CALCULATION OF VAPOR-LIQUID EQUILIBRIUM AVAILABILITY FUNCTION FOR MULTICOMPONENT MIXTURES

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Abstract—A computational method of an availability function, which is essential to thermodynamic efficiency analysis of separation processes, is provided. The proposed subroutines of vapor-liquid equilibrium entropy and subsequent availability function are incorporated to the general thermodynamic properties estimation databanks of Fredenslund et al. [1] and Prausnitz et al. [2]. The improved databank can be used to calculate availability function of mixtures of up to 20 components made of any combination of 100 species of industrial importance. To illustrate the applicability of the method and the databank, the program is tested to calculate the minimum separation energy in adiabatic and isothermal equilibrium flash distillations for various mixtures. Regardless of close- and wide-boiling mixtures, the availability departures from ideal state are usually significant. Within the limits of thermodynamic frameworks derived here, the calculated ideal availabilities and minimum separation energies show large deviations from the values with nonideality corrections.

INTRODUCTION

Most of available energy sources needed in chemical and related industries are consumed by such processes as distillation, absorption and extraction. Especially, since such processes are designed and operated with high level of empiricism due to their complex nature of process characteristics, these separation processes consume large amount of extra useful energy. Thus, it is highly possible that those processes can be operated more efficiently through systematic thermodynamic analysis of existing separation processes.

The systematic thermodynamic efficiency analysis in separation processes or energy conversion facilities can be used as a criteria for new energy-integrated design and improving existing processes. However, the primary step in thermodynamic efficiency analysis of separation processes is the accurate calculation of minimum separation energy for nonideal vapor-liquid equilibrium mixtures.

With the realistic thermodynamic efficiency analysis in mind, a program package to calculate availability for vapor and liquid mixtures at equilibrium is provided in the present work. Even though proposed databank is basically the same as those general equilibrium property databanks of Fredenslund et al.[1] and Prausnitz et al.[2], the subroutines of entropies of nonideal vapor-liquid mixture and availability functions are added to extend the conventional databank for the availability calculations. Therefore, the propos-

ed databank can be used for process efficiency analysis as well as for conventional process simulation.

AVAILABILITY FUNCTION A MINIMUM SEPARATION ENERGY

The separation of a fluid mixture into two or more products of different compositions at the same temperature and pressure necessarily requires a sort of process device which consumes useful energy. The total energy demand is entirely dependent on the characteristics of equipment and its mode of heat and mass transfer, or internal mixing. However, to analyse the thermodynamic efficiency for an equipment or a subsystem, the minimum separation energy demand must be analysed first. The minimum work demand for a separation is found by postulating a hypothetical ideal process no matter what process is employed to accomplish it. Then, the minimum work requirement is dependent upon the composition, temperature and pressure of the mixture to be separated and of the products. The minimum work required to separate mixtures is obtained by calculating the increase of availability of products with respect to the feed. The availability B, sometimes called the energy, is defined as

$$b = \frac{B}{m} = h - T_o S \tag{1}$$

where T_o is the reference temperature, from or to which heat can be transferred on a free basis as discus-

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sed by one of the authors[3,4] and by other[5]. The balance of availability change between products and feeds is a measure of the minimum separation energy required for separation

$$\Delta B = W_{min,T_0} = \sum_{product}(mb) - \sum_{feed}(mb) \qquad (2)$$

Therefore, the calculation of availability or minimum energy is reduced to the calculation of enthalpy and entropy changes with respect to reference temperature, T_o. The minimum separation energy represents only a lower bound on the energy that must be consumed by a separation processes. In most cases the energy requirement for a real process will be many times greater than this minimum. In the coming sections we discussed in detail the thermodynamic framework for the accurate calculation of the availability function.

ENTROPIES OF VAPOR-LIQUID EQUILIBRIUM MIXTURES

Vapor Phase

The entropy of a vapor mixture is first obtained from zero pressure heat capacities of the pure components and then is corrected for the effect of mixing and pressure. The heat capacity of an ideal vapor is a function of temperature. Among various proposed correlations, we used the following relation;

$$C_{pi}^* = D_{1i} + D_{2i}/T + D_{3i}T + D_{4i}\ln T \qquad (3)$$

where the units of C_{pi}^* and T are J/mole-K and Kelvin, respectively.

