2-1

The vapor pressure of mercury is obtained from Perry's Chemical Engineers' Handbook, 6th ed., p. 3-201 as

T, °C	Vapor press, bar
10	7.101×10^{-7}
20	1.729×10^{-6}
30	3.968×10^{-6}

By interpolation, the vapor pressure of mercury at 23°C is 2.2×10^{-6} bar. For low pressures, at equilibrium, the vapor phase mol fraction of mercury can be obtained with the use of Dalton's law, or

$y = p_v^{\circ}/p$ where p = system pressure of 1.013 bar

$y = 2.2 \times 10^{-6}/1.013 = 2.17 \times 10^{-6}$ kg mols Hg/kg mols air

but y = mols Hg/(mols air + mols Hg) $\cong$ mols Hg/mols air

The specific volume of air is obtained from the ideal gas relation $v = RT/p = (8314)(296.1)/101{,}300 = 24.305\ \text{m}^3/\text{kg mol}$

The concentration of mercury in air at equilibrium is then

$$c = (2.17 \times 10^{-6}/24.305)(200.6) = 17.9 \times 10^{-6}\ \text{kg Hg/m}^3$$
$$= 17.9\ \text{mg Hg/m}^3$$

Since the PEL (permissible exposure limit is 0.1 mg Hg/m³, the concentration of mercury in the air greatly exceeds this limit and therefore is not acceptable.

Answer

2-2

This problem has been simplified considerably with a number of assumptions. Actually, the corrosion rate for the iron (carbon steel) over a year is not in a fixed oxygen level atmosphere. It is most likely that the corrosion rate of iron is limited by the diffusion rate of oxygen to the tank surface. Under the circumstances, the analysis would require a corrosion model, information on the initial rate before corrosion product buildup, and need some indication of the diffusivity of the oxygen in the corrosion layer. As indicated in the problem, the reaction rate is a function of the surface are inside the tank. For a 7.6-m (inside) diameter spherical container, the inside area is given by

$$A = 4\pi r_i^2 = \pi D_i^2 = \pi (7.6)^2 = 181.5 \text{ m}^2$$

Iron corrosion = $(181.5)(0.127 \times 10^{-3})(7850)$ $\qquad \rho_{Fe} = 7850$ kg/m^3

= 180.9 kg/y

= $(180.9)/(365)(24) = 0.02065$ kg/h

= $0.02065/55 = 3.7545 \times 10^{-4}$ kg mol/h

Oxygen rate = $(3.7545 \times 10^{-4})(1.5$ kg mol O_2 / 2.0 kg mol Fe)

= 2.816×10^{-4} kg mol/h

Volume of sphere = $(4/3)\pi r_i^3 = \pi D_i^3/6 = \pi (7.6)^3/6 = 229.8$ m^3

At room temperature (21.1°C) and 1 atm, the specific volume inside the tank, assuming an ideal gas, is

$$v = (22.4)(294.2/273.1) = 24.147 \text{ m}^3/\text{kg mol air}$$

The oxygen concentration under these conditions is $(0.21)(24.147) = 8.696$ kg mol O_2/m^3

For a first order reaction,

$$\frac{dc}{d\theta} = -kc$$ where k = reaction rate constant, θ = time, and c = concentration

2-2 (continued)

When $c = 8.696 \times 10^{-4}$ kg mol/m^3, the O_2 rate is 2.816×10^{-4} kgmol/h, and the tank volume is 229.8 m^3. At this condition

$$\frac{dc}{d\theta} = \frac{-2.816 \times 10^{-4}}{229.8} = -1.225 \times 10^{-6} \text{ kgmol/m}^3\cdot\text{h}$$

Solving for the reaction rate constant gives

$$k = -\left(\frac{dc}{d\theta}\right)/c = (1.225 \times 10^{-6})/8.696 \times 10^{-3} = 1.408 \times 10^{-4} \text{ h}$$

Now solve for the time when O_2 concentration is reduced to 19.5 mol percent. Integrating the original rate equation results in

$$\ln(c_1/c_2) = k(\theta_2 - \theta_1) \qquad \text{where } \theta_1 = 0$$

$$\theta_2 = \ln(c_1/c_2)/k$$

$$= \ln(0.21/0.195)/1.408 \times 10^{-4}$$

$$= \underline{\underline{526 \text{ h or approx. } 22 \text{ days}}}$$

Answer

2-3

Assume that the dilution air is available at a temperature of 20°C and a pressure of 1 atm. The evaporation rate is 7.5 g/min or 0.0075 kg/min; Thus,

$\dot{n}_{vc} = 0.0075/78 = 9.62\times10^{-5}$ kg mol vinyl chloride/min

At 1 atm use the ideal gas to obtain the volumetric flow rate

$\dot{m}_{v,vc}\ n_{cv}RT/p = (9.62\times10^{-5})(8314)(293/1.013\times10^{5}$

$= 2.31\times10^{-3}\ m^3/min$

Since the PEL for vinyl chloride is 1ppm,

$\dot{m}_{v,air} = (\dot{m}_{v,vc})(10^6) = (2.31\times10^{-3})(10^6)$

$= 2.31\times10^{3}\ m^3/min$

If a safety factor of 5 is required,

$\dot{m}_{v,air} = (5)(2.31\times10^{3})/60 = \underline{\underline{192.5\ m^3/s}}$

Answer

This is a fairly high flow rate and would need one or two large blowers.

2-4

The density of benzene at 22°C is 879 kg/m³. The molecular weight is 78.1 kg/kg mol.

Since the pressure is low, assume the ideal gas law is applicable to the air stream that is used for ventilation.

$$\dot{n}_{Bz} = \left(2.0\times10^{-6}\,\frac{m^3}{min}\right)\left(879\,\frac{kg}{m^3}\right)\Big/78.1\,\frac{kg}{kg\,mol}$$

$$= 2.2506\times10^{-5}\ kg\ mol/min$$

$$\dot{m}_{v,Bz}\ nRT/p = \left(2.2506\times10^{-5}\,\frac{kg\ mol}{min}\right)\left(8314\,\frac{J}{kg\,mol\cdot K}\right)(295\ K)$$

$$6.27\times10^{-4}\ m^3/min$$

Assume complete mixing of the benzene with the dilution air

$$\dot{m}_{v,air} = \left(6.27\times10^{-4}\,\frac{m^3\,Bz}{min}\right)\left(10^6\,\frac{m^3\,air/min}{m^3\,Bz/min}\right)$$

$$= \underline{\underline{627\ m^3\ air/min}}$$

Answer

2-5

To determine the length of time the cannister will be usable, we will need to find a relationship between the amount adsorbed and $(T/V)\log(f_s/f)$. Let $x = (T/V)\log(f_s/f)$ and y the amount adsorbed in $cm^3(liq)/100\ g$ charcoal. From the data given,

when $y = 1 \quad x = 21$

$y = 10 \quad x = 11$

assuming a linear relation of $\log y = ax + b$

$\log 1 = 21a + b$

$\log 10 = 11a + b$

or $\log(1/10) = 10a \quad a = -0.1$

$b = \log 10 - 11(-0.1) \quad b = 2.1$

The molecular weight of dichloropropane (DCP) is 113, density is 1160 kg/m^3, and molar volume = 0.1 m^3/kg mol. The vapor pressure from <u>Perry's Chemical Engineers' Handbook</u>, 6ed., p.354,

