R & D NOTES

Free Energy Explanation of Separative Work

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Separative work is a commodity traded in the nuclear fuels markets at the current price of nearly \$80/SWU (Nuclear Engineering International, 1977). Typically, a 1 000 MWe light-water-reactor nuclear power station, presently the most common type in the United States., will daily consume 220 lb of nuclear fuel representing 360 SWUs of separative work. The light-water reactor requires uranium enriched to approximately 3% U^{235}. The CANDU reactor, on the other hand, uses as fuel natural uranium requiring no separative work. Other types of reactors use fuel highly enriched in U^{235}.

One SWU is the amount of separative work involved in preparing 0.33 kg of uranium enriched to 2.8% U^{235} from 2 kg of natural uranium which contains 0.711% U^{235} (JCAE. 1973). The energy required to perform this separation through the gaseous diffusion process amounts to 2 750 kw-hr or 1×10^{10} J. Most of this energy leaves the process as heat rejected from compressors rather than as free energy stored in the separated isotopes. The gas centrifuge process for uranium enrichment is expected to require less than 10% as much energy as does gaseous diffusion. Even with this more efficient process, however, most if the input energy will reappear as waste heat.

The development of Congressional support for public investment in uranium enrichment has not required a free energy explanation of the term separative work (JCAE, 1973). Nuclear fuel buyers, too, find it sufficient to know that the amount of separative work represented in a unit weight of nuclear fuel is independent of the fuel's temperature, pressure, and density, although it does depend on the nuclear fuel's content of fissile uranium atoms, the U^{235} content of the uranium from which it was prepared, and the U^{235} content of the tails left behind. For purposes of pricing separative work, the traders assume that the assays of the uranium feed and tails are invariant, thereby allowing separative work to be used as a measure of the fissile atom content of the nuclear fuel. Chemical engineers will want to know, nevertheless, how separative work is related to energy even though it is traded in units of weight. Separative work is the measure of performance, per unit time, of separation devices and plants. It has been used extensively in the engineering of gaseous diffusion and gas-centrifuge uranium enrichment plants.

CONCEPT OF SEPARATIVE WORK

The concept of separative work is not restricted to uranium enrichment, nor even to separating mixtures of isotopes. It can be applied generally to separations of mixtures of any two distinct species of atom or molecule for which a separation process can be visualized. Separative work δU has been defined (Cohen, 1951; Benedict and Pigford, 1957) by Equation (1):

$$\delta U = W_p(2x_p - 1)\ln[x_p/(1 - x_p)] + W_t(2x_t - 1) \ln[x_t/(1 - x_t)] - W_f(2x_f - 1)\ln[x_f/(1 - x_f)] \quad (1)$$

Generally, δU is expressed in units of weight of something common to the feed, heads, and tails streams of the separation process, something such as kilograms-of-binary-mixture units. In uranium enrichment, δU is expressed in units of kilograms of binary mixture of uranium isotopes, or briefly kg U. One SWU equals 1 kg U. The composition of the binary mixture is left unspecified because it is not common to all three streams.

THE VALUE FUNCTION CONCEPT

In the isotope-separation literature (Cohen, 1951; Shachter et al., 1965), $(2x - 1) \ln (x/(1 - x))$ is called the value function and is represented here by ϕ. It is an intensive (Sage, 1965) state property of the binary system whose composition is x mole fraction of one molecular or atomic species and $(1 - x)$ of the other.

THE FREE ENERGY EXPLANATION

The free energy explanations of separative work and the value function for binary mixtures of substances 1 and 2 are given in Equations (2) and (3), respectively:

$$\delta U = [W_p(G_p - \overline{G}_{1p}) + W_t(G_t - \overline{G}_{1t}) - W_f(G_f - \overline{G}_{1f})]/RT + [W_p(G_p - \overline{G}_{2p}) + W_t(G_t - \overline{G}_{2t}) - W_f(G_f - \overline{G}_{2f})]/RT \quad (2)$$

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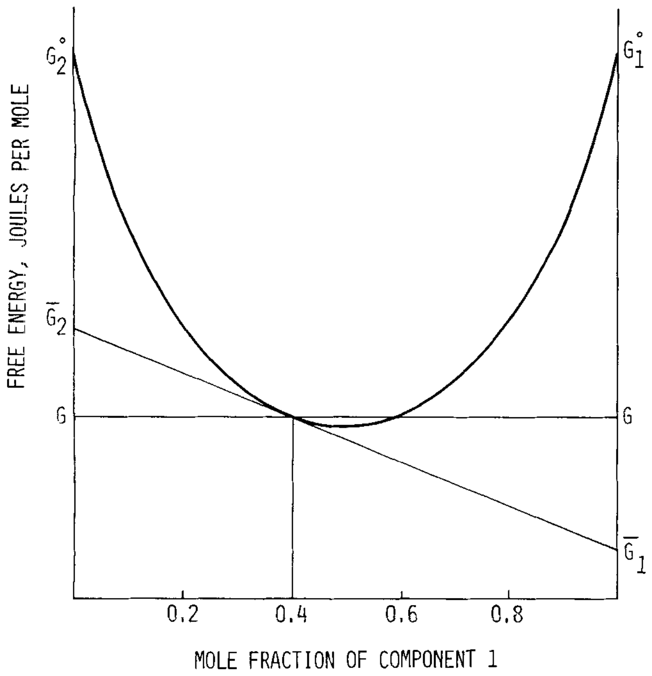

