

TRƯỜNG ĐẠI HỌC NÔNG LÂM TP HCM
BỘ MÔN CÔNG NGHỆ HÓA HỌC

GIỚI THIỆU CNHH

CHƯƠNG 4: VAI TRÒ VÀ TẦM QUAN TRỌNG CỦA KHOA HỌC CƠ BẢN TRONG CÔNG NGHỆ HÓA HỌC (Phần 2)

❖ Enthalpy và nhiệt dung riêng (Specific enthalpy and heat capacity):

For pure materials, with no phase change:

$$H_T = \int_{T_d}^T C_p dT \quad (3.11)$$

where H_T = specific enthalpy at temperature T ,

C_p = specific heat capacity of the material, constant pressure,

T_d = the datum temperature.

If a phase transition takes place between the specified and datum temperatures, the latent heat of the phase transition is added to the sensible-heat change calculated by equation 3.11. The sensible-heat calculation is then split into two parts:

$$H_T = \int_{T_d}^{T_p} C_{p1} dT + \int_{T_p}^T C_{p2} dT \quad (3.12)$$

where T_p = phase transition temperature,

C_{p1} = specific heat capacity first phase, below T_p ,

C_{p2} = specific heat capacity second phase, above T_p .

The specific heat at constant pressure will vary with temperature and to use equations 3.11 and 3.12, values of C_p must be available as a function of temperature. For solids and gases C_p is usually expressed as an empirical power series equation:

$$C_p = a + bT + cT^2 + dT^3 \quad (3.13a)$$

$$\text{or} \quad C_p = a + bT + cT^{-1/2} \quad (3.13b)$$

Absolute (K) or relative ($^{\circ}\text{C}$) temperature scales may be specified when the relationship is in the form given in equation 3.13a. For equation 3.13b absolute temperatures must be used.

Values for the constants in this equation for the more common gases can be found in the handbooks, and in Appendix C.

DELHF = Standard enthalpy of formation of vapour at 298 K, kJ/mol.

DELGF = Standard Gibbs energy of formation of vapour at 298 K, kJ/mol.

CPVAPA, CPVAPB, CPVAPC, CPVAPD = Constants in the ideal gas heat capacity equation:

$$C_p = \text{CPVAPA} + (\text{CPVAPB}) * T + (\text{CPVAPC}) * T ** 2 + (\text{CPVAPD}) * T ** 3,$$

C_p J/mol K, T deg K.

Table 8.4. Group contributions to ideal gas heat capacities, kJ/kmol°C (Rihani and Doraiswamy, 1965)

Group	<i>a</i>	<i>b</i> × 10 ²	<i>c</i> × 10 ⁴	<i>d</i> × 10 ⁶
Aliphatic hydrocarbon groups				
—CH ₃	2.5485	8.9740	−0.3567	0.004752
 —CH ₂	1.6518	8.9447	−0.5012	0.0187
=CH ₂	2.2048	7.6857	−0.3994	0.008264
 —C—H	−14.7516	14.3020	−1.1791	0.03356
 —C—	−24.4131	18.6493	−1.7619	0.05288
H C=CH ₂	1.1610	14.4786	−0.8031	0.01792
>C=CH ₂	−1.7472	16.2694	−1.1652	0.03083
H C=C<H	−13.0676	15.9356	−0.9877	0.02305
H C=C<H	3.9261	12.5208	−0.7323	0.01641
>C=C<H	−6.161	14.1696	−0.9927	0.02594
>C=C<	1.9829	14.7304	−1.3188	0.03854
H C=C=CH ₂	9.3784	17.9597	−1.07433	0.02474
>C=C=CH ₂	11.0146	17.4414	−1.1912	0.03047
H C=C=C<H	−13.0833	20.8878	−1.8018	0.05447
Aromatic hydrocarbon groups				
HC	−6.1010	8.0165	−0.5162	0.01250
—C	−5.8125	6.3468	−0.4476	0.01113
↔C↔	0.5104	5.0953	−0.3580	0.00888
Contributions due to ring formation				
Three-membered ring	−14.7878	−0.1256	0.3129	−0.02309
Four-membered ring	−36.2368	4.5134	0.1779	−0.00105
Five-membered ring:				
Pentane	−51.4348	7.7913	−0.4342	0.00898
Pentene	−28.8106	3.2732	−0.1445	0.00247
Six-membered ring:				
Hexane	−56.0709	8.9564	−0.1796	−0.00781
Hexene	−33.5941	9.3110	−0.80118	0.02291

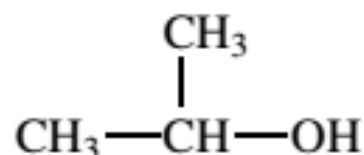
Table 8.4. (continued)

Group	a	$b \times 10^2$	$c \times 10^4$	$d \times 10^6$
Oxygen-containing groups				
—OH	27.2691	−0.5640	0.1733	−0.00680
—O—	11.9161	−0.04187	0.1901	−0.01142
$\begin{array}{c} \text{H} \\ \\ \text{—C=O} \end{array}$	14.7308	3.9511	0.2571	−0.02922
$\begin{array}{c} \diagup \\ \text{C=O} \end{array}$	4.1935	8.6931	−0.6850	0.01882
$\begin{array}{c} \text{O} \\ \\ \text{—C—O—H} \end{array}$	5.8846	14.4997	−1.0706	0.02883
$\begin{array}{c} \text{O} \\ // \\ \text{—C—O—} \end{array}$	11.4509	4.5012	0.2793	−0.03864
$\begin{array}{c} \swarrow \\ \text{O} \\ \searrow \end{array}$	−15.6352	5.7472	−0.5296	0.01586
Nitrogen-containing groups				
—C≡N	18.8841	2.2864	0.1126	−0.01587
—N≡C	21.2941	1.4620	0.1084	−0.01020
—NH ₂	17.4937	3.0890	0.2843	−0.03061
$\begin{array}{c} \diagup \\ \text{NH—} \end{array}$	−5.2461	9.1825	−0.6716	0.01774
$\begin{array}{c} \diagup \\ \text{N—} \end{array}$	−14.5186	12.3230	−1.1191	0.03277
$\begin{array}{c} \swarrow \\ \text{N} \\ \searrow \end{array}$	10.2401	1.4386	0.07159	−0.01138
—NO ₂	4.5638	11.0536	−0.7834	0.01989
Sulphur-containing groups				
—SH	10.7170	5.5881	−0.4978	0.01599
—S—	17.6917	0.4719	−0.0109	−0.00030
$\begin{array}{c} \swarrow \\ \text{S} \\ \searrow \end{array}$	17.0922	−0.1260	0.3061	−0.02546
—SO ₃ H	28.9802	10.3561	0.7436	−0.09397
Halogen-containing groups				
—F	6.0215	1.4453	−0.0444	−0.00014
—Cl	12.8373	0.8885	−0.0536	0.00116
—Br	11.5577	1.9808	−0.1905	0.0060
—I	13.6703	2.0520	−0.2257	0.00746