Temp., °C	Vapor press., mm Hg
19.4	40
28	60

Assuming the Antoine equation can be used to represent the vapor pressure of DCP

$\log p = A + B/T$

$\log 40 = A + B/292.55$

$\log 60 = A + B/301.15$

Solving the latter two equations simutaneously results in

$B = -1802 \quad A = 7.76$

At 26.9°C or 300.05 K

$\log p = 7.76 + (-1902/300.05) = 1.755$

$p = 56.9$ mm Hg

Determine the fugacity of DCP by assuming that it is essentially equal to the partial pressure. Thus,

2-5 (continued)

$f \simeq p$

$p = y\,p_T$ where p_T = total pressure and $y = 750/10^6$

$p = (750/10^6)(760) = 0.57\ \text{mm Hg}$

therefore, $f_s/f = 56.9/0.57 = 99.82$

$x = (T/V)\log(f_s/f) = (300/100)\log(99.82) = 5.99$

Now determine how much gas has been adsorbed

$\log y = -0.1x + 2.1 = (-0.1)(5.99) + 2.1 = 1.503$

$y = 31.84\ \text{cm}^3/100\ \text{g charcoal}$

For 100% saturation, amount adsorbed per 100g charcoal is

$m = (31.84\ \text{cm}^3/100\text{g C})(1.16\ \text{g/cm}^3) = 36.93\text{g}$

At 82% saturation, amount adsorbed before breakthrough is

$m_{82\%} = (36.93)(0.82) = 30.3\ \text{g}$

Now determine volume of air associated with 30.3 g DCP

$$n_{air} = \left(\frac{30.3\ \text{g DCP}}{113\ \frac{\text{g DCP}}{\text{g mol DCP}}}\right)\left(\frac{10^6\ \text{g mol air}}{750\ \text{g mol DCP}}\right) = 357.5\ \text{g mol air}$$

$$\text{Vol of air} = nRT/p = \frac{(357.5\ \text{g mol})}{1\ \text{atm}}\left(82.06\ \frac{\text{atm}\cdot\text{cm}^3}{\text{g mol}\cdot\text{K}}\right)(300\ \text{K})$$

$$= 8.8 \times 10^6\ \text{cm}^3 = 8{,}800\ \ell = 8.8\ \text{m}^3$$

At 45 ℓ/min

$$\theta = (8{,}800\ \ell)/(45\ \ell/\text{min}) = \underline{\underline{195\ \text{min} = 3.25\text{h}}}$$

Answer

Cannister should last 3.25h before break-through occurs.

2-6

If the mixture is at the flash point

$$\sum \frac{y_i}{LFL_i} = 1.0$$

Assuming Raoult's law applies

$$y_i = p_{v,i} \, x_i / p$$

where $p_{v,i}$ is the vapor pressure of component i, p the pressure, and x_i and y_i the mol fraction of component in the liquid and vapor, respectively. Vapor pressure of C_8 and C_9 are available from <u>Perry's Chemical Engineers' Handbook</u>, 6th ed., p. 3-58

Assume flash temperature of 18°C

Comp	x_i	$p_{v,i}$, atm	y_i	LFL_i
C_8	0.5	0.0123	0.00615	0.01
C_9	0.5	0.00365	0.00183	0.008

$$\sum \frac{y_i}{LFL_i} = \frac{0.00615}{0.01} + \frac{0.00183}{0.008} = 0.844 \quad \text{temp. too low}$$

Assume flash temperature of 21.1°C

Comp	x_i	$p_{v,i}$, atm	y_i	LFL_i
C_8	0.5	0.0145	0.00725	0.01
C_9	0.5	0.0044	0.0022	0.008

$$\sum \frac{y_i}{LFL_i} = \frac{0.00725}{0.01} + \frac{0.0022}{0.008} \cong 1.0$$

The flash point for this mixture is $\underline{\underline{21.1°C}}$
Answer

2-7

At equilibrium, $f_{i,L} = f_{i,v}$

Since

$$f_{i,L} = \gamma_i f_{0,L} x_i$$
$$f_{i,v} = \varphi_i f_{0,v} y_i$$
$$\gamma_i f_{0,L} x_i = \varphi_i f_{0,v} y_i$$

At low pressures

$$f_{0,v} = p$$
$$f_{0,L} = p_v^\circ$$
$$\varphi_i = 1.0$$

Therefore $\gamma_i p_v^\circ x_i = p y_i$

For an ideal solution, $\gamma_i = 1$

and $$x_i p_v^\circ = p y_i$$

Definitions

$f_{i,L}$ = fugacity of liquid
$f_{i,v}$ = fugacity of vapor
γ_i = liquid phase activity coeff,
φ_i = vapor phase activity coeff.
$f_{0,L}$ = pure comp. liq. fugacity
$f_{0,v}$ = pure comp. vapor fugacity
p = total pressure
p_v° = vapor pressure

If the acetone has no air dissolved in it, $x_i = 1.0$ and y_i is the LFL or $y_i = 0.0255$.

At a total pressure of 1 atm,

$$p_v^\circ = y_i p / x_i$$
$$= (0.0255)(1.0)/1.0$$
$$= 0.0255 \text{ atm} = 19.38 \text{ mm Hg}$$

Acetone has a vapor pressure of 19.38 mm Hg at a temperature of -21.4 °C (Perry's Chemical Engineers' Handbook, 6th ed., p. 3-50.

$$T_{flash} \text{ (calculated)} = \underline{\underline{-21.4\,°\text{C}}}$$

Answer

The handbook Dangerous Properties of Industrial Materials provides a measured flash point for acetone of -17.8°C.

2-8

At equilibrium, acetone, benzene, ethyl ether, and n-pentane are too rich to ignite. Carbon disulfide and methyl alcohol will always be in the flammable range. It should be noted that all of the vaporizing liquids can be ignited if not at equilibrium. Some are also quite toxic.

