

Nothing has been said about the fourth basic equation since it is generally used directly as is. Clearly, however, if an application is contemplated to an extremely high energy process, such as a nuclear reaction or high velocity particles, the Einstein relation,  $E = mc^2$ , must be employed. In such a case the individual mass and energy balances must be modified to allow for the equivalence of mass and energy.

NOMENCLATURE	
A	Helmholtz free energy, U-TS
a	Activity, $\xi/t^\circ$
c	Heat capacity, $T(dS/dT)$
F	Faraday number
f	Fugacity
G	Gibbs free energy, H-TS
g	Acceleration of gravity
H	Enthalpy
$J_a$	Ratio of activities $a_{C,D}^a/a_{A,B}^b$
$K_a$	Equilibrium ratio of activities
LW	Lost work
m	Mass
N,n	Number of moles
P	Pressure
P	Partial pressure
Q	Quantity of heat
S	Entropy
T	Temperature
U	Internal Energy
u	Velocity
V	Volume
W	Work
x	Mole fraction
Y	Mole fraction
Z	Height above datum plane
$\alpha, \beta$	Phases
$\gamma$	Activity coefficient
$\mu$	Chemical potential
$\omega$	Constant for regular solutions
—	Below an extensive property makes it per unit mass
—	Above an extensive property makes it a partial property of a mixture.
□	Denotes vapor pressure, as $P^\square$ .

Several example problems and solutions are presented in the following section.

## ChE problems for teachers

The following problems with solutions were submitted by Professor J. J. Martin.

No. 1. One hundred million standard cubic feet (60°F, 1 atm) per day of radioactive waste gas at 1000°F must be released at a height of 400 ft. above the ground to avoid contamination of the surrounding area. A circular stack of uniform diameter is to be used. A draft at the base of the stack of 1 in. of water will be required (pressure inside stack base is 1 in. H<sub>2</sub>O less than barometric pressure). The barometric pressure at the base of the stack is 740 mm Hg and the ambient temperature 60°F. The gas has a molecular weight of 32 and may be considered an ideal gas. What diameter will be required?

The lost work of gas flowing through the stack may be approximated by the equation:

$$LW = \frac{0.032 \text{ lu}^2}{g_c D}$$

LW = lost work in ft-lb<sub>F</sub>/lb<sub>M</sub>

l = height in ft

D = diameter in ft

u = velocity in feet per sec

$g_c$  = conversion factor from lb<sub>M</sub> to lb<sub>F</sub>

Solution: For barometric pressure at top consider a stagnant column of air outside the stack. Since it is at equilibrium (no flow) with no kinetic effects, Eqn. (17) applies as

$$0 = \int_{\text{base}}^{\text{top}} \frac{RT}{P} dP + g\Delta Z$$

$$RT \ln \frac{P_{\text{top}}}{P_{\text{base}}} = -g\Delta Z$$

$$\text{so } (10.73)(520) \ln \frac{P_{\text{top}}}{740} = - \frac{(400)(29)}{144}$$

$$\text{and } P_{\text{top}} = 729.41 \text{ mm Hg}$$

The pressure inside the base of the stack is

$$P_{\text{in base}} = 740 - \frac{(25.4)(1)}{13.6} = 738.13 \text{ mm Hg}$$

The gas velocity inside the stack at an average pressure of 734 mm Hg is

$$u = \frac{10^8 (760)(1460)(4)}{24(3600)(520)(734)\pi D^2} = \frac{4290 \text{ ft}}{D^2 \text{ sec}}$$

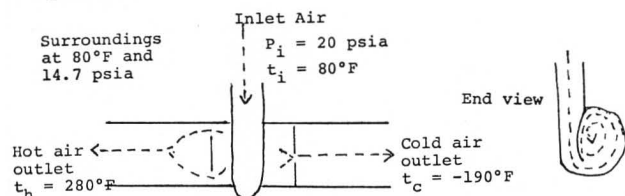
For flow inside the stack with no kinetic effects and no work, Eqn. (16) applies as

$$-LW = \int \frac{RT}{P} dP + g\Delta Z$$

$$\text{Thus, } - \frac{(0.032)(400)(4290)^2}{32.17 D^4} = \frac{(10.73)(1460)(144)}{(32)} \ln \frac{729.41}{738.13} + 400$$