Estimate the specific heat capacity of isopropyl alcohol at 500 K.

Solution

Structural formula



Group	No. of	a	$b \times 10^2$	$c \times 10^4$	$d \times 10^6$
—CH ₃	2	5.0970	17.9480	−0.7134	0.0095
— $\begin{array}{c} \\ \text{CH} \\ \end{array}$	1	−14.7516	14.3020	−1.1791	0.03356
—OH	1	27.2691	−0.5640	0.1733	−0.0068
Total		17.6145	31.6860	−1.7190	0.0363

$$C_p^\circ = 17.6145 + 31.6860 \times 10^{-2}T - 1.7192 \times 10^{-4}T^2 + 0.0363 \times 10^{-6}T^3.$$

At 500 K, substitution gives:

$$C_p = \underline{\underline{137.6 \text{ kJ/kmol}^\circ\text{C}}}$$

Experimental value, 31.78 cal/mol°C = 132.8 kJ/kmol°C, error 4 per cent.

Estimate the specific enthalpy of ethyl alcohol at 1 bar and 200°C, taking the datum temperature as 0°C.

$$C_p \text{ liquid } 0^\circ\text{C } 24.65 \text{ cal/mol}^\circ\text{C}$$

$$100^\circ\text{C } 37.96 \text{ cal/mol}^\circ\text{C}$$

$$C_p \text{ gas } (t^\circ\text{C}) 14.66 + 3.758 \times 10^{-2}t - 2.091 \times 10^{-5}t^2 + 4.740 \times 10^{-9}t^3 \text{ cal/mol}$$

Boiling point of ethyl alcohol at 1 bar = 78.4°C.

Latent heat of vaporisation = 9.22 kcal/mol.

Solution

Note: as the data taken from the literature are given in cal/mol the calculation is carried out in these units and the result converted to SI units.

As no data are given on the exact variation of the C_p of the liquid with temperature, use an equation of the form $C_p = a + bt$, calculating a and b from the data given; this will be accurate enough over the range of temperature needed.

$$a = \text{value of } C_p \text{ at } 0^\circ\text{C}, \quad b = \frac{37.96 - 24.65}{100} = 0.133$$

$$\begin{aligned}
H_{200^{\circ}\text{C}} &= \int_0^{78.4} (24.65 + 0.133t) dt + 9.22 \times 10^3 + \int_{78.4}^{200} (14.66 + 3.758 \times 10^{-2}t \\
&\quad - 2.091 \times 10^{-5}t^2 + 4.740 \times 10^{-9}t^3) dt \\
&= \int_0^{78.4} [24.65t + 0.133t^2/2] + 9.22 \times 10^3 + \int_{78.4}^{200} [14.66t + 3.758 \times 10^{-2}t^2/2 - 2.091 \\
&\quad \times 10^{-5}t^3/3 + 4.740 \times 10^{-9}t^4/4] \\
&= 13.95 \times 10^3 \text{ cal/mol} \\
&= 13.95 \times 10^3 \times 4.18 = \underline{\underline{58.31 \times 10^3 \text{ J/mol}}}
\end{aligned}$$

Specific enthalpy = 58.31 kJ/mol.

Molecular weight of ethyl alcohol, $\text{C}_2\text{H}_5\text{OH} = 46$

Specific enthalpy = $58.31 \times 10^3 / 46 = 1268 \text{ kJ/kg}$

Approximate values can be calculated for solids, and liquids, by using a modified form of Kopp's law, which is given by Werner (1941). The heat capacity of a compound is taken as the sum of the heat capacities of the individual elements of which it is composed. The values attributed to each element, for liquids and solids, at room temperature, are given in Table 8.2; the method illustrated in Example 8.6.

Table 8.2. Heat capacities of the elements, J/mol°C

Element	Solids	Liquids
C	7.5	11.7
H	9.6	18.0
B	11.3	19.7
Si	15.9	24.3
O	16.7	25.1
F	20.9	29.3
P and S	22.6	31.0
all others	26.0	33.5

For organic liquids, the group contribution method proposed by Chueh and Swanson (1973a,b) will give accurate predictions. The contributions to be assigned to each molecular group are given in Table 8.3 and the method illustrated in Examples 8.7 and 8.8.