Answer

The types of fire extinguishers recommended when a small spill is ignited are as follows:

Liquid	Extinguishers recommended
acetone	alcohol foam, dry chemical, CO_2
benzene	foam, dry chemical, CO_2
carbon disulfide	foam, water blanket
ethyl ether	alcohol foam, dry chemical, CO_2
methyl alcohol	alcohol foam, dry chemical, CO_2
n-pentane	foam, dry chemical, CO_2

Answer

2-9

The stoichiometric balance for the reaction is given by

$$C_3H_8 + 5O_2 + 5(3.76)N_2 \longrightarrow 3CO_2 + 4H_2O + 5(3.76)N_2$$

For 200% theoretical air, the balance becomes

$$C_3H_8 + 10O_2 + 10(3.76)N_2 \longrightarrow 3CO_2 + 4H_2O + 5O_2 + 10(3.76)N_2$$

Since all the energy generated from the combustion process is absorbed by the product gases, the final temperature of the products is determined by means of an adiabatic flame temperature calculation. The heat capacities for each component is a function of the temperature and requires a knowledge of the Cp-temperature relation of those components. Present software is available and can be used to rapidly converge with a heat balance on the appropriate flame temperature. When this is done, a temperature of $\underline{\underline{1527\,K}}$ is obtained. Answer

The iterative calculation can also be done by using an enthalpy table as a function of temperature for each of the coponents. The latter is available in Holman's <u>Thermodynamics</u>, 4th ed., Table A-18, pp 755-6 and is used in the hand calculation of this problem. The energy balance is

$$(\bar{h}_f^\circ)_{C_3H_8} = 3(\bar{h}_f + \bar{h}_T - \bar{h}_{298})_{CO_2} + 4(\bar{h}_f^\circ + \bar{h}_T - \bar{h}_{298})_{H_2O} + 5(\bar{h}_f^\circ + \bar{h}_T - \bar{h}_{298})_{O_2}$$
$$+ 37.6(\bar{h}_f + \bar{h}_T - \bar{h}_{298})_{N_2}$$

where $\bar{h}_f^\circ$ is the molar heat of formation, $\bar{h}_T$ the molar enthalpy at temperature T, and $\bar{h}_{298}$ the molar enthalpy at 298 K for the components as designated by the subscripts. Molar heats of formation for these components are from Table A-6 of the same text.

Heat losses to the surroundings are assumed to be negligible.

2-9 (continued)

To obtain the final temperature, assume different values of temperature until the energy balance is consistent. Units in kJ/kg mol.

Assume $T = 1555\,K$

$$-103{,}925 = 3(-393{,}782 + 74{,}392 - 9374) + 4(-241{,}997 + 60{,}680 - 9904)$$
$$+ 5(51{,}307 - 8664) + 37.6(49{,}034 - 8676)$$

$$-103{,}925 \neq -20{,}500$$

Temperature assumed is too high; assume $T = 1500\,K$

$$-103{,}925 = 3(-393{,}782 + 71{,}131 - 9374) + 4(-241{,}997 + 58{,}050 - 9904)$$
$$+ 5(49{,}272 - 8664) + 37.6(47{,}092 - 8676)$$

$$-103{,}925 \neq -123{,}997$$

Temperature assumed is too low. By interpolation, the final temperature under adiabatic conditions is 1511 K

The ideal gas law is valid at low pressures and high temperatures. Thus,

$$V_f = n_f RT/p$$

$$n_f = 3 + 4 + 5 + 37.6 = 49.6 \text{ kg mol/kg mol fuel}$$
$$= 4960 \text{ kg mol}/100 \text{ kg mol fuel}$$

$$V_f = (4960)(8314)(1511)/101{,}300 = 615{,}000\ m^3$$
$$= \underline{\underline{6.15 \times 10^5\ m^3}}$$

Answer

Ratio of final volume to initial volume is given by

$$V_f/V_i = \frac{n_f T_f}{n_i T_i} = \frac{(4960)(1511)}{(4860)(298)} = 5.17$$

2-10

Since the lower flammability limit (LFL) for acetone vapor in air is 2.55%, the maximum vapor pressure the acetone could have would be

$$p_v^\circ = (0.0255)(760) = 19.38 \text{ mm Hg}$$

The temperature equivalent to this vapor pressure may be determined utilizing the experimental data provided in Perry's Chemical Engineers' Handbook, 6th ed., p. 3-50 and the use of the Antoine equation with the form

$$\ln p_v^\circ = a - b/(t + 273)$$

The vapor pressure of acetone in the range of interest is

t, °C	p_v°, mm Hg
-40.5	5
-20.8	20

Substituting these values in the expression

$$\ln 5 = a - b/(-40.5 + 273)$$
$$\ln 20 = a - b/(-20.8 + 273)$$

Solving the equations simultaneously gives $a = 19.36$ and $b = 4126.3$. Thus,

$$\ln 19.38 = 19.36 - 4126.3/(t + 273)$$
$$t = -21.3^\circ\text{C}$$

The acetone would have to be cooled below -21.3°C to avoid an acetone-air mixture that could be ignited with a discharge of static electricity. Such cooling is not very practical and the use of an inert gas blanket should be considered during the filling operation.

Answer

2-11

The decomposition reaction is the following

$$C_2H_2 \rightleftharpoons 2C + H_2$$

Component	mols in	mols at temp. T	mol fraction
C_2H_2	1	$1-x$	$1-x$
C	0	$2x$	0*
H_2	0	x	x

*Assumes solid carbon product

Using the nomenclature and methodology from Sandler's Chemical and Engineering Thermodynamics

$$K_a(T) = \frac{a_C^2 a_{H_2}}{a_{C_2H_2}} \simeq \frac{y_{H_2}}{y_{C_2H_2}} = \frac{x}{1-x} \quad \text{where } x = \text{extent of reac.}$$

$$K_a(T) = e^{-(\Delta G_{rx}(T)/RT)}$$

Assume for both carbon and hydrogen

$$\Delta G_f(25°C) = 0 \quad \text{and} \quad \Delta H_f(25°C) = 0$$

$$\Delta G_{rx}(25°C) = -\Delta G_f(25°C)_{C_2H_2} = -50{,}000 \text{ cal/g mol}$$

$$\Delta H_{rx}(25°C) = -\Delta H_f(25°C)_{C_2H_2} = -54{,}194 \text{ cal/g mol}$$

The heat capacities for C, H_2 and C_2H_2 fit the relation $Cp_i = a_i + b_iT + c_iT^2 + d_iT^3 + e_i/T^2$ cal/g mol·K where T is in kelvins.

Comp.	a	$b \times 10^2$	$c \times 10^5$	$d \times 10^7$	e
C	2.673	0.2617	-	-	116,900
H_2	6.952	-0.04576	0.09563	-0.2079	-
C_2H_2	5.21	2.2008	-1.559	4.349	-

Data are from Sadler and Perry's Chemical Engineers' Handbook

For heats of reaction at other temperatures besides 25°C or T_1

$$\Delta H^\circ_{rx}(T) = \Delta H^\circ_{rx}(T_1) + \Delta a(T-T_1) + (\Delta b/2)(T^2-T_1^2) + (\Delta c/3)(T^3-T_1^3) + (\Delta d/4)(T^4-T_1^4) - \Delta e\left(\frac{1}{T} - \frac{1}{T_1}\right)$$

Where $\Delta a = \sum \nu_i a_i$, etc. and ν_i = stoichiometric coefficient

2-11 (continued, 1)