$$\text{Solving } D = 7.2 \text{ ft}$$

No. 2. A Ranque-Hilsch vortex cylinder is a device to expand a stream of air in steady flow from high pressure and ambient temperature down to two streams at atmospheric pressure, one of which is at low temperature and the other at high temperature. Air enters the cylinder through a tangential tube, creating a vortex from which the hot air is withdrawn from the outer periphery and the cold air is withdrawn from the central region, as shown below. In a certain test of the equipment the temperatures and pressures were measured and reported to be as indicated on the diagram. The mass flow rate of the hot air was stated to be 1.35 times that of the cold air. Show by calculations whether the reported measurements are possible.



Solution: Apply the energy balance Eqn. (2) to the whole device. Assuming negligible kinetic and potential effects, and

$$\delta Q = \delta W = dE_{\text{sys}} = 0,$$

$$\sum_j H_j \delta m_j = 0 \text{ or } (H\delta m)_i = (H\delta m)_h + (H\delta m)_c$$

$$\text{Let } \delta m_h = 1.35, \delta m_c = 1.0, \delta m_i = 2.35$$

Taking the reference state of air at 80°F and 20 psia, and assuming ideal gas behavior with  $C_p = 7.0$  Btu/lb mole-°R,

$$H_i = 0, H_h = 7(280-80) = 1400, \text{ and } H_c = 7(-190-80) = -1890$$

Substituting in the energy balance

$$0 = (1400)(1.35) + (-1890)(1) = 0. \text{ So energy balance OK.}$$

Apply the entropy balance as

$$dS = \frac{\delta LW}{T_0} + \sum_j S_j \delta m_j = 0 \text{ for steady state}$$

or

$$- \frac{\delta LW}{T_0} = (S\delta m)_i - (S\delta m)_h - (S\delta m)_c$$

Integrating Eqn. (8),  $\Delta S = C_p \ln T - R \ln P$

Using this to calculate entropies with respect to the reference state,

$$S_i = 0, S_h = 7 \ln \frac{740}{540} - 1.99 \ln \frac{14.7}{20} = 2.815 \text{ and } S_c =$$

$$7 \ln \frac{270}{540} - 1.99 \ln \frac{14.7}{20} = -4.24$$

Putting these into the entropy balance gives

$$-\frac{\delta LW}{T_0} = 0 - (2.815)(1.35) - (1)(-4.24) = 0.44$$

$$\text{or } \delta LW = -0.44 T_0$$

$T_0$  is the temperature at which heat may be rejected to the surroundings, 540, so

$$\delta LW = (-0.44)(540) = -237$$

This, however, is impossible because the minimum value of lost work in a perfect process (reversible) is zero. There is no such thing as negative lost work (gained work). Thus, the data from the experiment must be in error. In other words, do not invest in this device if successful exploitation is dependent upon the above data. No. 3. A mixture consisting of 33-1/3% by volume methane and 66-2/3% oxygen at 25°C and 1 atmosphere total pressure is fed to a combustion chamber where the methane is burned completely at 1800°C. The combustion products are then cooled and expanded at constant composition to 25°C and 1 atmosphere pressure. Assume ideal gases and surroundings at 25°C and no condensation of H<sub>2</sub>O.

a) What is the maximum work obtainable from the above process?

b) What would be the maximum work obtainable if the combustion reaction were carried out irreversibly at 1800°C, but all other steps were reversible?

DATA: For the reaction at 9 atmospheres pressure,



At 25°C:

$$\Delta H = -208,500 \text{ cal/gm mole CH}_4$$

$$\Delta S = -1.23 \text{ cal/gm mole CH}_4/\text{°K}$$

At 1800°C:

$$\Delta H = -211,110 \text{ cal/gm mole CH}_4$$

$$\Delta S = -4.07 \text{ cal/gm mole CH}_4/\text{°K}$$

Solution:

$$(a) \text{ At } 25^\circ\text{C}, \Delta G = \Delta H - T\Delta S = -208,500 - 298(-1.23) = -208,140$$

