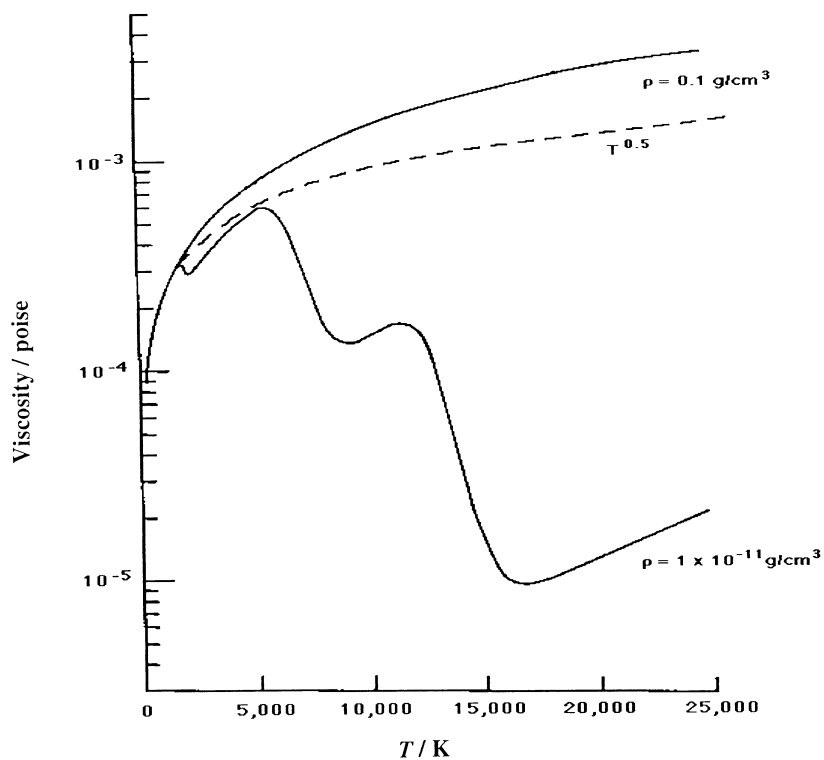


Fig. 2 Viscosity of a helium + hydrogen mixture at mole fraction helium = 0.11 as function of temperature at two fixed mass densities.

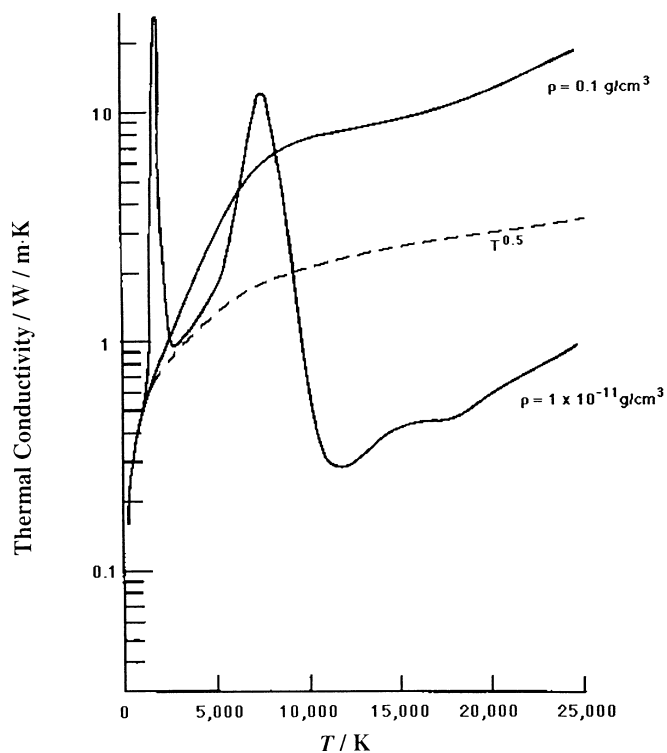


Fig. 3 Thermo conductivity of (helium + hydrogen) mixture at mole fraction helium = 0.11 as function of temperature at two fixed mass densities.

very slow. Nonetheless, it is interesting to examine the implications of this phase equilibrium model of the environment.

To start the thermodynamic analysis, the environment is first divided into compartments or regions in which the chemical will be approximately homogeneously distributed. These compartments include air and water that are well defined and easy to include in a model, and also biota (including humans), soil and sediment that are more difficult to characterize for inclusion in a thermodynamic model.

The criterion for phase equilibrium of a chemical between any two phases (denoted as I and II) is:

$$\bar{G}_i^I(T, p, x_i^I) = \bar{G}_i^{II}(T, p, x_i^{II}), \text{ or } \bar{\mu}_i^I(T, p, x_i^I) = \bar{\mu}_i^{II}(T, p, x_i^{II}) \text{ or } \bar{f}_i^I(T, p, x_i^I) = \bar{f}_i^{II}(T, p, x_i^{II}) \quad (1)$$

where \bar{G}_i^I , $\bar{\mu}_i^I$ and \bar{f}_i^I denote the partial molar Gibbs free energy, chemical potential and fugacity, respectively, of chemical i in solution, and the superscript denotes the environmental compartment. These equations are equivalent; and it is the last of these that will be used.