$K_a(T)$ for other temperatures besides at T_1 or 25 °C

$$\frac{\ln K_a(T)}{\ln K_a(T_1)} = \frac{\Delta a}{R}\ln\frac{T}{T_1} + \frac{\Delta b}{2R}(T-T_1) + \frac{\Delta c}{6R}(T^2-T_1^2) + \frac{\Delta d}{12R}(T^3-T_1^3) + \frac{\Delta e}{2}\left(\frac{1}{T^2}-\frac{1}{T_1^2}\right) + \frac{1}{R}\left\{-\Delta H^\circ_{rx}(T_1) + \Delta a T_1 + \frac{\Delta b}{2}T_1^2 + \frac{\Delta c}{3}T_1^3 + \frac{\Delta d}{4}T_1^4 - \frac{\Delta e}{T_1}\right\}\left(\frac{1}{T}-\frac{1}{T_1}\right) \quad (1)$$

For this reaction $K_a(T) = x/(1-x)$ or

$$x = \frac{K_a(T)}{1+K_a(T)} \quad (2)$$

From an energy balance for an adiabatic constant volume reaction

$$x = \frac{-\sum\int n_{i,in}\, C_{v_i}\, dT}{\Delta H^\circ_{rx}(T)} \quad (3)$$

where $n_{i,in}$ are the mols that enter into the reaction. Using the heat capacity constants tabulated earlier

$\Delta a = 7.088$

$\Delta b = -1.7232 \times 10^{-2}$

$\Delta c = 1.6546 \times 10^{-5}$

$\Delta d = -4.5569 \times 10^{-9}$

$\Delta e = 2.338 \times 10^{5}$

$$K_a(25\,^\circ C) = e^{-[(-50{,}000)/(1.987)(298.1)]} = 4.5 \times 10^{36}$$

Since the final temperature will be relatively high, the ideal gas law may be assumed to be valid. Thus,

$$C_{v,i} = C_{p,i} - R = a_i - R + b_i T + c_i T^2 + d_i T^3 + e_i/T^2$$

$\sum[n_i(a_i - R)]_{in} = 3.223$ $\quad \sum(n_i b_i)_{in} = 2.2008 \times 10^{-2}$ $\quad \sum(n_i e_i)_{in} = -1.559 \times 10^{-5}$

$\sum(n_i d_i)_{in} = 9.34 \times 10^{-9}$ $\quad \sum(n_i e_i)_{in} = 0$

With this information, Eqs. (1), (2) and (3) can be solved simultaneously. The results are

$T = 2967$ K and $x = 0.984$

The pressure will then be obtained from

2-11 (continued, 2)

$$p(T) = p_1(T_2/T_1) = 10(2967/298) = 99.6 \text{ atm}$$

With a safety factor of 4, the tank should be able to withstand a pressure of essentially 400 atm.

For spherical containers, Table 12-10 provides a relation to obtain the minimum wall thickness t of the tank as

$$t = \frac{Pr_i}{2SE_j - 0.2P}$$

Where P is the maximum allowable pressure, r_i the inside radius, S the maximum allowable working stress, E_j the efficiency of the welded joint. Assume that the carbon steel used in the tank is SA-442 Grade 55 with an S value of 94.7 MPa and that the welds are butt joints with complete penetration and spot examined resulting in a weld efficiency of 85%.

The diameter of the spherical tank was not given. Assume inside diameters of 1, 2, and 5 meters. For a 1-m diameter sphere

$$t = \frac{(400)(1.013\times10^5)(0.5)}{2(94.7\times10^6)(0.85) - (0.2)(400)(1.013\times10^5}$$

$$= 0.1324 \text{ m} \quad \text{or} \quad 5.21 \text{ in}$$

For 2 and 5 m inside diameters, the minimum thicknesses are $\underline{\underline{0.265 \text{ m and } 0.662}}$ m.

Answer

The results show the advantage of having a properly designed relief valve and burst disk assembly closely tied in with the reactor containing the decomposition reaction of acetylene. It would be imprudent to recommend a spherical container with a wall thickness greater than 0.0125 m because of the reactor costs involved.

2-12

The rate at which energy is produced in a reactor is given by the relation

$$\frac{dq}{d\theta} = \Delta H_{rx}\, k_o C V e^{-(E/RT)}$$

where $dq/d\theta$ is the heat liberated over time, ΔH_{rx} the heat of reaction, C the concentration of the reactant, V the volume of the reactor, E the activation energy, R the gas constant, and T the temperature.

When the reaction is exothermic, heat must be removed from the reactor to keep the temperature from increasing beyond control. The heat transfer rate can be written as

$$\frac{dq}{d\theta} = UA(T - T_o)$$

where U is the overall heat transfer coefficient, A the heat transfer area, and T_o the coolant temperature. If heat can be removed as rapidly as heat is generated by the reaction, the reaction can be kept under control. Thus, at steady state

$$\Delta H_{rx} k_o C V e^{-(E/RT)} = UA(T - T_o)$$

To simplify the relation, let $B = \Delta H_{rr} k_o C V$ and $K = UA$. Thus,

$$B e^{-(E/RT)} = K(T - T_o)$$

or $$B e^{-(E/RT)} - K(T - T_o) = 0$$

The maximum temperature where the steady-state energy balance is valid can be found by setting its derivative with respect to temperature equal to zero. Doing this, resuts in

$$B e^{-(E/RT)} (E/RT_c^2) - K = 0$$

where T_c is the critical or maximum temperature. However,

$$B e^{-(E/RT)} = K(T_c - T_o)$$

at the maximum temperature. Substituting this into the previous equation and solving for K gives

2-12 (continued)

$$K(T_c - T_0)(E/RT_c^2) = K$$

or $(T_c - T_0) = RT_c^2/E$ which can be used to find T_c

Substituting values

$$(T_c - 288.1) = 1.987\,T_c^2/28{,}000$$

$$T_c = 294.3 \text{ K}$$

This means that if the temperature in the reactor rises above 294.3 K (21.1°C), the reactor will begin to generate energy faster than it can be removed and the reaction will run away. Note that only a 6.2°C rise in temperature in the reactor can be tolerated.

Answer

For safe operation of the reactor some or all of the following actions can be taken:

1. Increase the size of the heat exchanger
2. Inject an inhibitor into the reactor or quench the reaction if it is ready to go out of control
3. Reduce the feed to the reactor
4. Provide adequate venting for the reactor for emergency use
5. Add diluents to the reactor to reduce the reaction rate. (These will probably have to be separated from the product after the reaction is completed)

2-13

A system for transferring liquid chlorine from a chlorine storage container with pressurized chlorine gas is shown below. A feature of this design is a relief system that utilizes a duplicate burst system to simplify replacement of the discs with a mechanical interlock between the two burst systems. Bottom outlets have been avoided so that joints are not exposed to liquid chlorine and the only leakage will be of a gaseos nature.