We used the data of Prausnitz et al.[2] for the sets of constants D_{ij} for pure components Eq. 3 appears to be the best available for typical vapors over the temperature range 200-600K. Eq. 3 should not be extrapolated outside the range of fit to avoid the serious error. The entropy of a pure ideal vapor at temperature T, relative to reference temperature T_o, is given by

$$S_i^{id} = \int_{T_o}^{T} C_{pi}^* / T \ dT \qquad (4)$$

For an ideal vapor mixture of m components, the entropy is then,

$$S^{id} = \sum_{i=1}^{m} y_i \{S_i^{id} - R\ln(y_i P / P_o)\} \qquad (5)$$

where y_i is the mole fraction, P_o the reference pressure.

For a real vapor mixture, entropy can be calculated from an equation of state with the departure correction from ideal vapor mixture

$$S^v = S^{id} + \Delta S^{correct} \qquad (6)$$

where $\Delta S^{correct}$ is the molar entropy correction for the

vapor mixture which is given by

$$\Delta S^{correct} = -\int_0^P (\frac{\partial V}{\partial T})_{p,y} dP \qquad (7)$$

where V is the vapor phase molar volume. To integrate Eq. 7 for nonassociating mixtures, the values of second virial coefficients are calculated based on the correlation of Hayden and O'Connell[6]. The virial coefficients after second are truncated in the present work. The result is

$$\Delta S^{correct} = -JP \sum_i^m \sum_j^m y_i y_j (\frac{\partial B_{ij}}{\partial T}) \qquad (8)$$

where J is the unit conversion factor (0.0988 J/cm³-bar)

For an associating vapor mixture, where strong dimerization occurs (i.e., either the association parameter $\eta_{ij} > 4.5$ or $\eta_{ii} > 4.5$), the molar entropy based on one stoichiometric (apparent) mole of the vapor is

$$S_{assoc}^v = S^{id} + \Delta S^{assoc} \qquad (9)$$

where ΔS^{assoc} is the entropy correction per apparent mole of the vapor at the same T and P relative to the ideal vapor at the same T and composition.

For such associating vapor mixtures, the chemical theory is used as done elsewhere[1,2,6]. The final derivation result based on Eq. 7 is

$$\Delta S^{assoc} = \Delta S_{chem}^D + \Delta S_{phys}^F \qquad (10)$$

where

$$\Delta S_{chem}^D = -(\frac{n_t}{n_t^a})R \sum_i^m \sum_j^m Z_{ij}\{(1 - \frac{T}{B_{ij}^D} (\frac{\partial B_{ij}^D}{\partial T})$$
$$- \frac{\ln B_{ij}^D (\delta_{ij} - 2)}{RT})\} \qquad (11)$$

$$\Delta S_{phys}^F = -(\frac{n_t}{n_t^a})P\{\sum_i^m Z_i (\frac{B_{ii}^F}{T})$$
$$+ \sum_i^m \sum_j^i Z_{ij} (\frac{\partial B_{ij}^F}{\partial T})\} \qquad (12)$$

Here, n_t/n_t^a is the ratio of the true number of moles to the apparent number of moles. Kronecker delta $\delta_{ij}= 0$ when $i \ne j$ and 1 when $i = j$. The superscript D represents the dimerization contribution, and F the free contribution to the real vapor entropy.

Liquid Phase

The entropy of a liquid mixture is given by

$$S^L = S^{id} + \sum_{i=1}^{m} X_i \Delta \bar{S}_i \qquad (13)$$

where S^{id} is given by Eq. 5 with y's replaced by x's. Here $\Delta\bar{S}_i$ is the partial molar entropy of component i, at T,P and composition of liquid mixture relative to the molar entropy of pure ideal vapor i at the same temperature. The partial molar entropy for every compo-

nent i is found from an appropriate form of the Gibbs-Helmholtz equation

$$(\frac{\partial \ln f_i^L}{\partial T})_{p,x} = -\frac{\Delta \bar{h}_i}{RT^2} = -\frac{\Delta \bar{g}_i}{RT^2} - \frac{\Delta \bar{S}_i}{RT^2} \qquad (14)$$

where the fugacities of liquid for condensable component and for noncondensable component are given by

$$f_i^{L(Po)} = \gamma_i^{(Po)} x_i f_i^{(Po)} \exp(\frac{\bar{v}_i P}{RT}) \qquad (15)$$

$$f_i^{L(\infty)} = \gamma_i^{(\infty)} x_i f_i^{(oL)} \exp(\frac{\bar{v}_i^\infty P}{RT}) \qquad (16)$$

where the superscript (Po) represents pure liquid i at T corrected to zero pressure and (oL) represents the hypothetical state (the fugacity of pure liquid i at system temperature T) and denotes at infinite dilution.