The fugacity of a chemical in air, which at environmental conditions is an ideal gas, is equal to its partial pressure:

$$\bar{f}_i^A(T, p, x_i^A) = x_i^A p = \frac{C_i^A}{C^A} p = C_i^A RT \quad (2)$$

Here x_i^A is the mole fraction of chemical i in the air, C_i^A and C^A are the molar concentrations of the chemical and the air, respectively, R is the gas constant and T is the absolute temperature. The fugacity of chemical i in water is

$$\bar{f}_i^W(T, p, x_i^W) = x_i^W \gamma_i(T, p, x_i^W) f_i^0 = x_i^W \gamma_i(T, p, x_i^W) p_i^{\text{vap}} \quad (3)$$

where the superscript W indicates the aqueous phase, the pure component fugacity of chemical i as a liquid, f_i^0 , has been replaced by its vapor pressure, p_i^{vap} , and γ_i is the activity coefficient of the chemical in water. In most cases of environmental interest the concentration of the chemical (pollutant) in the aqueous phase is quite low, so γ_i can be replaced with its value at infinite dilution, γ_i^∞ i.e.

$$\bar{f}_i^W(T, p, x_i^W) = x_i^W \gamma_i^\infty(T, p, x_i^W) p_i^{\text{vap}} = x_i^W H_i = C_i^W H_i' \quad (4)$$

where C_i^W is the molar concentration of the chemical in aqueous solution. Consequently, if the infinite dilution activity coefficient of a species in water is known, as well as its vapor pressure, we can estimate its fugacity in rivers, lakes, estuaries and the ocean. For many chemicals γ_i^∞ and p_i^{vap} are not known individually, but the Henry's law coefficient on a mole fraction basis, H_i , or on a concentration basis H_i' has been measured.

Information on species vapor pressures can be found in standard chemical handbooks; data on infinite dilution activity coefficients are less readily available (see, for example, books in the DECHEMA series [4]). However, such information can sometimes be obtained from solubility data as follows. If the organic chemical is a liquid and only partially soluble in water from the equality of fugacities for each species when a two-liquid phase chemical-water mixture is formed, we have that

$$x_i^C \gamma_i^C = x_i^W \gamma_i^W \quad (5)$$

where the superscript C represents the chemical-rich phase, W the aqueous phase, and the pure component vapor pressures have cancelled. Many organic chemicals (especially if they do not contain a hydroxyl or similar group) are only very slightly soluble in water, and likewise water is not very soluble in them. In this case x_i^C is approximately 1, as is γ_i^C (since the activity coefficient of a species approaches unity as it becomes pure). Also, in the aqueous phase, we have that $\gamma_i^W \approx \gamma_i^\infty$, because of the low solubility of the chemical in water. In this case we have

$$x_i^W \gamma_i^\infty = 1 \text{ or } \ln \gamma_i^\infty = -\ln x_i^W \quad (6)$$

where x_i^W is the mole fraction saturation solubility of the chemical in water. Consequently, for a species that is liquid when pure at the temperature of interest, we can determine its infinite dilution activity coefficient in water from aqueous solubility data, if the reported solubility is very low as is usually the case for the hydrophobic chemicals of interest here. For a species that is a solid at environmental

conditions, both the aqueous solubility and heat of fusion [5] are needed to obtain the infinite dilution activity coefficient

$$\ln \gamma_i^\infty = -\ln x_i^W - \frac{\Delta H_i^{\text{fus}}(T_m)}{RT} \left[1 - \frac{T}{T_m} \right] \quad (7)$$

Here $\Delta H_i^{\text{fus}}(T_m)$ is the heat of fusion at the melting point T_m , T is ambient temperature, and a small term related to the difference in solid and liquid heat capacities has been neglected. [The extra term in equation 7 is a result of the fugacity change on melting below the normal melting point]. It should be emphasized that the infinite dilution activity coefficients of a hydrophobic chemical in water can be very large. For example, the value for benzo[*a*]pyrene calculated using the equation above, and the solubility and heat of fusion we measured [6] is 3.78×10^8 . While this may seem high, it is not unusual for an almost insoluble, very hydrophobic chemical in water.

Equating the fugacity of the chemical in the air and water, we obtain

$$\bar{f}_i^A = C_i^A RT = C_i^W H_i' = \bar{f}_i^W \quad (8)$$

Defining the air-water concentration ratio or partition coefficient of chemical i , $K_{AW,i}$, we have

$$K_{AW,i} = \frac{C_i^A}{C_i^W} = \frac{H_i'}{RT} = \frac{\gamma_i^\infty p_i^{\text{vap}}}{C_i^W RT} \quad (9)$$

where C_i^W is the molar concentration of pure water. Consequently, if we know the equilibrium concentration of a chemical in either air or water, and its Henry's law constant (or its infinite dilution activity coefficient and vapor pressure), we can compute its value in the other phase.

To describe the distribution of a chemical between water and the aquatic biota (fish) we again apply the condition of phase equilibrium

$$\bar{f}_i^W = \bar{f}_i^B \text{ or } x_i^W \gamma_i^W = x_i^B \gamma_i^B \quad (10)$$

How one is to compute the fugacity or activity coefficient of a chemical in biota (assuming the biota to be liquid-like), for example a fish, is not immediately obvious. Since the discussion here is restricted to organic chemicals, the starting point is to use the octanol-water partition coefficient, K_{OW} , as a characterizing parameter. When *n*-octanol is mixed with water, two liquid phases form, one almost pure water and the other about 0.74 mole fraction *n*-octanol. If a very small amount of a third chemical is added and allowed to reach equilibrium, its concentration will generally be very different in these two phases. In particular, an added hydrophilic compound will have a higher concentration in the water phase, while an organic, hydrophobic chemical will be concentrated in the octanol-rich phase. The octanol-water partition coefficient of a chemical i , $K_{ow,i}$ is defined to be

$$K_{ow,i} = \frac{\text{concentration of chemical } i \text{ in the octanol-rich phase}}{\text{concentration of chemical } i \text{ in the water-rich phase}} = \frac{C_i^O}{C_i^W} \quad (11)$$

where C_i^O and C_i^W are the equilibrated concentrations of the chemical in the octanol-rich and water-rich phases, respectively.