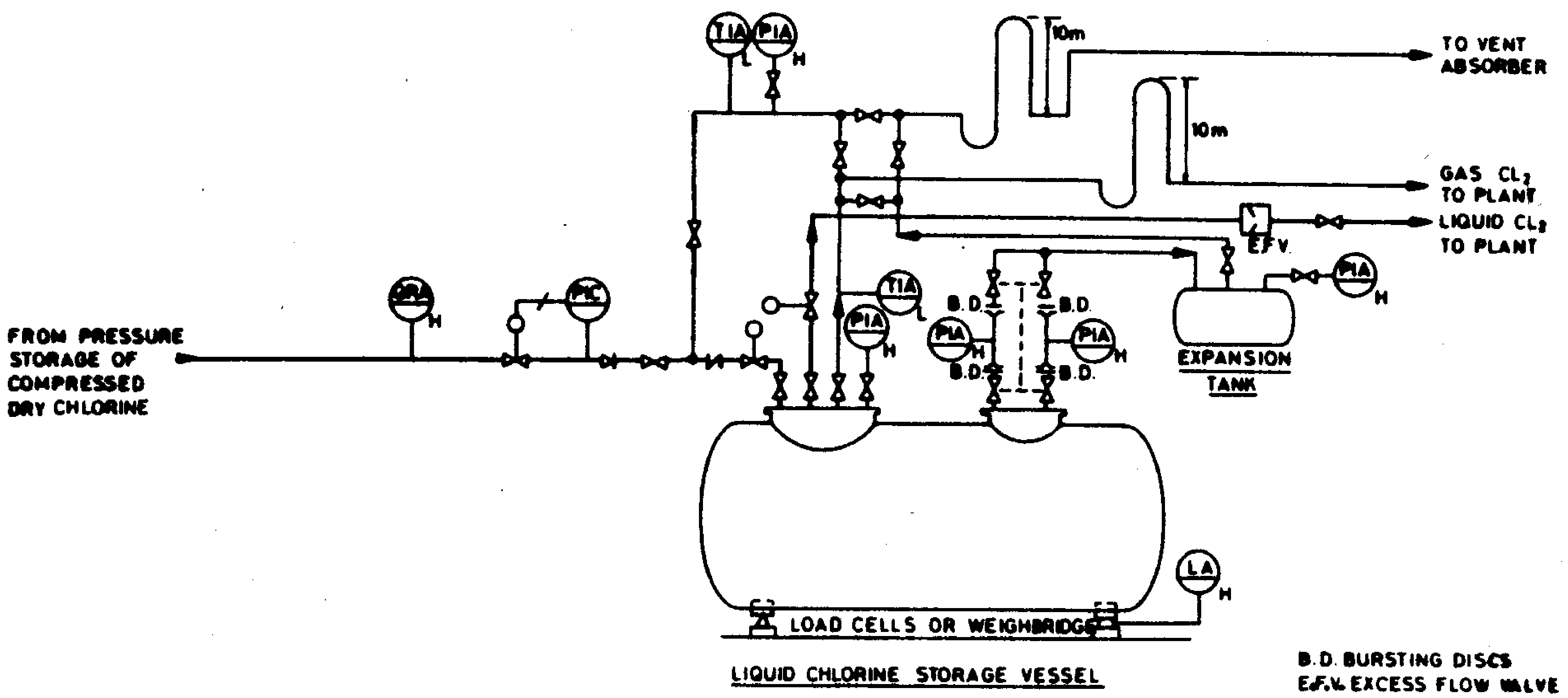
The severity of the leak is reduced by lowering the pressure within the storage container or system. A facility must be available to accomplish this pressure reduction during chlorine transfer as well. A waste Chlorine absorption unit that uses caustic or some simular chlorine consuming process is recommended. In addition, an expansion vessel is provided with an alarm to handle any pressure build-up in the container. The expansion tank is automatically vented to the absorption system (see figure).

The recompressed dry chlorine can be stored in a pressure storage receiver fitted with a relief valve set to discharge to the waste chlorine absorption unit at a predetermined pressure.

Pressurization with vaporized chlorine can function with a pressure storage tank that can utilize an external heater to vaporize the liquid chlorine. Control of the vaporization heater is tied to the pressure control system for the storage tank. Relief valves must permit over-pressurization to be relieved with excess chlorine vapor going to the waste chlorine absorption unit described above.

One possible instrumented arrangement for the chlorine vaporizer is shown in the second figure.

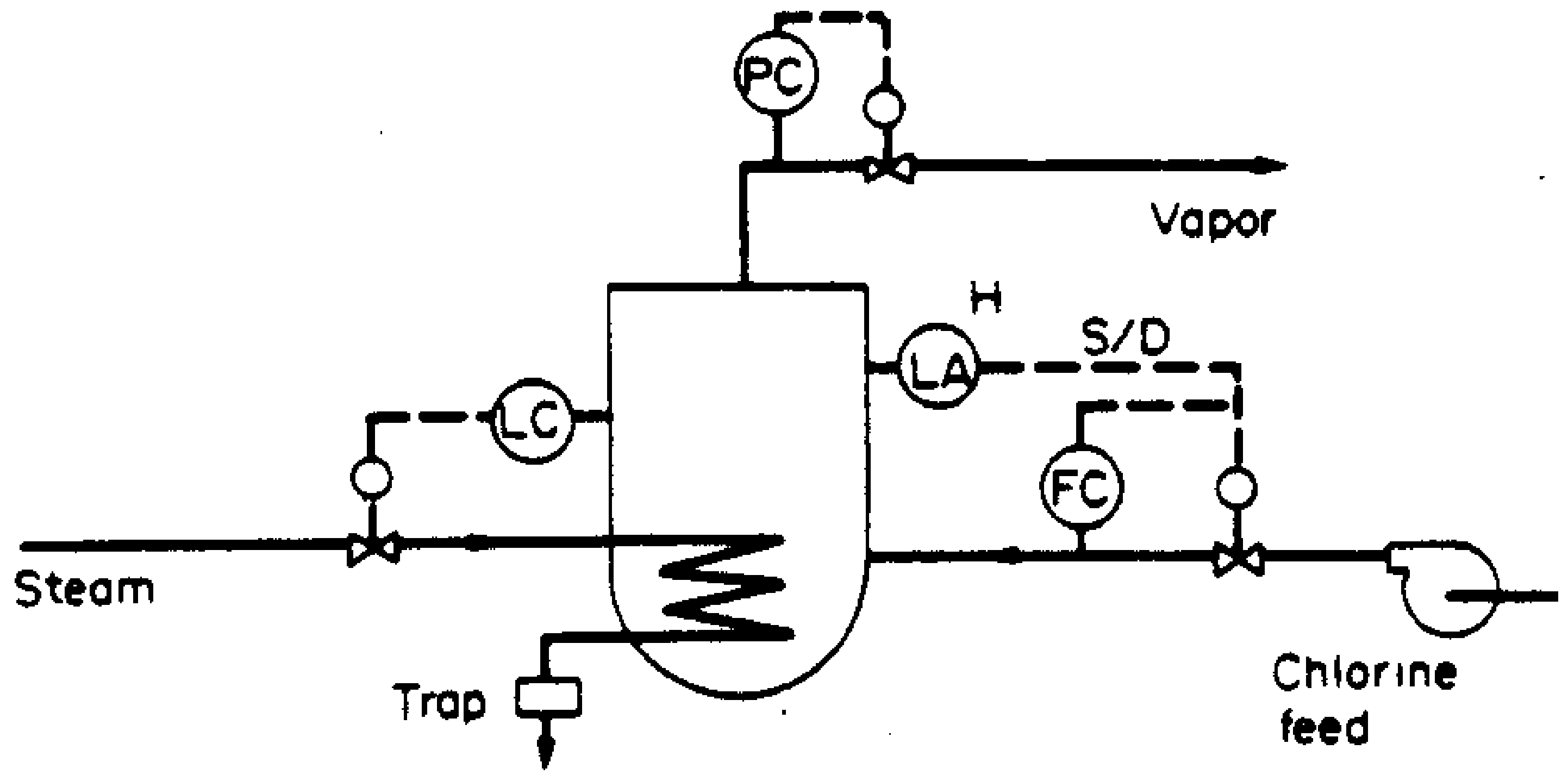
2-13 (continued, 1)