To expand 3 moles of products from 9 atm to 1 atm

$$\Delta G = \int v dp = n \int \frac{RT}{P} dP = nRT(\ln P) = 3(1.99)(298) \ln \frac{1}{9} = -3900 \text{ cal}$$

$$\text{From Eqn. (18) } -W_r = \Delta G_T = -208,140 - 3900 = -212,040 \text{ cal}$$

(b) Irreversible combustion at 1800°C means that the work which could have been produced in a reversible engine is converted to heat. This could be put through a reversible heat engine to recover some work.

$$\text{Thus, } \Delta G = -211,110 - (2073)(-4.07) = -202,680 \text{ cal}$$

$$\text{Using Eqn. (14) } W_r = 202,680 \left( \frac{2073 - 298}{2073} \right) = 173,580 \text{ cal}$$

Therefore the lost work due to the irreversible combustion is

$$LW = 202,680 - 173,580 = 29,100 \text{ cal}$$

Net work by this process is

$$W = 212,040 - 29,100 = 182,940 \text{ cal}$$

No. 4. One hundred lb-mole of a solution of 10 mole percent carbon disulfide and 90 mole percent acetone are to be separated into pure acetone and the azeotrope which forms at 39.25°C under atmospheric pressure. The azeotrope which forms 61 mole percent carbon disulfide and 39 mole percent acetone.

It is desired to estimate the minimum work to carry out the above separation in a distillation column if the feed solution is all liquid at 39.25°C and the products are withdrawn as liquids at the same temperature.

At 39.25°C the vapor pressure of CS<sub>2</sub> is 604 mm Hg, while the vapor pressure of (CH<sub>3</sub>)<sub>2</sub>CO at the same temperature is 400 mmHg. At atmospheric pressure the vapor phase may be assumed to behave as an ideal gas. The liquid solution does not behave as an ideal solution, but its activity coefficients may be represented by the Van Laar equation,

$$\ln \gamma_A = \frac{A}{\left(1 + \frac{Ax_A}{Bx_B}\right)^2} \quad \text{and} \quad \ln \gamma_B = \frac{B}{\left(1 + \frac{Bx_B}{Ax_A}\right)^2}$$

Solution: Let acetone be component A and carbon disulfide be B.

For the equilibrium between the liquid and vapor, Eqns. (20) and

(27) show that  $\bar{f}_i^L = \bar{f}_i^G$ . For the liquid  $\bar{f}_i^L = \gamma_i x_i f_i^O$ . Taking

the standard state as pure liquid under its own vapor pressure

and since vapor pressure is low this may be taken as the fugacity  $f_i^O$ ,  $\bar{f}_i^L = \gamma_i x_i P_i^O$ . Also for the gas, assuming ideality,  $\bar{f}_i^G = P_i = \gamma_i P$ . Thus,

$$\gamma_i x_i P_i^O = \gamma_i P$$

$$\text{For an azeotrope } x_i = y_i \text{ so } \gamma_i = \frac{P}{P_i^O}$$

$$\text{Thus, } \gamma_A = \frac{760}{400} = 1.90 \text{ and } \gamma_B = \frac{760}{604} = 1.258$$

From equations for Van Laar constants

$$A = \ln \gamma_A \left[ 1 + \frac{x_B \ln \gamma_B}{x_A \ln \gamma_A} \right]^2 = \ln 1.90 \left[ 1 + \frac{0.61 \ln 1.258}{0.39 \ln 1.90} \right]^2 = 1.558$$

$$B = \ln \gamma_B \left[ 1 + \frac{x_A \ln \gamma_A}{x_B \ln \gamma_B} \right]^2 = \ln 1.258 \left[ 1 + \frac{0.39 \ln 1.90}{0.61 \ln 1.258} \right]^2 = 1.787$$

In feed solution,

$$\ln \gamma_A = \frac{1.558}{\left[ 1 + \frac{1.558(0.9)}{1.787(0.1)} \right]^2} \quad \text{or} \quad \gamma_A = 1.0202$$

and

$$\ln \gamma_B = \frac{1.787}{\left[ 1 + \frac{1.787(0.1)}{1.558(0.9)} \right]^2} \quad \text{or} \quad \gamma_B = 4.08$$

From  $\Delta G = \Delta G_{\text{Ex}} + \Delta G_{\text{ideal}}$  and Eqns. (43) and (44),

$$\Delta G = RT(n_A \ln x_A \gamma_A + n_B \ln x_B \gamma_B)$$

So

$$\Delta G_{\text{feed}} = (1.99)(561)[90 \ln(0.9)(1.0202) + 10 \ln(0.1)(4.08)] = -18,140 \text{ Btu}$$

(Continued on page 221.)

practical needs of society which application of our knowledge of reactor design offers hope of meeting. Teaching, understanding, and applying the principles of reactor design will long remain a major challenge to chemical engineers.