Most organic compounds are hydrophobic and have large values of the octanol-water partition coefficient. Indeed, values of 10^3 or 10^4 and larger are not unusual. The insecticide DDT has a value of about 10^6 . Thus, at equilibrium, the concentration of DDT will be about a million times greater in the octanol-rich phase than in the water with which it is in equilibrium. The octanol-water partition coefficient is thus a measure of hydrophobicity, and serves as a characterizing parameter in environmental studies. Octanol is used as the organic phase for this characterizing parameter because of its availability in high purity, and as it is a good surrogate for the lipids in aquatic and animal biota, and for the organic matter in soils and sediments. Other chemicals could be used, however, as there already exist much data on octanol-water partition coefficients [7–9] and this parameter has been used to correlate many other properties, it is the parameter that will be used here.

Since the chemical added to the octanol-water system is very dilute, equation 11 can be rewritten as

$$K_{OW,i} = \frac{C_i^O}{C_i^W} = \frac{C^O x_i^O}{C^W x_i^W} = \frac{C^O \gamma_i^W}{C^W \gamma_i^O} = \frac{C^O \gamma_i^{W,\infty}}{C^W \gamma_i^{O,\infty}} \quad (12)$$

where C^O and C^W are the total molar concentrations of the octanol-rich and water-rich phases, and $\gamma_i^{O,\infty}$ and $\gamma_i^{W,\infty}$ are the infinite dilution activity coefficients of chemical i in these two phases, and x_i^O and x_i^W are the respective mole fractions. Experimentally, it is found that the octanol-water partition coefficients of different organic chemicals range in value from about 0.1–10⁸. This is a result of the infinite dilution activity coefficient of such chemicals in octanol generally being of order unity, and that in water varying from 1 to 10⁹. The octanol-water partition coefficient is essentially a measure of how good a solvent water is for the chemical under study, or equivalently the magnitude of the infinite dilution activity coefficient of the chemical in water. Since the dominant term in the octanol-water partition coefficient is $\gamma_i^{W,\infty}$, several correlations have been proposed relating $K_{OW,i}$ to this quantity [10], for example:

$$\log_{10} K_{OW,i} = -0.486 + 0.8061 \log_{10} \gamma_i^{W,\infty} \quad (13)$$

Thus, the value of the octanol-water partition coefficient can be estimated from that somewhat easier-to-measure infinite dilution coefficient.

To proceed, it is common to use a biota-water partition coefficient of the chemical i , $K_{BW,i}$ as

$$K_{BW,i} = \frac{C_i^B}{C_i^W} = \frac{C^B x_i^B}{C^W x_i^W} = \frac{C^B \gamma_i^W}{C^W \gamma_i^B} \quad (14)$$

where C^B and C^W are the total molar concentrations of the biota and water, respectively. This partition coefficient is usually obtained from correlation; empirically, it is found that a reasonable approximation is

$$K_{BW,i} = \phi_B K_{OW,i} \quad (15)$$

where ϕ_B is the fraction of the biota that is lipid. The reason that this correlation is satisfactory is that most organic chemicals partition mainly into the fatty tissue or lipids of fish (and people), rather than into muscle, other tissues, skeletal structure, or the aqueous portions of biota, and octanol is a reasonable surrogate for these lipids. With this simple correlation, one distinguishes between aquatic and terrestrial biota, and between animal and vegetable matter only by the fraction of each that is lipids.

With these equations, if we know the composition of a chemical in one of the environmental compartments we have so far considered (air, water or biota), we can compute its equilibrium concentration in the other compartments. For simplicity, as we consider to other environmental compartments, we will reference all compositions to that in water by using soil-water, sediment-water, etc., partition coefficients, as this is the most convenient and common choice.

The partitioning of a chemical between water and other environmental compartments, such as soil, the sediment at the bottom of lakes and rivers, and sediment suspended in water are also obtained from simple correlations. The concentrations of chemicals in soils and sediments are usually given in units of p.p.m. by weight (mg/kg); for water, since its density is unity, this is also mg/L. The soil-water partition coefficient is typically defined to be

$$K'_{sw} = \frac{\text{Chemical content of soil, mg/kg}}{\text{Concentration of chemical in water, mg/L}} \quad (16)$$

though we will use a concentration-based partition coefficient defined as follows

$$K_{sw} \frac{\text{Concentration of chemical in soil, mg/L}}{\text{Concentration of chemical in water, mg/L}} = K'_{sw} \rho_s \quad (17)$$

where ρ_s is the density of the soil (kg/L). For soil, sediment and suspended sediment, it has been found that organic chemicals adsorb largely into the organic matter in each of these compartments. Further, to a good approximation, the partition coefficient for an organic chemical between the organic carbon in each of these compartments and water based on weight fraction, $K'_{OC,i}$, is also correlated with the

octanol-water partition coefficient of the species

$$K'_{OC,i} = 0.41K_{OW,i} \quad (18)$$

Consequently, we have that for the soil-water partition coefficient

$$K_{SW,i} = \frac{C_i^S}{C_i^W} = \rho_S \phi_S K'_{OC,i} = 0.41 \rho_S \phi_S K_{OW,i} \quad (19)$$

for the sediment-water partition coefficient

$$K_{DW,i} = \frac{C_i^D}{C_i^W} = \rho_D \phi_D K'_{OC,i} = 0.41 \rho_D \phi_D K_{OW,i} \quad (20)$$

and for the suspended sediment-water partition coefficient

$$K_{MW,i} = \frac{C_i^M}{C_i^W} = \rho_M \phi_M K'_{OC,i} = 0.41 \rho_M \phi_M K_{OW,i} \quad (21)$$

Here S, D and M represent soil, sediment, and suspended sediment, respectively, and ϕ is the fraction of organic matter in each of these compartments.