One possible arrangement with appropriate controls and alarm system for transferring liquid chlorine by using recompressed chlorine vapor.

Answer

2-13 (continued, 2)



Answer

2-14

Reducing the inventory of a hazardous material in a process includes, but is not limited to the following items:

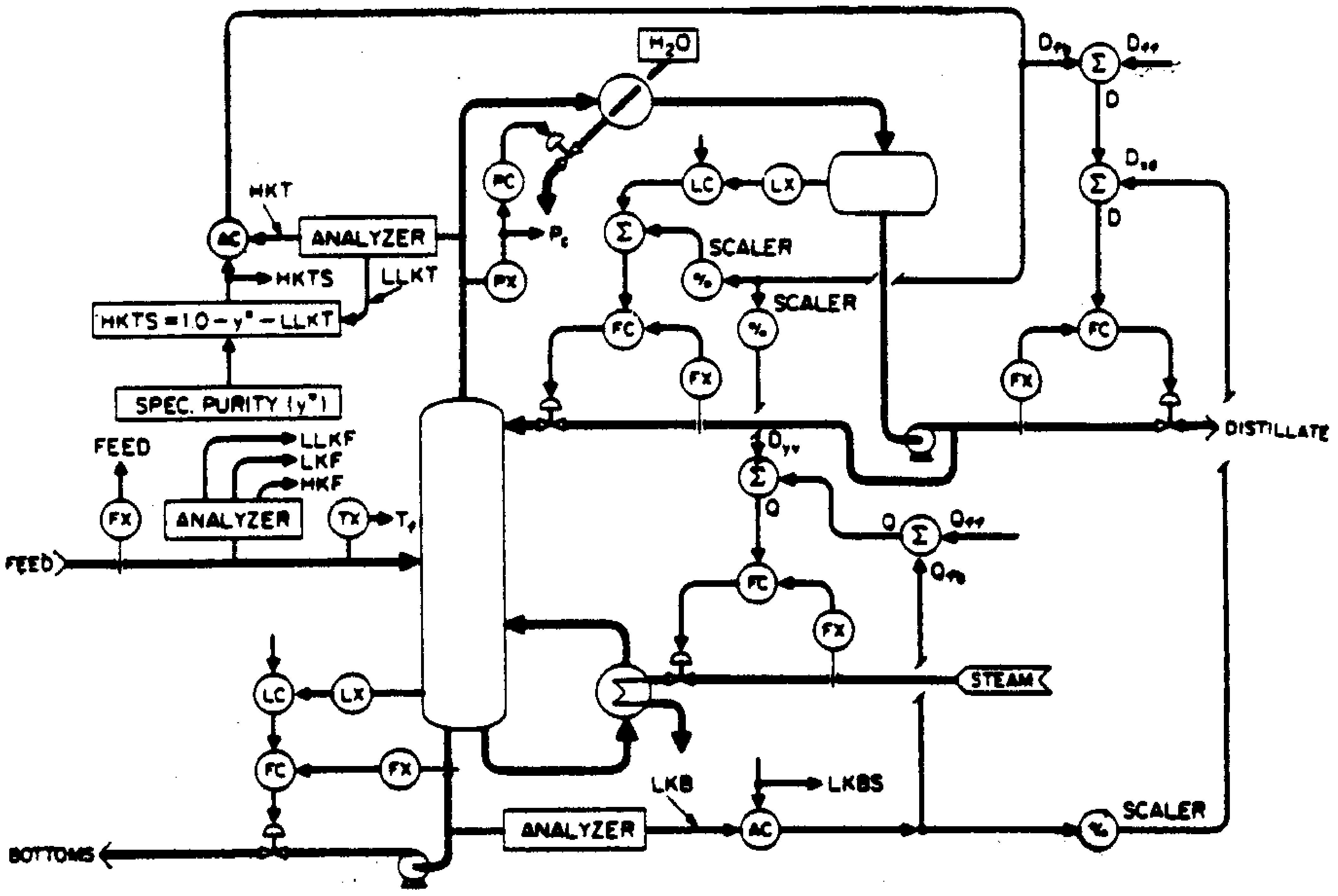
1. Investigate the possibility of producing the end product by another process that does not the use of a very hazardous material.
2. Determine whether the hazardous material may be reacted or combined before the distillation step to form a non-hazardous material. If the hazardous material is a reactant, recycle the stream back to the process to reduce the hazardous material content before the distillation step.
3. Depending upon how the hazardous material is used in the process, determine whether there are more efficient ways of absorbing, adsorbing, trapping, complexing, etc, the hazardous materials to avoid using a distillation operation that generally has considerably greater difficulty in attaining ppm concentrations in a product stream.
4. If elimination of the hazardous material is not possible, operate the distillation operation on a continuous basis. This will require less material being handled, smaller equipment used with possible elimination of the buffer storage, and improved chances of containment should there be a leak.
5. Improve the efficiencies of the column to reduce build-up of Hazardous materials. Guidelines for such improvements are given by K.E. Nelson, Hydrocarbon Processing 69(3), 93-98 (1990).

Answer

A distillation column can be controlled in many ways. Generally, there is no one "best" way. Which one is to be prefered depends on the purpose of the separation, the types of controls available for each service, the variability of the feed, and the relative importance of the product recovery and product purity. Each case needs to be analyzed separately.

2-14 (continued)

A typical distillation column with appropriate instrumentation in which basic controls are assisted with predictive and analyzer loops is outlined in Perry's Chemical Engineers' Handbook, 6th ed., p. 22-118 and is reproduced below with the permission of McGraw-Hill.



Nomenclature Summary for Fig.