For condensable components, the pure liquid fugacity at zero-pressure is given by

$$\ln f_i^{(Po)} = C_{1i} + C_{2i}/T + C_{3i}T + C_{4i}\ln T + C_{5i}T^2 \qquad (17)$$

where the C's are constants for liquid i. These constants can be determined primarily from vapor pressure data and secondarily from vapor phase and liquid-phase volumetric data. However, in the present work, the values of constants are taken from the works of previous investigators[1,2].

For noncondensable components, the fugacity at hypothetical state is an essentially arbitrary function of temperature and we used the correlation in the original databank[2]

$$\ln(\frac{f_i^{oL}}{P_{ci}}) = 7.224 - 7.534(\frac{T}{T_{ci}})^{-1} - 2.598 \ln(\frac{T}{T_{ci}}) \qquad (18)$$

where P_{ci} and T_{ci} are the critical pressure and temperature, respectively.

With appropriate integrations of Eq. 14-16, the following equations are derived and programmed into the databank. First, for condensable liquid mixtures, the total entropy is given by

$$S^L = S^{id} + \sum_{i=1}^{m} x_i \frac{\Delta \bar{h}_i}{T} - R\sum_{i=1}^{m} x_i \ln x_i \gamma_i^{(Po)} \qquad (19)$$

where h_i is the partial molar enthalpy which is relatively well defined in the literatures[1,2] and we used those same equations in the present databank. Also, for liquid mixtures containing both condensable and noncondensable components, the partial molar enthalpy equation is used

$$\Delta \bar{h}_i = h_i^{ex} - RT^2 \underbrace{(\frac{d \ln f_i^{(Po)}}{dT})_{pure}}_{\text{all condensable}}$$

$$\underbrace{- RT^2(\frac{\partial \ln \gamma_i^{(\infty)}}{\partial T})_{p,x} - RT^2(\frac{d \ln f_i^{oL}}{dT})_{pure}}_{\text{all noncondensable}} \qquad (20)$$

OTHER EQUILIBRIUM PROPERTIES AND DATABANK STRUCTURE

In order to calculate accurately the availability functions for vapor and liquid phases, enthalpies are required in addition to entropies. Also, for an accurate calculation of enthalpy and entropy, the other properties such as activity coefficient and fugacity coefficient are required. However, all those additional properties calculations are well defined in the original databanks which are improved in the present work. Thus, a detailed discussion of such properties is inappropriate here. Interested readers are referred to the works of Fredenslund et al.[1] and Prausnitz et al.[2]. The subroutine of availability for vapor and liquid mixture system of up to 20 components at specified T, P and composition is programmed by FORTRAN 77 for IBM-PC-XT.

EXAMPLE CALCULATIONS OF EQUILIBRIUM SEPARATIONS IN MULTICOMPONENT SYSTEM

Effects of Nonideality Corrections for Equilibrium Mixtures

To test the applicability of the method for calculating availabilities, the vapor-phase and liquid-phase enthalpies and entropies for ideal state and nonideality corrections results for various equilibrium mixtures are compared in Table 1. The deviations of ideality and nonideality corrections of the calculated enthalpies and entropies in the vapor-phase are usually small.

However, the deviations of calculated values in liquid phase are large, especially, when a liquid mixture forms an association between molecules.