Group		Value	Group	Value
	Alkane		$\begin{array}{c} \text{O} \\ \\ -\text{C}-\text{O}- \end{array}$	60.71
$-\text{CH}_3$		36.84	$-\text{CH}_2\text{OH}$	73.27
$-\text{CH}_2-$		30.40	$\begin{array}{c} \\ -\text{CHOH} \end{array}$	76.20
$\begin{array}{c} \\ -\text{CH}- \end{array}$		20.93	$\begin{array}{c} \\ -\text{COH} \\ \end{array}$	111.37
$\begin{array}{c} \\ -\text{C}- \\ \end{array}$		7.37	$-\text{OH}$	44.80
	Olefin		$-\text{ONO}_2$	119.32
$=\text{CH}_2$		21.77	Halogen	
$\begin{array}{c} \\ =\text{C}-\text{H} \end{array}$		21.35	$-\text{Cl}$ (first or second on a carbon)	36.01
$\begin{array}{c} \\ =\text{C}- \end{array}$		15.91	$-\text{Cl}$ (third or fourth on a carbon)	25.12
	Alkyne		$-\text{Br}$	37.68
$-\text{C}\equiv\text{H}$		24.70	$-\text{F}$	16.75
$-\text{C}\equiv$		24.70	$-\text{I}$	36.01
	In a ring		Nitrogen	
$\begin{array}{c} \\ -\text{CH}= \end{array}$		18.42	$\begin{array}{c} \text{H} \\ \\ \text{H}-\text{N}- \end{array}$	58.62
$\begin{array}{c} \\ -\text{C}= \end{array}$ or $\begin{array}{c} \\ -\text{C}- \\ \end{array}$		12.14	$\begin{array}{c} \text{H} \\ \\ -\text{N}- \end{array}$	43.96
$-\text{C}=$		22.19	$\begin{array}{c} \\ -\text{N}- \end{array}$	31.40
$-\text{CH}_2-$		25.96	$-\text{N}=\text{N}$ (in a ring)	18.84
	Oxygen		$-\text{C}\equiv\text{N}$	58.70
$-\text{O}-$		35.17	Sulphur	
$\begin{array}{c} \diagup \\ \text{C}=\text{O} \\ \diagdown \end{array}$		53.00	$-\text{SH}$	44.80
$\begin{array}{c} -\text{C}-\text{O} \\ \\ \text{H} \end{array}$		53.00	$-\text{S}-$	33.49
$\begin{array}{c} \text{O} \\ \\ -\text{C}-\text{OH} \end{array}$		79.97	Hydrogen	
			$\text{H}-$ (for formic acid, formates, hydrogen cyanide, etc.)	14.65

Exceptions to the above 18.84 rule:

1. No such extra 18.84 additions for $-\text{CH}_3$ groups.
2. For a $-\text{CH}_2-$ group fulfilling the 18.84 addition criterion add 10.47 instead of 18.84. However, when the $-\text{CH}_2-$ group fulfils the addition criterion in more ways than one, the addition should be 10.47 the first time and 18.84 for each subsequent addition.
3. No such extra addition for any carbon group in a ring.

Estimate the specific heat capacity of urea, $\text{CH}_4\text{N}_2\text{O}$.

Solution

Element	mol. mass	Heat capacity
C	12	$7.5 = 7.5$
H	4	$4 \times 9.6 = 38.4$
N	28	$2 \times 26.0 = 52.0$
O	16	$16.7 = 16.7$
	<hr/> 60	<hr/> <u>114.6</u> J/mol°C

$$\text{Specific heat capacity} = \frac{114.6}{60} = \underline{\underline{1.91 \text{ J/g}^\circ\text{C}}} \text{ (kJ/kg}^\circ\text{C)}$$

Experimental value 1.34 kJ/kg°C.

Kopp's rule does not take into account the arrangement of the atoms in the molecule, and, at best, gives only very approximate, "ball-park" values.

Estimate the specific heat capacity of chlorobutadiene at 20°C, using Chueh and Swanson's method.

Solution

Structural formula $\text{CH}_2=\underset{\substack{| \\ \text{Cl}}}{\text{C}}-\text{CH}=\text{CH}_2$, mol. wt. 88.5

Group	Contribution	No. of	Addition rule		Total
$=\text{CH}_2$	21.77	2	—	=	43.54
$=\text{C}-$ 	15.91	1	18.84	=	34.75
 $=\text{CH}$	21.35	1	18.84	=	40.19
$-\text{Cl}$	36.01	1	—	=	36.01
					<u>154.49</u> kJ/kmol°C

$$\text{Specific heat capacity} = \frac{154.49}{88.5} = \underline{\underline{1.75 \text{ kJ/kg}^\circ\text{C}}}$$

❖ Nhiệt phản ứng (Heats of reaction):

If a process involves chemical reaction, heat will normally have to be added or removed. The amount of heat given out in a chemical reaction depends on the conditions under which the reaction is carried out. The standard heat of reaction is the heat released when the reaction is carried out under standard conditions: pure components, pressure 1 atm (1.01325 bar), temperature usually, but not necessarily, 25°C.



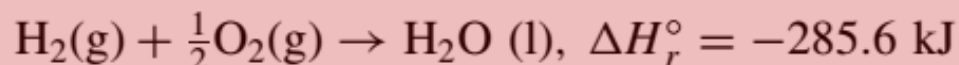
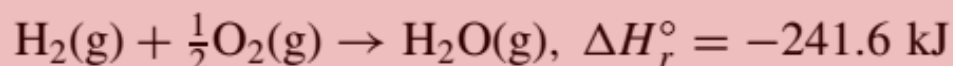
(The equation implies that the quantity of reactants and products are mols)

Or, by stating to which quantity the quoted value applies:

$$\Delta H_r^\circ = -56.68 \text{ kJ per mol NO}_2$$

The reaction is exothermic and the enthalpy change ΔH_r° is therefore *negative*. The heat of reaction $-\Delta H_r^\circ$ is *positive*. The superscript $^\circ$ denotes a value at *standard* conditions and the subscript *r* implies that a chemical reaction is involved.

The state of the reactants and products (gas, liquid or solid) should also be given, if the reaction conditions are such that they may exist in more than one state; for example:



The difference between the two heats of reaction is the latent heat of the water formed.

Standard heats of reaction can be converted to other reaction temperatures by making a heat balance over a hypothetical process, in which the reactants are brought to the standard temperature, the reaction carried out, and the products then brought to the required reaction temperature; as illustrated in Figure 3.4.

$$\Delta H_{r,t} = \Delta H_r^\circ + \Delta H_{\text{prod.}} - \Delta H_{\text{react.}} \quad (3.22)$$