Symbol	Explanation
D_{fb}	Contribution of feedback control to distillate-flow set point
D_{ff}	Contribution of predictive control
D_{xd}	Contribution of noninteractive decoupler to distillate-flow set point
D_{yv}	Contribution of noninteractive decoupler to reboiler-heat set point
HKF	Heavy key feed-stream component
HKT	Heavy key overhead-product-stream-component concentration, weight percent
HKTS	Specified concentration of heavy key component in overhead product, weight percent
LKBS, x^*	Specified concentration of light key component in bottoms product, weight percent
LKF, z	Light-key-feed-stream-component concentration, weight percent
LLKF	Lighter-than-light-key-feed-stream-component concentration, weight percent
LLKT	Lighter-than-light-key-overhead-product-stream-component concentration, weight percent
Q	Reboiler heat, BTU/unit time
Q_{fb}	Contribution of feedback control to steam-flow set point
Q_{ff}	Contribution of predictive control to steam-flow set point
Q_r/F	Weight ratio, reboiler-heat-to-feed
x^*, *LKBS*	Specified concentration of light key component in bottoms product, weight percent
z, *LKF*	Light-key-feed-stream-component concentration, weight percent

2-15

HAZOP for Line L-102

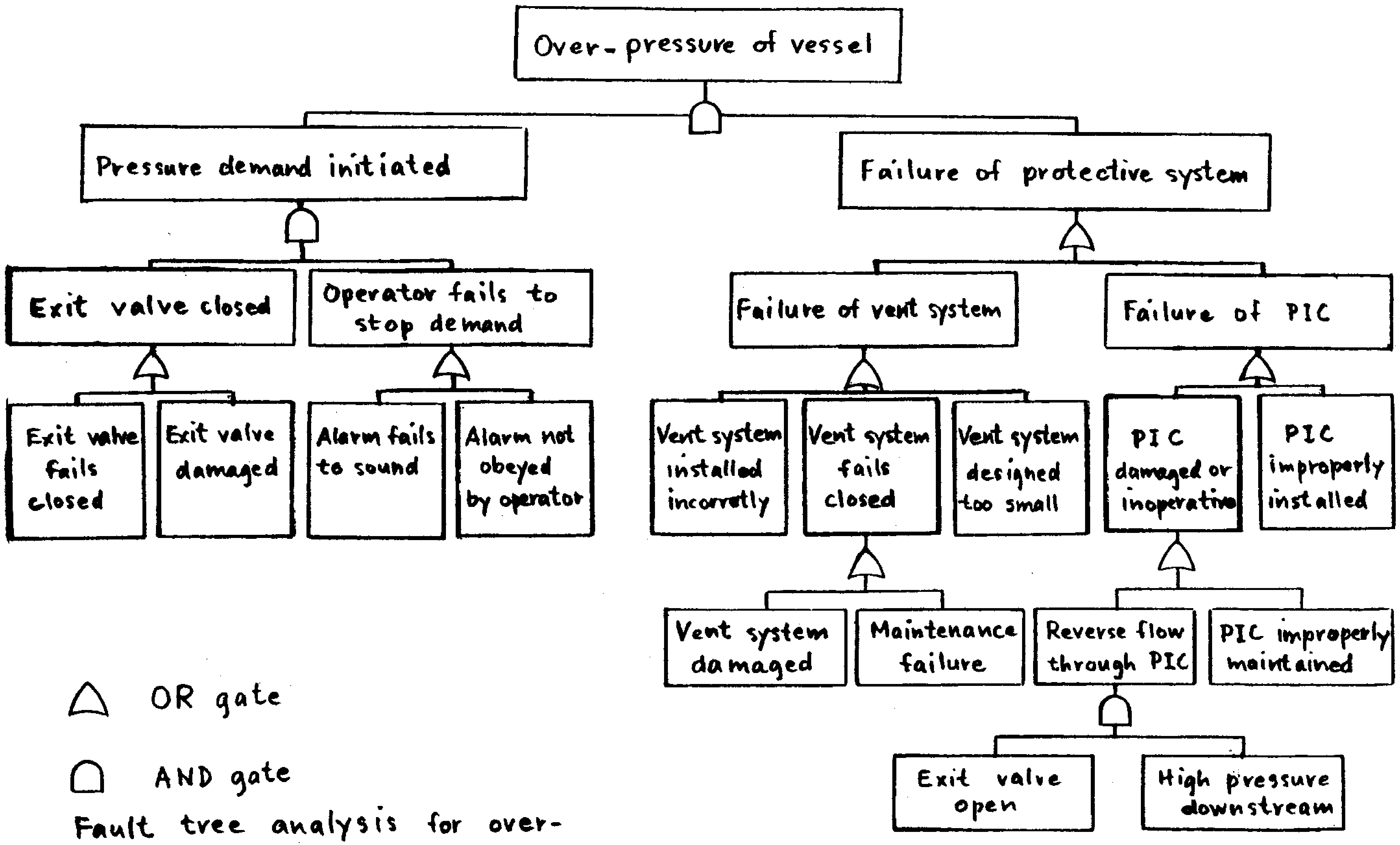
Guide word	Property	Possible cause	Possible consequence	Action required
More	Temperature	A	Pump seal failure, vapor lock	Install a feed-back line
Less	Temperature	Low ambient temperature	B	steam tracing
More	Flow	Line fracture	Spillage (possible large explosion)	C
		Pump seal failure	Spillage (possible small explosion)	D
		Control fault		Consider bypass
No	Flow	E	Shutdown	Low level alarm
		F	Shutdown	Automatic start-up of standby pump
Reverse	Flow	Pump failure	Backpressure on storage vessel	G
As well as	Impurities	H	Possible small detonation	Priming line

The missing items below complete the HAZOP study above:

A. Steam tracing operating incorrectly or downstream valve closed
B. Thermal stress on line
C. Install flow control with automatic shutoff
D. Flow diverted through standby pump capable of automatic startup
E. Tank empty
F. Pump failure
G. Relieve backpressure, divert flow through standby pump with automatic startup
H. Pump drawing in air or operator error

Answer

2-16



Fault tree analysis for over-pressurizing vessel

2-17

The important factors to be considered for plant location in the fertilizer industry are (1) raw materials, (2) markets, (3) transportation facilities, (4) power and fuel availability, (5) waste disposal, and (6) water supply. The order of importance varies with the fertilizer considered and to some extent to the size of plant contemplated. Analysis of this situation for ammonia, urea, and phosphate fertilizer requires a knowledge of the raw materials required and the most commonly used process for each fertilizer. A concise review of these requirements is given by G.T. Austin in Shreve's Chemical Process Industries, 5th ed. About 90% of US ammonia production uses natural gas as the feedstock. The reactions are

$$CH_{4(g)} + H_2O \xrightarrow[2860\text{ kPa},\ 515^\circ C]{\text{Ni catalyst}} CO_{(g)} + 3\,H_{2(g)}$$

$$CH_{4(g)} + \text{air} \xrightarrow[670^\circ C]{\text{Ni catalyst}} CO_{(g)} + 2H_{2(g)} + N_{2(g)}$$

$$1/2\,N_{2(g)} + 3/2\,H_{2(g)} \xrightarrow[\text{pressure}]{\text{Fe catalyst}} NH_{3(g)}$$

The process requires large amounts of power and cooling water. Since natural gas is easily transported by pipeline, the plant need not be located near the gas well. Rather, it is more profitable to locate the plant close to the markets. Thus, the latter is the most important factor in plant location. Adequate power and water supply would also rank quite high. As the size of the plant increased, more consideration would have to be given to transportation facilities since the markets would be from the plant. Adequate supply of natural gas would also become important with plant size.