These relationships are very simple approximations, but given that all environmental calculations have considerable uncertainty, they are not unreasonable first approximations. In particular, soil is an especially complex, heterogeneous material and under the single heading of soils one finds material ranging from clays to sand. Also, some soils, especially clays, have quite different chemical and physical properties depending on whether they are wet or dry. For the purposes here we will neglect all of these important complexities and characterize soils only by their organic carbon content.

As the first example of the use of the equations developed here, we start with the observation that the mass fraction of polychlorinated biphenyls (PCBs) in the St. Lawrence River has been reported to be about 0.3×10^{-9} . There are more than a hundred different PCB congeners, and a reasonable average value of their octanol-water partition coefficient is $\log_{10} K_{OW} = 5.5$. Using this information, and that aquatic biota are approximately 0.05 mass fraction lipids, we find that the expected whole body average concentration of PCBs in fish in the St. Lawrence River is

$$C_i^B = f_B K_{OW,i} C_i^W = 0.05 \times 10^{5.5} \times 0.3 \times 10^{-9} = 4743 \times 10^{-9} = 4.7 \times 10^{-6}$$

Consequently, based solely on phase equilibrium, we expect that the concentration of PCBs in fish and other aquatic biota to be almost 16000 times higher than the concentration of this chemical in the water. The mass fraction of PCBs in eels (which are low on the food chain) in the St Lawrence River has been found to be about 7.9×10^{-6} . Consequently, our very approximate calculation of this complex process is accurate to within a factor of 2.

As another example, it has been reported [11] that the mass fraction of benzo[a]pyrene in water in the southern part of the Canadian province of Ontario is 2.82×10^4 mg/m [3]. The vapor pressure [7] of this compound is 2.13×10^{-5} Pa at $T = 298.15$ K, $\log_{10} K_{OW} = 6.04$, and the value of $\gamma^{W,\infty}$ we measured is 3.78×10^8 as mentioned earlier. Assuming that the organic contents of soil and sediment are 0.02 and 0.05, respectively, and that the densities of the compartments are 1.5 and 1.42, we obtain the results in Table 1 for the concentration of the benzo[a]pyrene in each of the environmental compartments.

The agreement between the results of the calculations and reported data, while not perfect, is reasonable given the absolute simplicity of the thermodynamic model compared to the complexity of environmental processes and the uncertainty in the parameters used. The results do show that the many orders of magnitude difference in the concentration of a long-lived pollutant in the various environmental compartments can be explained using the concept of phase equilibrium. The results also show the importance of accurate thermodynamic data (especially the infinite dilution activity coefficient in water) in environmental calculations. Had we naively assumed ideal solution behavior (case III), our results for the concentration of the chemical in the soil, sediment and biota would have been in error by about six orders of magnitude!

From this analysis it is evident that the relevant thermodynamic quantities for predicting how a

Table 1 Environmental distribution of benzo[*a*]pyrene

Compartment	Concentration/(ng/m ³)			
	I	II	III	Reported data
Water				2.82 × 10 ⁴
Air	1.648	1.648	0	1.3 to 7.1
Soil	3.71 × 10 ⁸	9.06 × 10 ⁸	1.11 × 10 ²	1.1 × 10 ⁸
Sediment	8.78 × 10 ⁸	2.14 × 10 ⁹	2.62 × 10 ²	(0.8 to 3) × 10 ⁸
Biota	1.55 × 10 ⁹	3.77 × 10 ⁹	4.61 × 10 ²	1.4 × 10 ⁸

I. Using reported value of $\log_{10} K_{OW} = 6.04$.

II. K_{OW} calculated from equation 3 with $\gamma^{W,\infty} = 3.78 \times 10^8$.

III. Ideal solution calculation and K_{OW} calculated from equation 3 with $\gamma^{W,\infty} = 1$.

chemical will partition between various environmental compartments are its infinite dilution activity coefficient in water, its vapor pressure (or Henry's Law constant), and its octanol-water partition coefficient. However, with equation 13 one can make estimates of the distribution of a long-lived chemical in the environment knowing only two quantities, its vapor pressure and its infinite dilution activity coefficient.

The discussion above has been based on the assumption that a chemical is in phase equilibrium throughout the food chain, from the lowest level protozoa to high level predators. While this is a reasonable assumption for many long-lived pollutants, there is evidence that chemicals with high values of the octanol-water partition coefficient accumulate up the food chain. By this we mean that as a result of a predator ingesting a chemical contained in its prey, and then eliminating this chemical only very slowly, that the concentration of the chemical increases with position in the food chain. One example of this was the higher concentration of DDT found in birds of prey, such as eagles (and especially in their eggs) in the United States in the 1950s, than in the fish they ate.

Food chain bioaccumulation has been described by a simple steady-state model [12]

Rate of elimination of chemical *i* by decomposition and excretion = rate of uptake of chemical *i* from water + rate of uptake of chemical *i* from

or, in equation form

$$R_{i,\eta} C_i^\eta = k_{i,\eta} C_i^W + \sum_{j=1} \alpha_{j \rightarrow \eta}^i F_{\eta,j} C_j^j \quad (22)$$

where the sum is over all species on which the predator preys, and $R_{i,\eta}$ is the overall rate constant for both excretion and decomposition of the chemical *i* in predator species η . Further $k_{i,\eta}$ is the rate constant of this species for the uptake of the chemical *i* from the water, and $F_{\eta,j}$ is the rate at which predator species η feeds on species *j* below it in the food chain ($\eta > j$). Finally $\alpha_{j \rightarrow \eta}^i$ is the assimilation factor or fraction of the chemical *i* in the prey *j* that is absorbed by the predator η . If there were no food chain accumulation (as occurs when the phase equilibrium model is correct, or if only one species is present in an ecosystem), then

$$\frac{C_i^\eta}{C_i^W} = \frac{k_{i,\eta}}{R_{i,\eta}} = K_{BW,i}^\eta = \phi_B^\eta K_{OW,i} \quad (23)$$

where $K_{BW,i}^\eta$ is the biota-water partition coefficient of chemical *i* for species η computed as discussed earlier.