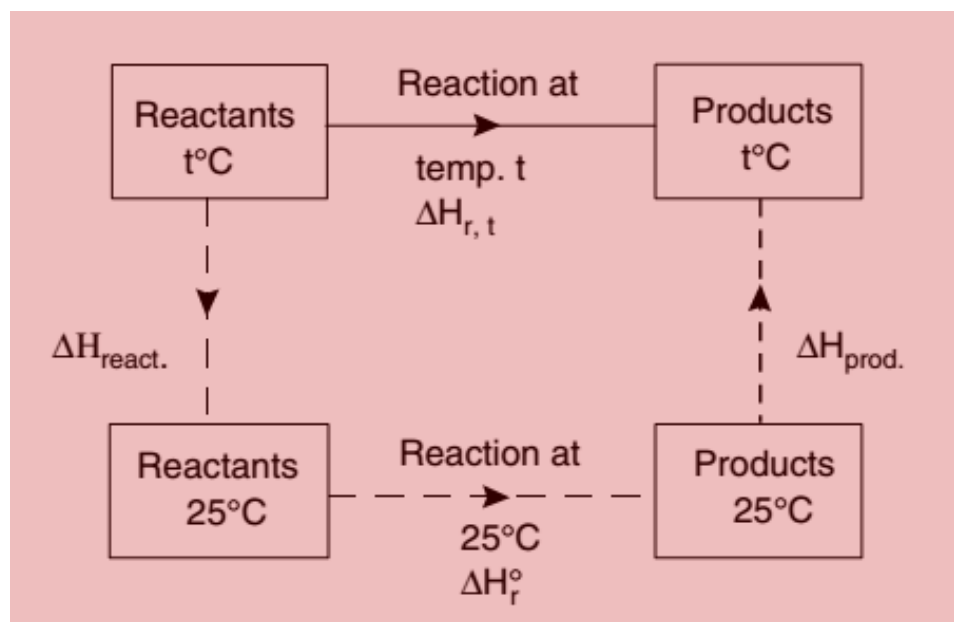


Figure 3.4. ΔH_r at temperature t

where $-\Delta H_{r,t}$ = heat of reaction at temperature t ,
 $\Delta H_{\text{react.}}$ = enthalpy change to bring reactants to standard temperature,
 $\Delta H_{\text{prod.}}$ = enthalpy change to bring products to reaction temperature, t .

For practical reactors, where the reactants and products may well be at temperatures different from the reaction temperature, it is best to carry out the heat balance over the actual reactor using the standard temperature (25°C) as the datum temperature; the standard heat of reaction can then be used without correction.

It must be emphasised that it is unnecessary to correct a heat of reaction to the reaction temperature for use in a reactor heat-balance calculation. To do so is to carry out two heat balances, whereas with a suitable choice of datum only one need be made. For a practical reactor, the heat added (or removed) Q_p to maintain the design reactor temperature will be given by (from equation 3.10):

$$Q_p = H_{\text{products}} - H_{\text{reactants}} - Q_r \quad (3.23)$$

where H_{products} is the *total* enthalpy of the product streams, including unreacted materials and by-products, evaluated from a datum temperature of 25°C;
 $H_{\text{reactants}}$ is the total enthalpy of the feed streams, including excess reagent and inerts, evaluated from a datum of 25°C;
 Q_r is the total heat generated by the reactions taking place, evaluated from the standard heats of reaction at 25°C (298 K).

$$Q_r = \sum -\Delta H_r^\circ \times (\text{mol of product formed}) \quad (3.24)$$

where $-\Delta H_r^\circ$ is the standard heat of reaction per mol of the particular product.

The standard enthalpy of formation ΔH_f° of a compound is defined as the enthalpy change when one mol of the compound is formed from its constituent elements in the standard state. The enthalpy of formation of the elements is taken as zero. The standard heat of any reaction can be calculated from the heats of formation $-\Delta H_f^\circ$ of the products and reactants; if these are available or can be estimated.

Conversely, the heats of formation of a compound can be calculated from the heats of reaction; for use in calculating the standard heat of reaction for other reactions.

The relationship between standard heats of reaction and formation is given by equation 3.26 and illustrated by Examples 3.8 and 3.9

$$\Delta H_r^\circ = \sum \Delta H_f^\circ, \text{ products} - \sum \Delta H_f^\circ, \text{ reactants} \quad (3.26)$$

A comprehensive list of enthalpies of formation is given in Appendix D.

As with heats of reaction, the state of the materials must be specified when quoting heats of formation.

Calculate the standard heat of the following reaction, given the enthalpies of formation:



Standard enthalpies of formation kJ/mol

$$\text{NH}_3(\text{g}) \quad -46.2$$

$$\text{NO}(\text{g}) \quad +90.3$$

$$\text{H}_2\text{O}(\text{g}) \quad -241.6$$

Solution

Note: the enthalpy of formation of O_2 is zero.

$$\begin{aligned}\Delta H_r^\circ &= \sum \Delta H_f^\circ, \text{ products} - \sum \Delta H_f^\circ, \text{ reactants} \\ &= (4 \times 90.3 + 6 \times (-241.6)) - (4 \times (-46.2)) \\ &= \underline{\underline{-903.6 \text{ kJ/mol}}}\end{aligned}$$

$$\text{Heat of reaction } -\Delta H_r^\circ = \underline{\underline{904 \text{ kJ/mol}}}$$

❖ Chuyển đổi và năng suất (Conversion and Yield):

Conversion is to do with reactants (reagents); yield with products.

Conversion is a measure of the fraction of the reagent that reacts.

To optimise reactor design and to minimise by-product formation, the conversion of a particular reagent is often less than 100 per cent. If more than one reactant is used, the reagent on which the conversion is based must be specified.

Conversion is defined by the following expression:

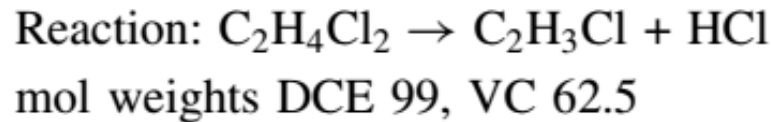
$$\begin{aligned}\text{Conversion} &= \frac{\text{amount of reagent consumed}}{\text{amount supplied}} \\ &= \frac{(\text{amount in feed stream}) - (\text{amount in product stream})}{(\text{amount in feed stream})}\end{aligned}\quad (2.8)$$

This definition gives the total conversion of the particular reagent to all products. Sometimes figures given for conversion refer to one specific product, usually the desired product. In this instance the product must be specified as well as the reagent. This is really a way of expressing yield.