Fig. 1. Relationship of free energy to partial molal free energy.

$$\phi = [(G - \overline{G}_1) + (G - \overline{G}_2)]/RT \qquad (3)$$

Separative work is a weighted sum of free energy differences, wherein the free energy is expressed in multiples of RT. Because both free energy and RT have the same dimensions, their ratio is dimensionless.

Figure 1 shows how the partial molal free energies, chemical potentials, are related to the free energy of the binary mixture (Lewis and Randall, 1923). The tangent to the curve at the mole fraction corresponding to the composition of the binary mixture crosses the left and right coordinates at $\overline{G}_2$ and $\overline{G}_1$, respectively. If the two substances form an ideal solution (no enthalpy of mixing), then the entropy of mixing is related to the free energy of mixing by Equation (4).

$$\Delta S = -\Delta G/T \qquad (4)$$

Separative work is, then, also a weighted sum of entropy differences wherein entropy is expressed in multiples of the universal gas constant R.

RELATION TO THE DEFINITIONS

From Figure 1.

$$G - \overline{G}_2 = x\frac{dG}{dx} \qquad (5)$$

$$G - \overline{G}_1 = (1-x)\frac{dG}{d(1-x)} \qquad (6)$$

So, at constant temperature

$$\phi = x\frac{dM}{dx} + (1-x)\frac{dM}{d(1-x)} \qquad (7)$$

where

$$M = G/RT \qquad (8)$$

Now the entropy of mixing of an ideal solution (Lewis and Randall, 1923) is given by Equation (9)

$$\Delta S = -R[x\ln(x) + (1-x)\ln(1-x)] \qquad (9)$$

and the corresponding free energy by

$$\Delta G = RT[x\ln(x) + (1-x)\ln(1-x)] \qquad (10)$$

From Equations (8) and (10)

$$\frac{dM}{dx} = \ln\left(\frac{x}{1-x}\right) \qquad (11)$$

$$\frac{dM}{d(1-x)} = -\ln\left(\frac{x}{1-x}\right) \qquad (12)$$

so

$$\phi = x\ln\left(\frac{x}{1-x}\right) - (1-x)\ln\left(\frac{x}{1-x}\right) \qquad (13)$$

which is equivalent to

$$\phi = (2x-1)\ln[x/(1-x)] \qquad (14)$$

but Equation (14) is exactly the definition of the value function. Replacement of the quantities equivalent to ϕ in Equation (2) with the right-side term in Equation (14) will yield Equation (1), thereby confirming that Equation (2) is consistent with the conventional definition definition of separative work for ideal solutions.

Equation (2) might be considered the more fundamental definition of separative work and Equation (1) the form it may take for ideal solutions such as mixtures of uranium isotopes. Equation (2) can be generalized to define separative work for multicomponent separations by adding the corresponding terms for components 3, 4, and so on. If multiple product, tails, or feed streams are involved in the separation process, the corresponding terms for these streams would be included with appropriate signs.

NOTATION

G = free energy (Gibbs) of a mole of mixture, J/mole
G_f = free energy of a mole of feed mixture, J/mole
$\overline{G}_{1f}$ = partial molal free energy (chemical potential) of feed component 1, J/mole
$\overline{G}_{2f}$ = partial molal free energy (chemical potential) of feed component 2, J/mole
G_p = free energy of a mole of product mixture, J/mole
$\overline{G}_{1p}$ = partial molal free energy (chemical potential) of heads component 1, J/mole
$\overline{G}_{2p}$ = partial molal free energy (chemical potential) of heads component 2, J/mole
G_t = free energy of a mole of tails mixture, J/mole
$\overline{G}_{1t}$ = partial molal free energy (chemical potential) of tails component 1, J/mole
$\overline{G}_{2t}$ = partial molal free energy (chemical potential) of tails component 2, J/mole
G_1^0 = free energy of pure component 1 at same temperature and pressure, J/mole
G_2^0 = free energy of pure component 2 at same temperature and pressure, J/mole
M = free energy normalized by RT, dimensionless
R = universal gas constant, J/mole-°K
S = entropy of a mole of mixture, J/mole-°K
T = temperature, °K
W_f = amount of feed mixture used to obtain W_p units of product, kg of binary mixture
W_p = amount of product mixture obtained in the separation of W_f units of feed, kg of binary mixture
W_t = amount of tails mixture obtained in the separation of W_f units of feed, kg of binary mixture
x_f = mole fraction of component 1 in feed mixture
x_p = mole fraction of component 1 in product mixture
x_t = mole fraction of component 1 in tails mixture
δU = separative work, SWU or kg U
ϕ = value function, dimensionless