Common notation is to define a biomagnification factor for chemical *i* in species η as follows

$$\theta_{\eta,j} = \frac{C_i^\eta}{K_{BW,i}^\eta C_i^W} = \frac{C_i^\eta}{\phi_B^\eta K_{OW,i} C_i^W} \quad (24)$$

Defined in this way, if $\theta_{\eta,i} = 1$ the chemical i in organism η is in phase equilibrium with the water with which it is in contact (which is the assumption of the phase equilibrium model discussed earlier). Thomann [12] has assumed that in aquatic systems predators prey upon species only one level below them in the food chain, and has correlated the model parameters as a function of the octanol-water partition coefficient. [By equation 13 this correlation can be transformed into one in terms of the infinite dilution activity coefficient of the chemical in water.]

Using his correlation, the extents of biomagnification as a function of the octanol-water partition coefficient shown in Fig. 4 were obtained. There are several messages to be drawn from this figure. First we see that there is no significant biomagnification of a chemical up the food chain unless its octanol-water partition coefficient is above about 10^4 (corresponding to a value of $\gamma^{W,\infty}$ about 3×10^5), and that there will be significant biomagnification for values of K_{OW} of 10^6 and larger. Thus we can conclude that insecticides such as malathion ($\log_{10} K_{OW} = 2.90$) and lindane ($\log_{10} K_{OW} = 3.85$) will not biomagnify in the food chain, their concentrations in different biotic species will be approximately the same, and this concentration can be computed based on phase equilibrium. However, dieldrin ($\log_{10} K_{OW} = 5.48$), DDT ($\log_{10} K_{OW} = 6.19$) and mirex ($\log_{10} K_{OW} = 7.5$) are likely to increase significantly up the food chain. Further, since DDT and mirex have long persistence times in the environment (greater than 15 and 5 years, respectively), this is likely to occur. In these cases we first compute the equilibrium concentration in the biota, and then multiply it by the appropriate biomagnification factor to obtain the concentration of the chemical in the species. This biomagnification up the food chain is in addition to the already large equilibrium concentration differences that result from the hydrophilic character of many of these compounds.

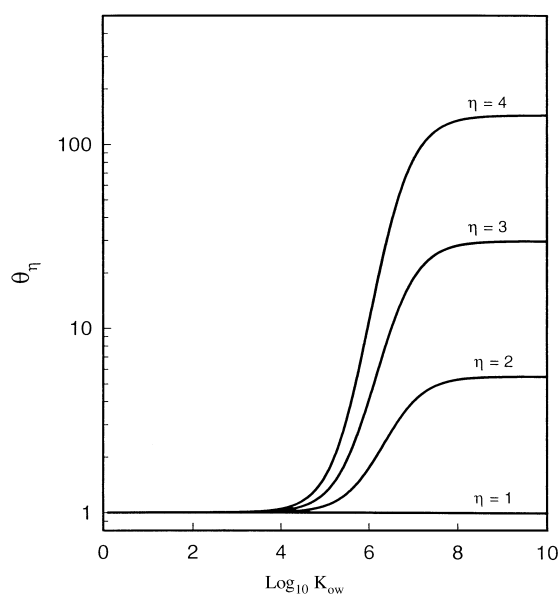


Fig. 4 Biomagnification factor θ_{η} as a function of the octanol-water partition coefficient K_{OW} and trophic level η .

An example of a biomagnification effect can be seen by re-examining biotic PCB concentrations in Lake Michigan. From the first example in this section, the equilibrium aquatic biota concentration of PCBs is expected to be 16 000 times greater than the concentration of PCBs in Lake Michigan water based on a phase equilibrium calculation only. However, biomagnification (Fig. 4) results in an additional factor of about 14 in PCB accumulation, leading to a predicted total PCB concentration in Lake Michigan trout of about 225 000 times greater than the concentration in the lake water. Frequently it is this additional concentration enhancement resulting from multiplicative biomagnification factor that produced the most serious biotic damage. That is why toxic chemicals PCBs and DDT are serious environmental hazards, but chemicals with lower octanol-water partition coefficients (or infinite dilution activity coefficients in water) may be less of an environmental hazard, unless they are especially toxic.

Consequently, the biomagnification of a chemical depends largely on the value of its octanol-water

partition coefficient, even when the kinetic effect just discussed is important. Since the octanol-water partition coefficient depends largely on the infinite dilution activity coefficient of the chemical in water, it is the value of $\gamma^{w,\infty}$ that determines not only the equilibrium distribution of a chemical in most environmental compartments, but also its further biomagnification up the biotic food chain. While the measurement of the infinite dilution activity coefficient of an organic chemical in water does not provide information on how toxic a chemical is to biotic species, it can tell us how whether the chemical is likely to bioaccumulate up the food chain.

APPLICATION OF QUANTUM MECHANICS TO PHASE EQUILIBRIUM CALCULATIONS

The last subject I want to consider is unusual in the sense of using computational quantum chemistry, and in particular *ab initio* molecular orbital calculations, both as a test of thermodynamic models and as basis for making phase behavior predictions. This is work currently in progress in my research group directed towards predicting mixture phase behavior without the use of any measured mixture data. Current group contribution methods such as the various forms of UNIFAC [13–15] and ASOG [16] are sometimes, but not always, successful in this regard, and the parameter base for DISQUAC [17,18] is presently too limited.