In the manufacture of vinyl chloride (VC) by the pyrolysis of dichloroethane (DCE), the reactor conversion is limited to 55 per cent to reduce carbon formation, which fouls the reactor tubes. Calculate the quantity of DCE needed to produce 5000 kg/h VC.

Solution

Basis: 5000 kg/h VC (the required quantity).



$$\text{kmol/h VC produced} = \frac{5000}{62.5} = \underline{\underline{80}}$$

From the stoichiometric equation, 1 kmol DCE produces 1 kmol VC. Let X be DCE feed kmol/h:

$$\text{Per cent conversion} = 55 = \frac{80}{X} \times 100$$

$$X = \frac{80}{0.55} = \underline{\underline{145.5 \text{ kmol/h}}}$$

In this example the small loss of DCE to carbon and other products has been neglected. All the DCE reacted has been assumed to be converted to VC.

Yield is a measure of the performance of a reactor or plant.

$$\text{Yield} = \frac{\text{mols of product produced} \times \text{stoichiometric factor}}{\text{mols of reagent converted}} \quad (2.9)$$

Stoichiometric factor = Stoichiometric mols of reagent required per mol of product produced

Plant yield (applied to the complete plant or any stage)

$$= \frac{\text{mols product produced} \times \text{stoichiometric factor}}{\text{mols reagent fed to the process}} \quad (2.10)$$

Where more than one reagent is used, or product produced, it is essential that product and reagent to which the yield figure refers is clearly stated.

With industrial reactors it is necessary to distinguish between “Reaction yield” (chemical yield), which includes only chemical losses to side products; and the overall “Reactor yield” which will include physical losses.

If the conversion is near 100 per cent it may not be worth separating and recycling the unreacted material; the overall reactor yield would then include the loss of unreacted material. If the unreacted material is separated and recycled, the overall yield *taken over the reactor and separation step* would include any physical losses from the separation step.

In the chlorination of ethylene to produce dichloroethane (DCE), the conversion of ethylene is reported as 99.0 per cent. If 94 mol of DCE are produced per 100 mol of ethylene fed, calculate the overall yield and the reactor (reaction) yield based on ethylene. The unreacted ethylene is not recovered.

Solution



Stoichiometric factor 1.

$$\begin{aligned}\text{Overall yield (including physical losses)} &= \frac{\text{mols DCE produced} \times 1}{\text{mols ethylene fed}} \times 100 \\ &= \frac{94}{100} \times 100 = \underline{\underline{94 \text{ per cent}}}\end{aligned}$$

$$\begin{aligned}\text{Chemical yield (reaction yield)} &= \frac{\text{mols DCE produced}}{\text{mols ethylene converted}} \times 100 \\ &= \frac{94}{99} \times 100 = \underline{\underline{94.5 \text{ per cent}}}\end{aligned}$$

The principal by-product of this process is trichloroethane.

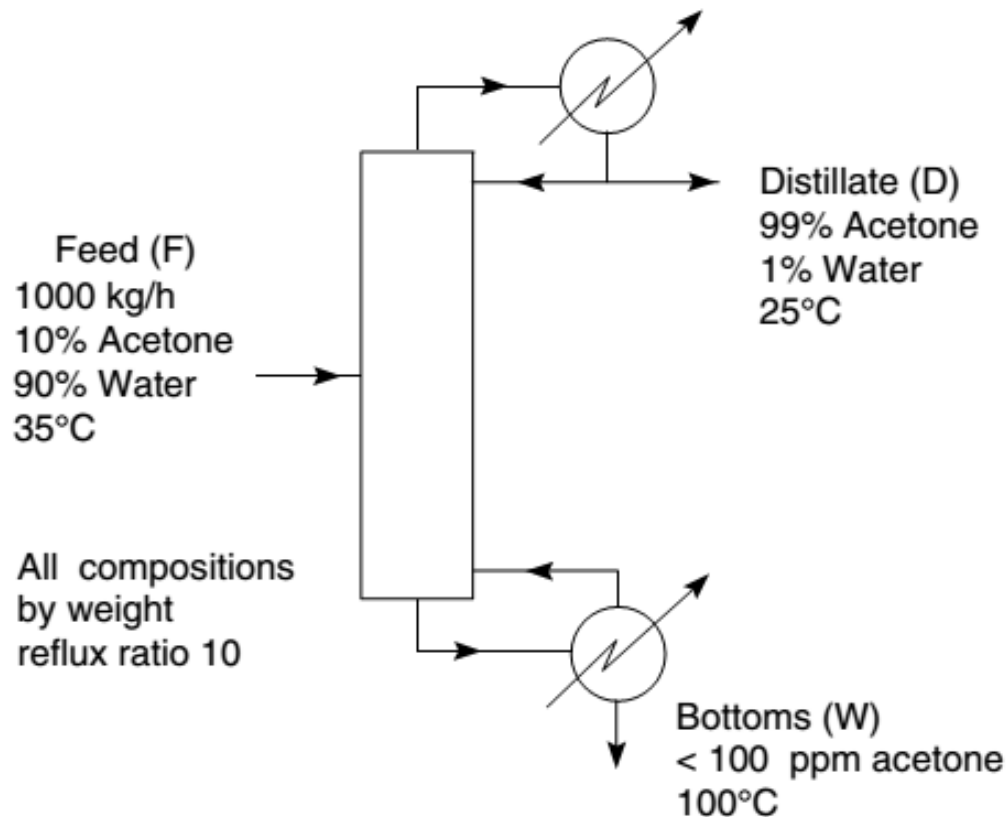
Ứng dụng các định luật bảo toàn

Balance with no chemical reaction. Estimate the steam and the cooling water required for the distillation column shown in the figure.

Steam is available at 25 psig (274 kN/m^2 abs), dry saturated.

The rise in cooling water temperature is limited to 30°C .

Column operates at 1 bar.



Material balance

It is necessary to make a material balance to determine the top and bottoms product flow rates.