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## PROBLEMS (Cont'd from p. 217.)

$$\Delta G_{\text{products}} = \Delta G_{\text{azeo}} + \Delta G_{\text{acetone}} - \Delta G_{\text{azeo}}$$

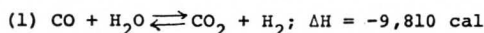
$$\Delta G_{\text{azeo}} = (1.99)(561) \left[ \frac{(10)(39)}{61} \right] \ln(0.39)(1.9) + 10 \ln(0.61)(1.258) \\ = -5,050 \text{ Btu}$$

$$-W_r = \Delta G = \Delta G_{\text{products}} - \Delta G_{\text{feed}}$$

$$= -5050 + 18140 = 13090 \text{ Btu/100 moles feed}$$

No. 5. Badische Anilin and Soda-Fabrik AG of Ludwigshafen am Rhein give this data.

"Water-Gas Shift Reaction--Conversion of the carbon monoxide proceeds according to the expression:

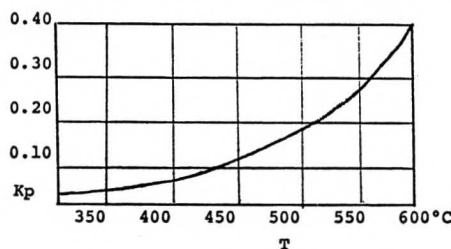


It is an equilibrium reaction with a temperature-dependent equilibrium constant,

$$(2) K_p = \frac{(\text{CO})(\text{H}_2\text{O})}{(\text{CO}_2)(\text{H}_2)}$$

The location of the equilibrium for a given gas composition is independent of the total pressure of the system." Also presented with the above statements is a graph which is reproduced below. Please study this information and demonstrate (a) by numerical calculations whether their data are concordant, and determine (b) the free energy change of the reaction at 500°C.

Temperature dependence of the equilibrium constant  $K_p$



(Continued on page 226.)

relates directly to the title of the curriculum. The award of a degree will be primarily the interest of the regional accrediting agency. Regional accreditation at the appropriate level (associate or bachelor's degree) must precede ECPD inspection. It is believed that this limited accrediting procedure by ECPD will eliminate, to the maximum degree possible, confusion between engineering education and engineering technician education.

## RECOGNITION OF CONTINUING EDUCATION

The significance of continuing education for engineers was recognized a few years ago by a comprehensive report sponsored by EJC, ECPD, ASEE and NSPE that emphasizes its great importance to the engineering profession. Nevertheless, continuing education operates under the handicap that the achievement of the individual receives no formal recognition. In contrast, a reasonable amount of effort directed toward part-time graduate study can result in a master's degree that receives nation-wide acceptance. If some type of formal recognition of perhaps an equivalent academic year of effort devoted to continuing education could be developed, the at-

tention given to continuing education would doubtless increase. Because of its extensive experience with the accreditation process, ECPD seems to be the logical agency to experiment with this concept of formal recognition of achievement in continuing education. It is hoped that an appropriate channel for such recognition may be devised. It seems to the writer that such recognition is a serious responsibility of the engineering profession that has been neglected merely because of its sensitive nature.

## DEFINING A PROFESSION

A profession may be defined in part by required steps of admission and advancement of its members. It can also be defined in part through aiding in the recognition of associated groups, who relate clearly to its activities, but by using distinctly different standards for recognition. Such a relationship exists between engineers and engineering technicians or technologists. There is reason to hope that these and other actions of engineering societies may aid in defining the profession of engineering which has resisted inclusive definition by words alone. Nevertheless, the writer believes that definitions can be improved.