Semi-theoretical activity coefficient models, such as UNIQUAC [19] and Wilson, [20] have explicit energy parameters that are interpreted as being interaction energies, but in fact are treated as adjustable and fitted to experimental data. For example, the energy parameters in the Maurer–Prausnitz [21] version of the UNIQUAC model are

$$\tau_{ij} = \exp\left(\frac{z E_{ij} - E_{jj}}{2 kT}\right) \quad (25)$$

while Kemeny & Rasmussen [22] suggest instead that the that the factor $z/2$ be eliminated

$$\tau_{ij} = \exp\left(\frac{E_{ij} - E_{jj}}{kT}\right) \quad (26)$$

where z is the coordination number, usually fixed at 10, and E_{ij} is the interaction energy between molecules of i and j . Based on perturbation theory, Fischer [23] has argued that the first of these equations is incorrect. When the UNIQUAC model is fitted to experimental data, since the two equations above differ by only a constant factor, it is not possible to distinguish between them. The analogous energy parameters in the Wilson model are

$$\Lambda_{ij} = \frac{V_j^L}{V_i^L} \exp\left(\frac{E_{ii} - E_{ij}}{RT}\right) \quad (27)$$

where V_i^L is the liquid molar volume of species i .

We have been using *ab initio* quantum mechanics methods to calculate the actual interaction energies resulting from hydrogen-bonding and van der Waals interactions for aqueous mixtures that can then be used in the UNIQUAC and Wilson models. Of course, activity coefficient models used in applied thermodynamics are approximate, and the parameters obtained at one temperature usually are not useful in predicting phase behavior at other temperatures. Also while these models may provide a reasonable description of the excess free energy, they are generally unsatisfactory for its component parts, the excess enthalpy and excess entropy. Nevertheless it is of interest to test these models using interaction energies determined for a cluster of molecules representing a condensed phase calculated by *ab initio* quantum mechanics methods.

It is important to devise a consistent, unambiguous procedure from which average interaction energies between pairs of molecules in a liquid mixture can be determined. The steps we use are as follows:

- (a) Construct a cluster composed of eight molecules, four of each species. This cluster size was selected as a compromise between computational cost and a reasonable representation of the phase space of a dense fluid.
- (b) Perform an energy minimization of the cluster using the computationally inexpensive PM3 semiempirical method [24] to obtain an approximate intermolecular geometry of the cluster.

- (c) Do more rigorous geometric energy minimization using the HF (Hartree–Fock) method with the 6–31G** basis set.
- (d) Select directly interacting molecular pairs from this optimized cluster, that is, like and unlike pairs that are in close proximity, and record their separation distances and relative orientations. Obtain an accurate interaction energy of each of these molecular pairs using 6–311++G(3d,2p) basis set and the separation and orientation obtained in the previous step. The pair interaction energy E_{AB}^{int} of interest to us is then computed from

$$E_{AB}^{\text{int}} = E_{AB}\{AB\} - E_A\{AB\} - E_B\{AB\} \quad (28)$$

where E is the energy of a single or pair of molecules, and $\{AB\}$ refers to the combined basis set for both A and B molecules (including accounting for the basis set superposition error).

- (e) Finally, since several of the same molecular pairs are found in each cluster (e.g. H₂O–H₂O), linearly average the energies of the sets of the same molecular pairs to obtain the interaction energies to be used in the activity coefficient model. Also, because of the large number of configurations possible, it is useful to try different initial geometries and include these results in the average to eliminate any dependence on the initial configuration.

All the *ab initio* computations were performed using the *Gaussian 94* program [25]. These calculated interaction energies were then used in the Wilson and UNIQUAC activity coefficient models to predict the vapor–liquid equilibrium for mixtures of water separately with methanol, ethanol, formic acid, and acetic acid. [26] One immediate conclusion is that the use of equation 25 greatly overpredicts the degree of solution nonideality of these mixtures. This result confirms Fischer’s conclusion, and consequently we will not consider this model further.

The computed interaction energy parameters for the Wilson model and the remaining UNIQUAC activity coefficient model are given in Table 2. The pure component parameters (the r and q parameters for the UNIQUAC equation and the constants for the Antoine equation) were obtained from Gmehling *et al.* [4]. Figures 5a and b show the (x - y) and (p - x - y) diagrams, respectively, for the [methanol (1) + water (2)] system. Figures 6, 7 and 8 show similar results for the [ethanol (1) + water (2)], [formic acid (1) + water (2)], and [acetic acid (1) + water (2)] systems, respectively, all at approximately ambient conditions. Plotted on those figures are the experimental data [4], predictions from both the UNIQUAC and Wilson models using the parameters determined by *ab initio* methods and, for comparison, predictions from the UNIFAC model. In these plots the predictions have been corrected for the vapor-phase association of the organic acid.

Table 2 Interaction energies E_{ij} from *ab initio* calculations

System	E_{11} (kJ/mol)	E_{22} (kJ/mol)	E_{12} (kJ/mol)	Δu_{12}^* (kJ/mol)	Δu_{21}^* (kJ/mol)
Methanol + water	-12.300	-11.852	-12.247	-0.395	0.053
Ethanol + water	-11.234	-11.675	-10.879	0.796	0.356
Formic acid + water	-22.813	-11.582	-15.573	-3.991	7.240
Acetic acid + water	-13.253	-9.578	-11.001	1.423	2.252

*Parameters for UNIQUAC model; $\Delta u_{ij} = E_{ij} - E_{jj}$.