Balance on acetone, acetone loss in bottoms neglected.

$$1000 \times 0.1 = D \times 0.99$$

Distillate, $D = 101 \text{ kg/h}$

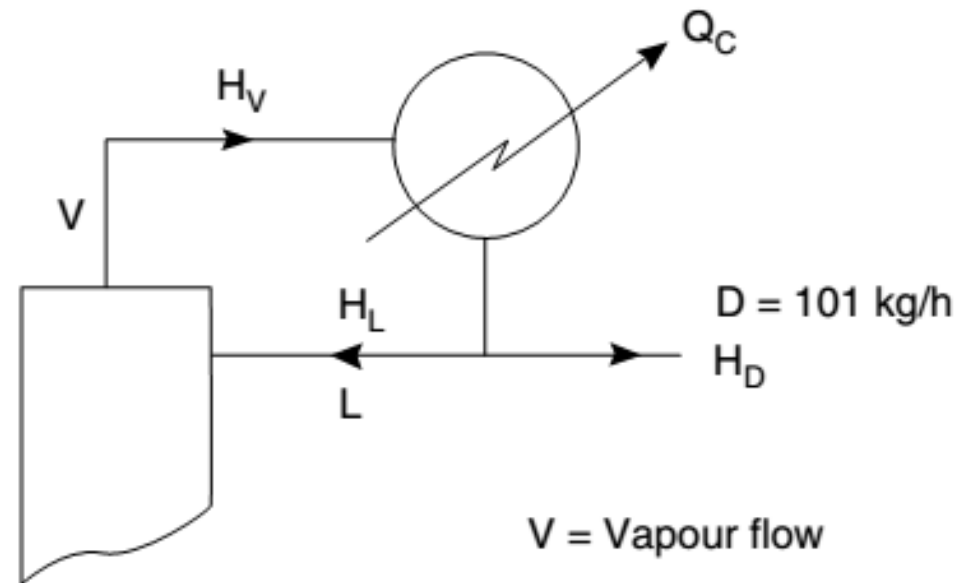
Bottoms, $W = 1000 - 101 = 899 \text{ kg/h}$

Reflux ratio

$$R = \frac{L}{D} = 10$$

$$L = 10 \times 101 = 1010 \text{ kg/h}$$

$$V = L + D = 1111 \text{ kg/h}$$



V = Vapour flow

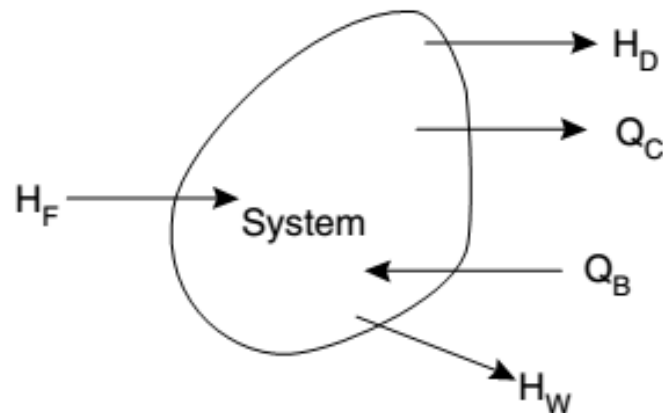
L = Reflux flow

H = Enthalpy

Energy balance

The kinetic and potential energy of the process streams will be small and can be neglected.

Take the first system boundary to include the reboiler and condenser.



Inputs: reboiler heat input Q_B + feed sensible heat H_F .

Outputs: condenser cooling Q_C + top and bottom product sensible heats $H_D + H_W$.

Q_C must be determined by taking a balance round the condenser.

At steady state: input = output

$$H_V = H_D + H_L + Q_C,$$

$$Q_C = H_V - H_D - H_L$$

Basis 25°C, 1h.

Heat capacity data, from Volume 1, average values.

Acetone: 25°C to 35°C 2.2 kJ/kg K

Water: 25°C to 100°C 4.2 kJ/kg K

Heat capacities can be taken as additive.

Feed, 10 per cent acetone = $0.1 \times 2.2 + 0.9 \times 4.2 = 4.00$ kJ/kg K

Tops, 99 per cent acetone, taken as acetone, 2.2 kJ/kg K

Bottoms, as water, 4.2 kJ/kg K.

From vapour–liquid equilibrium data:

boiling point of 99 per cent acetone/water = 56.5°C

Latent heat acetone at 56.5°C (330 K) = 620 kJ/kg

Water at 56.5°C (330 K) = 2500 kJ/kg

Enthalpy of vapour $H_V = \text{latent} + \text{sensible heat}$

$$H_V = 1111[(0.01 \times 2500 + 0.99 \times 620) + (56.5 - 25)2.2] = 786,699 \text{ kJ/h}$$

The enthalpy of the top product and reflux are zero, as they are both at the base temperature. Both are liquid, and the reflux will be at the same temperature as the product.

Hence $Q_C = H_V = \underline{\underline{786,699 \text{ kJ/h}}} \quad (218.5 \text{ kW})$

Q_B is determined from a balance over complete system

Input Output

$$Q_B + H_F = Q_C + H_D + H_W$$

$$H_F = 1000 \times 4.00(35 - 25) = 40,000 \text{ kJ/h}$$

$$H_W = 899 \times 4.2(100 - 25) = 283,185 \text{ kJ/h}$$

(boiling point of bottom product taken as 100°C).

hence
$$\begin{aligned} Q_B &= Q_C + H_W + H_D - H_F \\ &= 786,699 + 283,185 + 0 - 40,000 \\ &= \underline{\underline{1,029,884 \text{ kJ/h}}} \quad (286.1 \text{ kW}) \end{aligned}$$

Q_B is supplied by condensing steam.