Equilibrium Separation Availability Calculation

The improved databank presented here can be incorporated into many of the well documented calculational procedures or process simulators for the purpose of solving conventional design problems or analyses of separation energy audit in distillation columns and absorbers-strippers. The flash calculations are the most appropriate application of the phase-equilibria since multistage separations are usually arranged with countercurrent flow of the equilibrium phases between the stages. In this section, by adopting the step-limiting Newton's method[2,7], the databank is implemented for adiabatic and isothermal equilibrium flash calculations for six mixture cases as shown in Table 2. For mixtures that are not extremely wide-boiling, conver-

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Table 1. Significance of nonidealities corrections in enthalpy and entropy for various vapor-liquid equilibrium mixtures.

Components	Mole fraction		Press	Temp	Vapor-phase				Liquid-Phase			
					ideal only		corrected		ideal only		corrected mixing	
	vapor	Liquid	(bars)	(K)	H	S	H	S	h	s	h	s
Benzene	0.268	0.243	1.0	353.6	6.306	0.032	6.473	0.031	−23.69	−0.043	−23.82	−0.043
Cyclohexane	0.249	0.250										
Methylcyclo-hexane	0.155	0.286										
n-Hexane	0.328	0.220										
Carbon tetra-chloride	0.200	0.200	1.0	346.4	3.709	0.025	3.834	0.025	−30.63	−0.065	−30.65	−0.065
Ethanol	0.379	0.164										
n-Propanol	0.086	0.103										
Cyclohexane	0.214	0.197										
Toluene	0.121	0.336										
Acetic acid	0.003	0.021	1.0	353.9	3.738	0.021	3.324	0.022	−38.76	−0.101	−38.81	−0.101
Ethanol	0.243	0.089										
Ethyl acetate	0.315	0.061										
Water	0.440	0.829										
Carbon tetra-chloride	0.083	0.104	1.0	344.6	2.941	0.027	2.847	0.026	−33.15	−0.066	−33.03	−0.066
Ethanol	0.135	0.092										
n-Propanol	0.055	0.111										
Cyclohexane	0.094	0.101										
Toluene	0.129	0.217										
Acetone	0.122	0.095										
Methanol	0.185	0.080										
Water	0.196	0.201										

gence is usually achieved in three or four iterations. Case 1 through case 4 in Table 2 are typical of relatively close boiling mixtures, the latter case 3 exhibit significant liquid-phase nonidealities. Case 3 and 4 shown in Table 2 show strong vapor-phase nonidealities as well. In all of the cases the results of availability departure from ideal state are not negligible. Especially, when a mixture forms association species (Case 3 & 4), the ideality assumptions overestimate minimum separation energy more than several times with respect to the values calculated with nonideality correction. Within the limits of thermodynamic frameworks derived here for phase-equilibrium entropies, it is obvious that the nonidealities in vapor-liquid equilibrium mixtures must be corrected when an accurate availability analysis is needed.

CONCLUSION AND PROGRAM PACKAGE

Toward the realistic efficiency analysis, a reliable method to calculate availability is proposed. With thermodynamically consistent equations for calculating the vapor- and liquid-phase entropies, the existing conventional databanks are improved to be applicable for both conventional process design simulators and for purposes of analysing thermodynamic efficiency of energy audit in separation processes.

The program listing can be obtained from the authors upon request for further interested readers.

Table 2. Calculated availability functions for both adiabatic and isothermal flash calculations for various mixtures.