As seen in all of the figures, the predictions with the UNIQUAC model with quantum-mechanically determined parameters are in excellent agreement with the experimental data, and sometimes superior to the UNIFAC predictions. For all of these mixtures the UNIQUAC model resulted in better predictions based on parameters determined from *ab initio* methods than the Wilson model. It is important to emphasize that the results obtained here are truly predictions in that the only input required for the computation of the activity coefficient parameters was the molecular arrangement of the atoms.

All of the above predictions are for approximately ambient conditions. One might ask how this method could be extended to higher temperatures and pressures. This brings me to one of the most useful

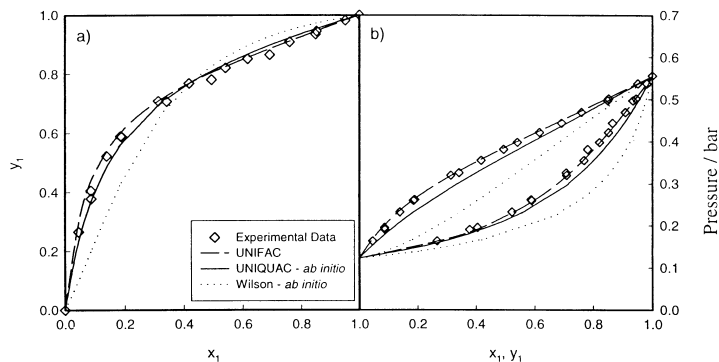


Fig. 5 Vapor-liquid equilibrium diagram for the methanol (1) + water (2) system at $T = 323.15$ K.

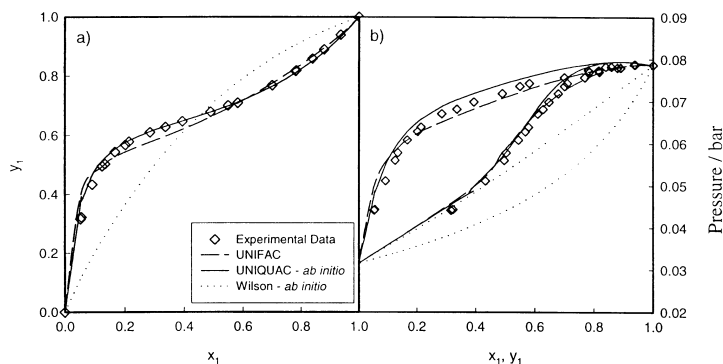


Fig. 6 Vapor-liquid equilibrium diagram for the ethanol (1) + water (2) system at $T = 298.15$ K.

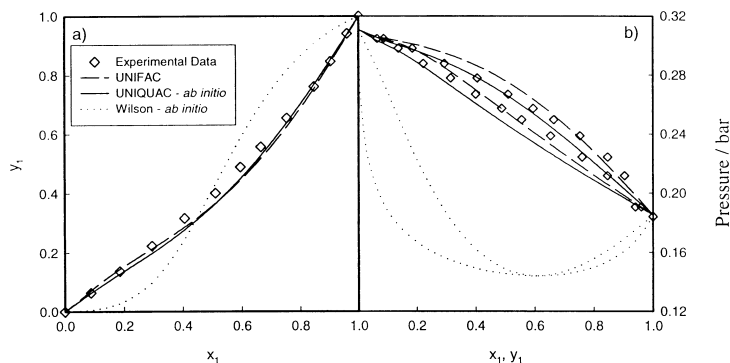


Fig. 7 Vapor-liquid equilibrium diagram for the formic acid (1) + water (2) system at $T = 333.15$ K.

developments in applied thermodynamics in this decade, the combination of equations of state and activity coefficient models using free energy-based mixing rules. There are now several such mixing rules; I will discuss only the Wong-Sandler [26,27] mixing rule as it has a simple theoretical basis, and is the one I know best. The basis of this mixing rule is the observation that cubic equations of state such as those of Peng & Robinson [28]:

$$P = \frac{RT}{V_{mix} - b} - \frac{a(T)}{V_{mix}(V_{mix} + b) + b(V_{mix} - b)} \quad (29)$$

or of Soave, Redlich & Kwong [29] have two adjustable parameters, a and b , and this provides two degrees of freedom in choosing their values in a mixture. We use the first degree of freedom to insure that the second virial coefficient B from the equation of state has the known quadratic dependence on

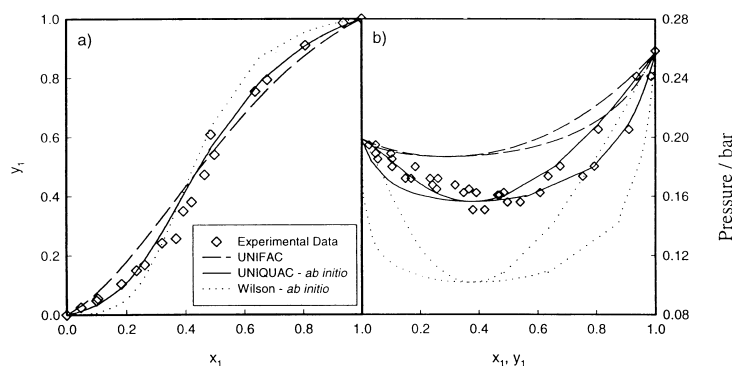


Fig. 8 Vapor-liquid equilibrium diagram for the acetic acid (1) + water (2) system at $T = 343.15$ K.

composition, i.e.

$$B(x, T) = \sum_i \sum_j x_i x_j B_{ij}(T) = \sum_i \sum_j x_i x_j \left(b_{ij} - \frac{a_{ij}}{RT} \right) = b - \frac{a}{RT} \quad (30)$$