Latent heat of steam (Volume 1) = 2174 kJ/kg at 274 kN/m²

$$\text{Steam required} = \frac{1,029,884}{2174} = \underline{\underline{473.7 \text{ kg/h}}}$$

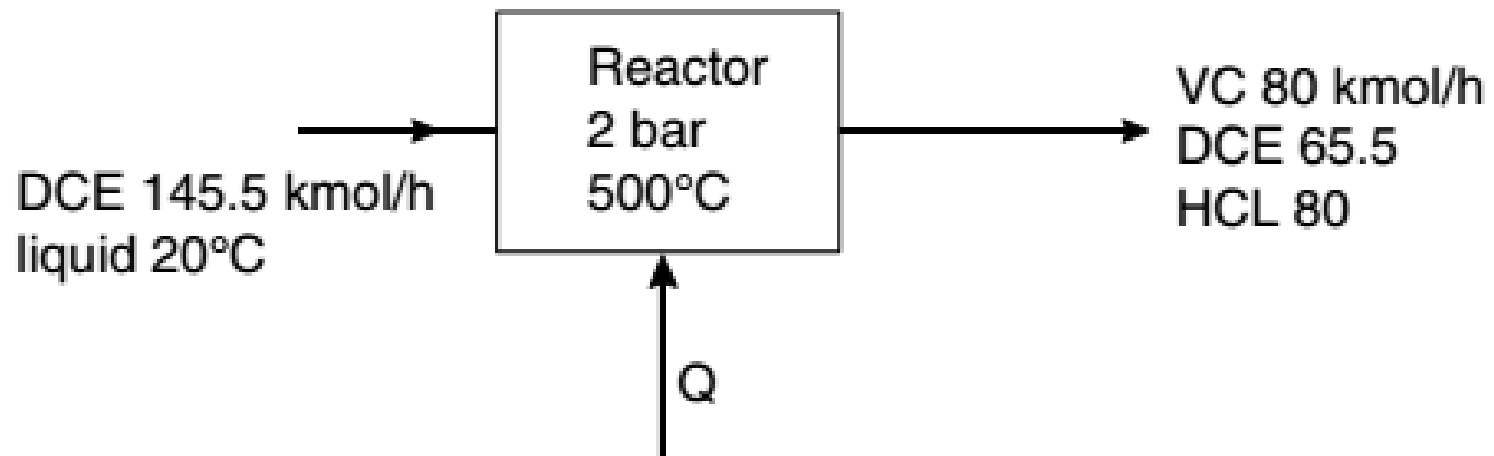
Q_C is removed by cooling water with a temperature rise of 30°C

$$Q_C = \text{water flow} \times 30 \times 4.2$$

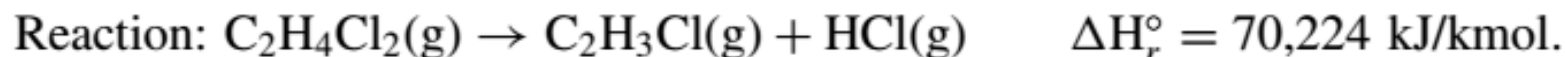
$$\text{Water flow} = \frac{786,699}{4.2 \times 30} = \underline{\underline{6244 \text{ kg/h}}}$$

Vinyl chloride (VC) is manufactured by the pyrolysis of 1,2-dichloroethane (DCE). The reaction is endothermic. The flow-rates to produce 5000 kg/h at 55 per cent conversion are shown in the diagram (see Example 2.13).

The reactor is a pipe reactor heated with fuel gas, gross calorific value 33.5 MJ/m³. Estimate the quantity of fuel gas required.



Solution



The small quantity of impurities, less than 1 per cent, that would be present in the feed have been neglected for the purposes of this example. Also, the yield of VC has been taken as 100 per cent. It would be in the region of 99 per cent at 55 per cent conversion.

Heat capacity data, for vapour phase

	$C_p^\circ = a + bT + cT^2 + dT^3 \quad \text{kJ/kmolK}$			
	a	$b \times 10^2$	$c \times 10^5$	$d \times 10^9$
VC	5.94	20.16	-15.34	47.65
HCl	30.28	-0.761	1.325	-4.305
DCE	20.45	23.07	-14.36	33.83

for liquid phase: DCE at 20°C, $C_p = 116 \text{ kJ/kmol K}$,

taken as constant over temperature rise from 20 to 25°C.

Latent heat of vaporisation of DCE at 25°C = 34.3 MJ/kmol.

At 2 bar pressure the change in C_p with pressure will be small and will be neglected. Take base temperature as 25°C (298 K), the standard state for ΔH_r° .

$$\text{Enthalpy of feed} = 145.5 \times 116(293 - 298) = -84,390 \text{ kJ/h} = \underline{\underline{-84.4 \text{ MJ/h}}}$$

$$\text{Enthalpy of product stream} = \int_{298}^{773} \sum (n_i C_p) dT$$

Component	n_i (mol/h)	$n_i a$	$n_i b \times 10^2$	$n_i c \times 10^5$	$n_i d \times 10^9$
VC	80	475.2	1612.8	-1227.2	3812.0
HCl	80	2422.4	-60.88	106.0	-344.4
DCE	65.5	1339.5	1511.0	-940.6	2215.9
$\sum n_i C_p$		4237.1	3063.0	-2061.8	5683.5

$$\begin{aligned}
 & \int_{298}^{773} \sum n_i C_p dT \\
 &= \int_{298}^{773} (4237.1 + 3063.0 \times 10^{-2} T - 2061.8 \times 10^{-5} T^2 + 5683.5 \times 10^{-9} T^3) dT \\
 &= \underline{\underline{7307.3 \text{ MJ/h}}}
 \end{aligned}$$

$$\begin{aligned}\text{Heat consumed in system by the endothermic reaction} &= \Delta H_r^\circ \times \text{mols produced} \\ &= 70,224 \times 80 = 5,617,920 \text{ kJ/h} = \underline{\underline{5617.9 \text{ MJ/h}}}\end{aligned}$$

$$\begin{aligned}\text{Heat to vaporise feed (gas phase reaction)} \\ &= 34.3 \times 145.5 = \underline{\underline{4990.7 \text{ MJ/h}}}\end{aligned}$$

Heat balance:

$$\text{Output} = \text{Input} + \text{consumed} + Q$$

$$\begin{aligned}Q &= H_{\text{product}} - H_{\text{feed}} + \text{consumed} \\ &= 7307.3 - (-84.4) + (5617.9 + 4990.7) = \underline{\underline{18,002.3 \text{ MJ/h}}}\end{aligned}$$

Taking the overall efficiency of the furnace as 70% the gas rate required

$$\begin{aligned}&= \frac{\text{Heat input}}{(\text{calorific value} \times \text{efficiency})} \\ &= \frac{18,002.3}{33.5 \times 0.7} = \underline{\underline{768 \text{ m}^3/\text{h}}}\end{aligned}$$

Vấn đề tối ưu hóa trong CNHH

Xét một bình chứa (**vessel**) có một nguồn gia nhiệt tốc độ Q (W/m^3) để làm ấm nước với một cuộn dây đốt bằng điện (**electrical heating coil**). Bình chứa hoạt động ở chế độ ổn định, xác định điều kiện để nhiệt độ ở bên trong bình chứa là cao nhất.