Flash Type	Case	Components	Feed			Flash					Availability(KJ/mole)						Minimum work (KJ/mole)	
									Mole fraction		Feed		Products					
											Liquid		Liquid		Vapor			
			Mole fraction	Press (bars)	Temp (K)	Press (bars)	Temp (K)	V/F	Liq	Vap	Ideal	Actual	Ideal	Actual	Ideal	Actual	Ideal	Actual
Adiabatic	system(1)	Benzene	0.25	3.0	394.0	1.0	353.6	0.275	0.243	0.268	-9.656	-9.688	-8.728	-8.748	-0.692	-0.582	0.236	0.358
		Cyclohexane	0.25						0.250	0.249								
		Methylcyclo-hexane	0.25						0.286	0.155								
		n-Hexane	0.25						0.220	0.328								
Adiabatic	system(2)	Carbon tetra-chloride	0.20	3.0	381.5	1.0	346.4	0.166	0.200	0.200	-11.47	-11.43	-10.74	-10.74	-0.535	-0.478	0.195	0.204
		Ethanol	0.20						0.164	0.379								
		n-Propanol	0.10						0.103	0.086								
		Cyclohexane	0.20						0.197	0.214								
		Toluene	0.30						0.336	0.121								
Iso-thermal	system(3)	Formic acid	0.35	1.0	550.0	1.0	380.6	0.572	0.348	0.351	-14.35	-23.20	-7.037	-7.182	-0.968	-14.68	6.350	1.345
		Acetic acid	0.35						0.373	0.333								
		Water	0.30						0.278	0.316								
Adiabatic	system(4)	Acetic acid	0.02	3.0	384.7	1.0	353.9	0.074	0.021	0.003	-10.72	-10.73	-10.47	-10.48	-0.139	-0.208	0.111	0.041
		Ethanol	0.10						0.089	0.243								
		Ethyl acetate	0.08						0.061	0.315								
		Water	0.80						0.829	0.440								
Adiabatic	system(5)	n-Butane	0.25	3.0	340.1	1.0	315.3	0.238	0.164	0.524	-8.534	-8.534	-7.081	-7.081	-0.534	-0.505	0.919	0.948
		i-Butane	0.15						0.084	0.361								
		n-Pentane	0.10						0.097	0.110								
		n-Decane	0.50						0.655	0.005								
Adiabatic	system(6)	Carbon tetra-chloride	0.10	5.0	393.3	1.0	344.6	0.193	0.104	0.083	-13.15	-13.07	-12.14	-12.13	-0.843	-0.817	0.166	0.123
		Ethanol	0.10						0.092	0.135								
		n-Propanol	0.10						0.111	0.055								
		Cyclohexane	0.10						0.101	0.094								
		Toluene	0.20						0.217	0.129								
		Acetone	0.10						0.095	0.122								
		Methanol	0.10						0.080	0.185								
		Water	0.20						0.201	0.196								

NOMENCLATURE

B   : total availability function, J
b   : molar availability function, J/mol
B_{ij} : second virial coefficients
C_{ij} : coefficients in the correlation of pure liquid state fugacity
D_{ij} : coefficients in zero-pressure heat capacity equation
C_{pi}^{*} : heat capacity, J/g-mol-K
h   : molar enthalpy, J/mol
J   : unit conversion factor, 0.0988 J/cm^3-bar
m   : number of component mass
n   : number of moles, mol
P   : pressure, bar
R   : gas constant
s   : molar entropy, J/mol-K
T   : absolute temperature, K
W   : separation energy
x   : liquid-phase mole fraction
y   : vapor-phase mole fraction

Greek Letters
δ : Kronecker delta
η : association parameter
γ : activity coefficient

Superscripts
oL   : hypothetical state pure liquid
Po   : zero pressure pure liquid

id   : ideal
V   : vapor
L   : liquid
D   : dimerization contribution
E   : Excess property
F   : free contribution
-     : partial molar quantity

Subscripts
assoc : association of vapor-phase
min   : minimum separation energy

REFERENCES

1. Fredenslund, A., Gmehling, J. and Rasmussen, P.: Vapor-Liquid Equilibria Using UNRFAC -a group contribution method , Elsevier Sci. Pub. Co. Armsterdam (1977).
2. Prausnitz, J., Anderson, T., Grens, E., Eckert, C., Hsieh, R. and O'Connell, J.: Computer Calculations for Multicomponent Vapor-Liquid and Liquid-Liquid Equilibria , Prentice-Hall Inc (1980).
3. Yoo, K.P. and Choi, C.S.: On the Thermodynamic Efficiency Evaluations of Process and Energy Facilities , Part I. Availability and its Application, *Korean J. of Chem. Ind. Tech.*, **3,** 2 (1985).
4. Yoo, K.P. and Choi, C.S.: Part II. Lost Energy Analysis , *ibid.,* **3,** 4 (1985).
5. King, C.J.: Separation Processes , 2nd. ed., Ch. 13 , McGraw-Hill Book Co(1980).
6. Hayden, J.G. and O'Connell, J.P.: *Ind. Eng. Chem. Process Des. Dev.,* **14,** 221 (1975).
7. Goldstein, R.P. and Stanfield, R.B.: *Ind. Eng. Chem. Process Des. Dev.,* **9,** 78 (1970).