The combining rule used with this equation is:

$$\left(b - \frac{a}{RT} \right)_{ij} = \frac{1}{2}(b_i + b_j) - \frac{\sqrt{a_i a_j}}{RT} (1 - k_{ij}) \quad (31)$$

which introduces the binary interaction parameter k_{ij} . The second equation is based on the observation that the excess Helmholtz free energy of mixing at liquid densities calculated from a cubic EOS is much less sensitive to pressure than is the Gibbs free energy. Consequently to an excellent approximation:

$$A^E(T, \text{liquid density}, x) = A^E(T, p = \infty, x) \cong A^E(T, \text{low } p, x) \cong G^E(T, \text{low } p, x) \quad (32)$$

The first of these approximate equalities is based on the fact that the equation of state will always predict liquid-like densities at high pressure. The second follows from the relative insensitivity of the excess Helmholtz free energy to pressure at liquid densities, and the third from the fact that $G^E = A^E + PV^E$, and that the PV^E term is very small at low pressures. In the limit of infinite pressure, $V_i \rightarrow b_i$ and $V_{mix} \rightarrow b_{mix}$ and for the Peng-Robinson equation

$$\frac{A^{ex}(T, p \rightarrow \infty, x_i)/C^* RT}{C^* RT} = \frac{1}{RT} \left[\frac{a}{b} - \sum_i x_i \frac{a_i}{b_i} \right] \quad (33)$$

with $C^* = [\ln(\sqrt{2}-1)]/\sqrt{2} = -0.62323$. Combining equations 31 and 33 gives the second mixing rule equation

$$\frac{G^E}{C^* RT} = \frac{a}{bRT} - \sum_i x_i \frac{a_i}{b_i RT} \quad (34)$$

Equations 30 and 34 are solved to obtain the mixture a and b parameters.

Using the UNIQUAC model with the parameters determined from the *ab initio* calculations as discussed above for G^E , the Stryjek & Vera [30] form of the Peng-Robinson EOS (in order to obtain the correct pure component vapor pressures), and a single value of the binary interaction parameter k_{ij} to reproduce the low pressure UNIQUAC predictions shown in Fig. 5, the predictions for the higher temperatures and pressures shown in Fig. 9 were obtained. Similar results have been obtained for the (acetone + water) system (are shown in Fig. 10) and for the other systems. It is remarkable that such reasonably good predictions could be made over large ranges of temperature and pressure without using any measured mixture data. Also, once again, we see the advantage of using a well-defined thermodynamic model for extrapolations to higher temperatures.

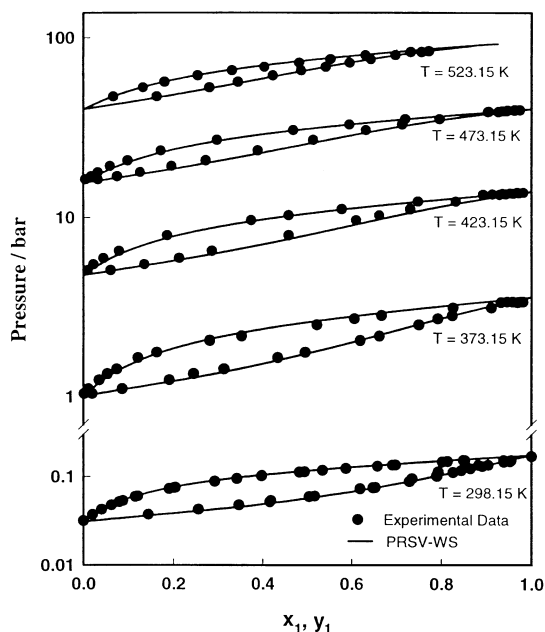


Fig. 9 Predictions of the vapor–liquid equilibrium diagram for methanol (1) + water (2) system at higher temperatures and pressures using UNIQUAC parameters determined from quantum mechanics.

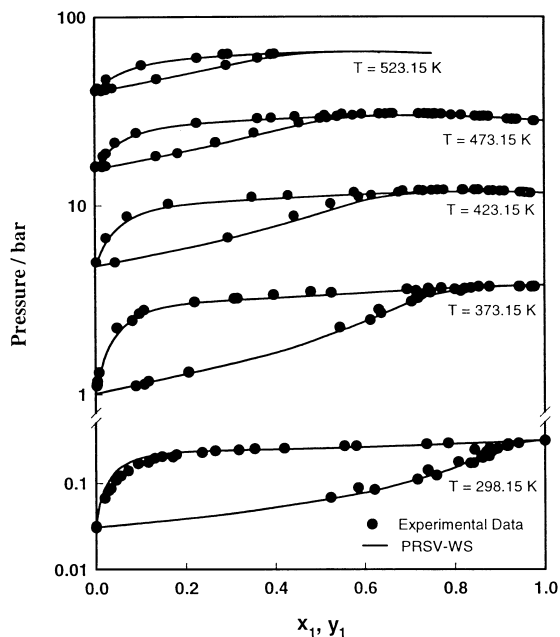


Fig. 10 Predictions of the vapor–liquid equilibrium diagram for acetone (1) + water (2) system at higher temperatures and pressures using UNIQUAC parameters determined from quantum mechanics.

CONCLUSIONS

I have tried to do two things here. The first was to illustrate the very broad range of applications of thermodynamics by two examples dealing first with the design of space probes, and a second with the prediction of the distribution of chemicals in the environment. The second is a method of obtaining thermodynamic parameters from quantum mechanics, which can then be used both to test thermodynamic models, and as a basis for making thermodynamic predictions in the absence of experimental data. Perhaps what I would like you to remember most from this talk is that there are many situations in which

simple models can be used to describe complex phenomena, and that a theoretically based model is generally much better than simple extrapolation.

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