Giải pháp (Solution)

Cho một thể tích xác định của khối điều khiển của bình chứa là V , tốc độ gia nhiệt cố định Q , diện tích bề mặt gia nhiệt (surface area) là A , hệ số truyền nhiệt (heat transfer coefficient) là h , nhiệt độ trong bình chứa là T và nhiệt độ bên ngoài là T_a .

$$Q \cdot V = h \cdot A \cdot \Delta T = h \cdot A \cdot (T - T_a)$$

Ở chế độ hoạt động ổn định với một thể tích xác định, nhiệt độ trong bình chứa cao nhất khi diện tích bề mặt truyền nhiệt A là nhỏ nhất.

Hình cầu (sphere) có diện tích bề mặt nhỏ nhất đối với một thể tích. Tuy nhiên, bình chứa hình cầu thì không có trong thực tế (vì nó có thể lăn) nên có thể chọn bình chứa hình trụ (cylindrical vessel) (bán kính r , chiều cao h) cùng thể tích với thể tích hình cầu bán kính R .

$$\pi r^2 h = \frac{4}{3} \pi R^3 \Rightarrow h = \frac{4}{3} \frac{R^3}{r^2} \quad (1)$$

Tổng diện tích bề mặt (DTBM) hình trụ: $A = (2\pi r) h + 2(\pi r^2)$

$$\text{Thay } h \text{ vào } A = f(r) = 2\pi \frac{4}{3} \frac{R^3}{r} + 2\pi r^2 \quad (2)$$

DTBM nhỏ nhất \Rightarrow Vi phân bậc 1 (first derivative) bằng 0

$$\text{Lưu ý: } f(x) = x^n \Rightarrow f'(x) = n \cdot x^{n-1}$$

$$f(r) = 2\pi \frac{4}{3} \frac{R^3}{r} + 2\pi r^2$$

$$f'(r) = 2\pi \frac{4R^3}{3}(-1)(r^{-1-1}) + 2\pi 2r^{2-1} = 2\pi \left[-\frac{4R^3}{3r^2} + 2r \right] = 0 \quad (3)$$

$$\Rightarrow -\frac{4R^3}{3r^2} + 2r = 0 \quad \Rightarrow \frac{4R^3}{3r^2} = 2r \quad \Rightarrow 4R^3 = 6r^3$$

$$\Rightarrow r = \left(\frac{2}{3}\right)^{1/3} R$$

$$(3) \Rightarrow f''(r) = \frac{8R^3}{3r^3} + 2 > 0$$

\Rightarrow Vì phân bậc 2 (second derivative) dương, điểm tối ưu là cực tiểu

$$(1) \Rightarrow h = 2 \left(\frac{2}{3}\right)^{1/3} R$$

$$(2) \Rightarrow A = 2\pi \left(2 \left(\frac{2}{3}\right)^{2/3} R^2 + \left(\frac{2}{3}\right)^{2/3} R^2 \right) = 6\pi \left(\frac{2}{3}\right)^{2/3} R^2$$

❖ BÀI TẬP CHƯƠNG 4 (EXERCISES)

Exercise 1: How much dry sugar must be added in 100 kg of aqueous sugar solution in order to increase its concentration from 20% to 50%?

Exercise 2: Carbon dioxide is added at a rate of 10 kg/h to an air stream contained 0.03 percent v/v CO_2 and the air is sampled at a sufficient distance downstream to ensure complete mixing. If the analysis shows 0.45 percent v/v CO_2 , calculate the air-flow rate.

Exercise 3: A mixture of calcium sulfate, potassium sulfide and potassium oxide is given to you. You are asked to find out the amount of each of the compounds present in the mixture. The mixture is analyzed quantitatively for the amount of each elements. The amount of calcium is found to be 20%, potassium is 30%, oxygen is 10% and the remaining is sulfur. Find the mass of each compound present in the mixture.

Exercise 4: The composition of a gas derived by the gasification of coal is, volume percentage: carbon dioxide 4, carbon monoxide 16, hydrogen 50, methane 15, ethane 3, benzene 2, balance nitrogen. If the gas is burnt in a furnace with 20 per cent excess air, calculate:

- (a) the amount of air required per 100 kmol of gas,
- (b) The amount of flue gas produced per 100 kmol of gas,
- (c) The composition of the flue gases, on a dry basis.

Assume complete combustion.

Exercise 5: Ammonia is removed from a stream of air by absorption in water in a packed column. The air entering the column is at 760 mmHg pressure and 20°C. The air contains 5.0 per cent v/v ammonia. Only ammonia is absorbed in the column. If the flow rate of the ammonia air mixture to the column is 200 m³/s and the stream leaving the column contains 0.05 per cent v/v ammonia, calculate:

- (a) The flow-rate of gas leaving the column.
- (b) The mass of ammonia absorbed.
- (c) The flow-rate of water to the column, if the exit water contains 1% w/w ammonia.

Exercise 6: 1000 kg/h of milk is heated in a heat exchanger from 45°C to 72°C. Water is used as the heating medium. It enters the heat exchanger at 90°C and leaves at 75°C. Calculate the mass flow rate of the heating medium, if the heat losses to the environment are equal to 1 kW. The heat capacity of water is given equal to 4.2 kJ/kg °C and that of milk 3.9 kJ/kg °C.

Exercise 7: In the manufacture of aniline, liquid nitrobenzene at 20°C is fed to a vaporizer where it is vaporized in a stream of hydrogen. The hydrogen stream is at 30°C, and the vaporizer operates at 20 bar. For feed-rates of 2500 kg/h nitrobenzene and 366 kg/h hydrogen, estimate the heat input required. The nitrobenzene vapor is not superheated.