## PROBLEMS (Cont'd from p. 221.)

Solution:

(a) Assuming heat capacity effects negligible, use Eqn. (30) in the form

$$\ln \frac{K_{a2}}{K_{a1}} = \frac{\Delta H^\circ}{R} \left( \frac{1}{T_1} - \frac{1}{T_2} \right) = \frac{\Delta H^\circ}{R} \left( \frac{T_2 - T_1}{T_1 T_2} \right)$$

From the graph  $K_a = 0.1$  at  $427^\circ\text{C}$  and  $0.4$  at  $600^\circ\text{C}$

$$\text{Thus } \Delta H^\circ = \frac{(1.99)(873)(700)}{.700-873} \ln \frac{0.4}{0.1} = -9750 \text{ cal/gm mole}$$

This agrees well with the  $-9810$  cal given. The slope of the  $\ln K_a$  vs  $1/T$  plot gives the same result.

(b) At  $500^\circ\text{C}$ ,  $K_a = 0.19$  for  $\text{CO}_2 + \text{H}_2 \rightarrow \text{CO} + \text{H}_2\text{O}$

$$\text{For the reverse reaction } K_a = \frac{1}{0.19}$$

Therefore, from Eqn. (29)

$$\begin{aligned} \Delta G^\circ &= -RT \ln K_a = -(1.99)(773) \ln \frac{1}{0.19} \\ &= -2550 \text{ cal/gm mole} \end{aligned}$$

No. 6. The heat of combustion of hydrogen with oxygen at atmospheric pressure and  $18^\circ\text{C}$  to form liquid water is  $68,300$  cal/gm mole  $\text{H}_2\text{O}$ . The reversible voltage for the electrolysis of water in a very dilute acid solution at  $18^\circ\text{C}$  is  $-1.23$  volts when all products and reactants are at atmospheric pressure. The latent heat of vaporization of water is  $10,500$  cal/gm mole, and both this and the heat of combustion vary negligibly with temperature. The vapor pressure of water at  $18^\circ\text{C}$  is  $15.48$  mm Hg (neglect effect of small acid content), while at  $40^\circ\text{C}$  the vapor pressure is  $55.31$  mm Hg.

Calculate the reversible voltage to electrolyze water at  $40^\circ\text{C}$  if the products and reactants are at  $5$  atm pressure. Assume ideal gas behavior and negligible effect of pressure on vapor pressure. For water take the standard state to be (a) pure liquid under atmospheric pressure and (b) pure gas under its vapor pressure at  $18^\circ\text{C}$ . Compare the two answers. The reaction is  $\text{H}_2\text{O} \rightarrow \text{H}_2 + \frac{1}{2} \text{O}_2$ .

Solution:

(a) Integrating Eqn. (33) assuming little change in  $\Delta H^\circ$ ,

$$\left| \frac{\mathcal{E}^\circ}{T} \right| = \frac{\Delta H^\circ}{N\mathcal{F}} \left| \frac{1}{T} \right|$$

or

$$\mathcal{E}_{40}^\circ = \frac{-1.23(313)}{291} + \frac{68,300(313)}{2(23,050)} \left[ \frac{1}{241} - \frac{1}{313} \right]$$

$$= -1.211 \text{ volts}$$

By Eqn. (35)

$$\mathcal{E}_r = \mathcal{E}_r^\circ - \frac{RT}{N\mathcal{F}} \ln \frac{a_{\text{O}_2}^{1/2} a_{\text{H}_2}}{a_{\text{H}_2\text{O}}}$$

$$= -1.211 - \frac{(1.99)(313)}{2(23,050)} \ln(5)^{1/2(5)} = -1.2438 \text{ volts}$$

(b) In producing gaseous water  $\Delta H = 68,300 - 10,500 = 57,800$  cal/gm mole

$$\text{Thus, } \mathcal{E}_r^\circ = \frac{-1.23(313)}{241} + \frac{(57,800)(313)}{2(23,050)} \left[ \frac{1}{291} - \frac{1}{313} \right] = -1.228 \text{ volts}$$

Now activity of gaseous water under own vapor pressure is

$$a_{\text{H}_2\text{O}} = \frac{55.31}{15.48} = 3.57$$

So

$$\mathcal{E}_r = -1.228 - \frac{(1.99)(313)}{2(23,050)} \ln \frac{(5)^{1/2(5)}}{3.57}$$

$$= -1.2434 \text{ volts which agrees well with } -1.2438$$