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A Note on Modeling Laboratory Batch Crystallizations

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The classic analysis of Randolph and Larson (1962, 1971) serves as the basis for characterizing suspension crystallization systems. In particular, laboratory experiments employing well-mixed suspension crystallizer techniques yield crystal size distributions which are very revealing of those characteristics through application of the analysis. This has been well demonstrated with the steady state operation of the laboratory crystallizer (Randolph and Larson, 1971). The analysis of distributions from batch crystallizations is not so informative. Yet, there is a good reason for designing and carrying out experiments batchwise. For example, laboratory batch crystallizations are much more easily performed than continuous ones, especially when sampling distributions during the active crystallization period are not considered. This type of operation is particularly relevant for consideration when working with chemical systems difficult to process, for example, owing to toxic or highly viscous properties, or considerations of monetary expense; or when time to develop appropriate apparatus for continuous operation is not available; or as a first step in preparing for continuous operation in the laboratory in order to obtain experimental design information.

A particular characteristic of batch generated size distributions which appears to be encountered when the seeds charge is not too great is the plateau or hump within the domain of the distribution. This characteristic appears in the published distributions of Baliga (Randolph and Larson, 1971) and Weed (Wey and Estrin, 1973). One apparent explanation for this peculiar behavior of the distribution is size dependent growth; successful reproduction of the experimental distributions was demonstrated using this hypothesis for the potassium sulfate-water system. Other reasons for such distributions may be attrition—agglomeration phenomena and surface energy effects which may become significant at low supersaturations when the sizes influenced are within the readily measurable range.

Another reason for this behavior may be inherent in the nucleation law and typical batch operation which is associated with decreasing supersaturation as the batch proceeds. Qualitatively, the process may be described as follows: nucleation occurs initially owing to the relatively high levels of supersaturation despite low concentrations of suspended solids; in the mid period of operation, the plateau in the distribution is generated because a decrease

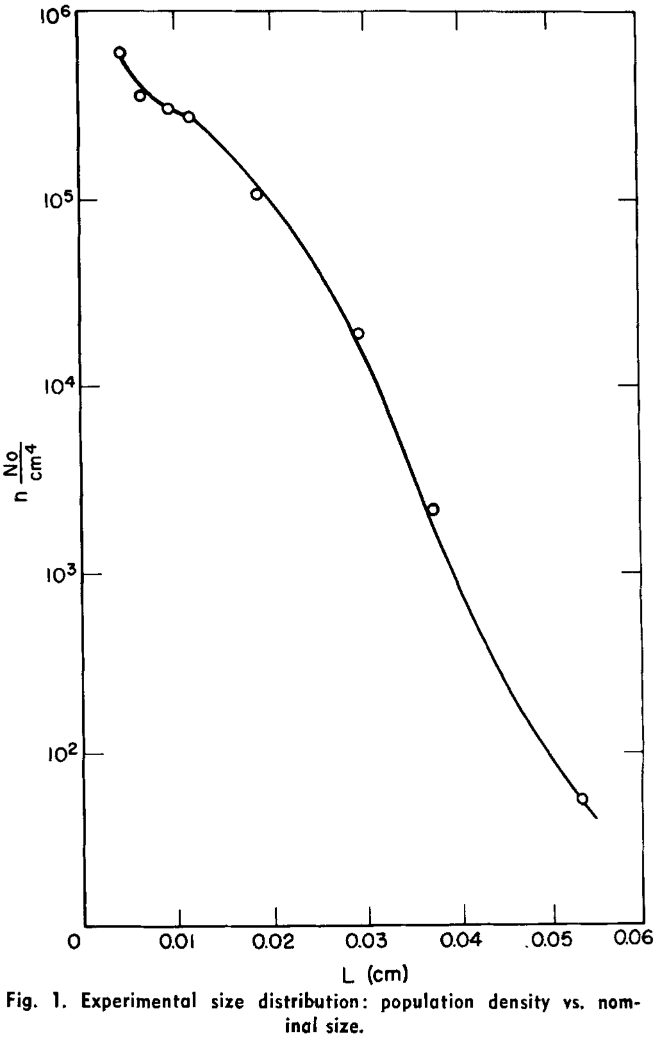

Fig. 1. Experimental size distribution: population density vs. nominal size.

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