The commercial processes in current use for the manufacture of urea are based on two reactions, namely

$$CO_{2(g)} + 2NH_{3(l)} \xrightarrow[185^\circ C - 193^\circ C]{22\text{ MPa}} NH_4CO_2NH_{2(l)}$$

2-17 (continued)

$$NH_4CO_2NH_2 \rightleftharpoons NH_2CONH_{2(l)} + H_2O_{(l)}$$

This process requires approximately 1/4 the power and cooling water of that required for the ammonia process per unit weight of fertilizer produced. Since ammonia is one of the principal raw materials required for the process, it is much more important to consider the source of the raw materials in a selection of the plant site for the production of urea. This factor will be the most important consideration even with an increase in plant size. However, since the fertilizer markets are not as large as for the raw material, careful consideration must be given to markets and the transportation necessar to reach those markets.

Phosphate fertilizer is obtained from phosphate rock ore. The accidulation of phosphate rock to produce superphosphate fertilizer can probably best be described by the following reaction:

$$CaF_2 \cdot 3Ca_3(PO_4)_2 + 7\,H_2SO_4 + 3H_2O \longrightarrow 3CaH_4(PO_4)_2 \cdot H_2O + 2HF + 7CaSO_4$$

Since the phosphate rock must be concentrated after it is mined, plant location is determined by the location of the phosphate rock ore regardless of plant size. The aspects of waste disposal of the non-phosphate rock is directly related to the mining operation. Markets directly affect plant size.

Answer

2-18

The diluted waste sample contains 15g of waste and 485g of dilution water. The total oxygen available for consumption by the waste is

$$g \text{ of } O_2 = (485)(9)/10^6 = 4.365 \times 10^{-3} g$$

The final oxygen content of the diluted sample is

$$g \text{ of } O_2 = (500)(4)/10^6 = 2.0 \times 10^{-3} g$$

The oxygen depletion due to the 15 g waste sample is

$$O_2 \text{ depletion} = 4.365 \times 10^{-3} - 2.0 \times 10^{-3} = 2.365 \times 10^{-3} g$$

The BOD, defined as the oxygen depletion in parts oxygen consumed per 10^6 parts of waste is then

$$BOD = (2.365 \times 10^{-3})(10^6/15) = \underline{\underline{158 \text{ parts } O_2/10^6 \text{ parts waste}}}$$

Answer

2-19

The solution to this problem involves some of the same safety aspects as considered in the solution of Problem 2-13.
The most common method to vaporize chlorine is to use steam in a heating coil immersed in the chlorine liquid in the vaporizer. A schematic with typical instrumentation is shown in the solution of Problem 2-13 and will not be repeated here.
The disadvantage of using hot water to vaporize the chlorine is the need for a larger coil and a greater potential for freezing of the coil (NBP of Cl_2 is - 34°C). Economics is probably the major deterrent for not using a closed circuit heating with a heat transfer fluid that is inert to chlorine.

The use of a heating coil immersed below the liquid level in a chlorine vaporizer is the preffered arrangement to accomplish the vaporization. Not only is the coiled tube less expensive, it is also less susceptible to leaks and failures.

Answer

2-20

The net heat transfer flux to a storage tank during a fire comes from radiation and convection attributed to the fire that surrounds tank and can be approximated by

$$q_{net} = q_r + q_c + q_{rr}$$

where q_r is the radiation flux from the fire, q_c the convection flux from the fire, and q_{rr} the radiation flux back from the tank. The radiation fluxes are proportional to the differences in the fourth powers of the absolute temperatures for the radiating and absorbing surfaces. The convection flux can be estimated of natural convection heat transfer. Since the surface of interest in this problem is large and vertical, the relations for natural convection on vertical plane surfaces are the most appropriate ones to use. The flame can be assumed to have transport properties equal to that of hot air in the flame and the fact that most of the gas in the flame is nitrogen. Flame temperatures vary from fuel to fuel, but a temperature of about 1500K will provide a reasonable average value for most situations.

If the benzene tank, assumed to be a vertical cylinder, is to store 1600 m^3, its minimum height is given by

$$V = \pi D_i^2 Z/4$$
$$Z = 4V/\pi D_i^2 = (4)(1600)/\pi(15)^2 = 9.05 \text{ m}$$

Storage tanks generally have an ullage volume of 10% or more to take care of liquid expansion and provide additional volume for some vaporization to occur without appreciably increasing the tank pressure. Heat transfer to the surface area surrounding the ullage space will be minimal compared to the surface area wetted by the full tank contents. Thus, only the latter area will be used in the heat transfer calculation. Also assume that the temperature of the wetted wall to be at the boiling point temperature of the fluid being stored in the tank. There will be a temperature gradient through the tank wall, but this will be small and have minimal effect on the re-

2-20 (continued, 1)

quired venting rate during a fire.

$$q_r = 95{,}000 \text{ W/m}^2$$

is given in the problem statement and assumes that the external fire completely surrounds the storage tank. The convective flux from the fire is given by

$$q_c = h(T_f - T_w)$$

where T_f is the flame temperature and T_w is the wall temperature, assumed to be the same as the normal boiling temperature of the fluid in the tank. The heat transfer coefficient in US customary units for natural convection along a vertical surface may be obtained numerically from

$$Nu = \left\{ 0.825 + \frac{0.387\, R_a^{1/6}}{\left[1 + \left(\frac{0.492}{P_r}\right)^{9/16}\right]^{8/27}} \right\}^2$$

as given in Perry's Chemical Engineers' Handbook, 6th ed., where $Nu = hL/k$, $Pr = C_p\mu/k$, $Ra = Gr\,Pr$, and $Gr = L^3\rho^2 g\,\beta\,\Delta T/\mu^2$. Since this calculation is rather lengthy and natural convective heat transfer coefficients for air generally have values of 5 to 10 W/m²·K, we will assume an average value of 7.5 W/m²·K and only calculate a better value if analysis warrants it.

Using this assumption

$$q_c = (7.5)(1500 - 353) = 8600 \text{ W/m}^2\cdot\text{K}$$

The heat flux radiated back from the tank surface to space can be estimated from

$$q_{rr} = \epsilon\,\sigma\,T_w^4 \qquad \text{assume } \epsilon = 1.0$$

$$= (1.0)(0.972\times10^{-8})(353)^4 = 150 \text{ W/m}^2\cdot\text{K}$$

From these calculations

$$q_{net} = 950{,}000 + 8600 - 150 = 103{,}450 \text{ W/m}^2\cdot\text{K}$$

2-20 (continued, 2)

The vapor boil-off rate is then

$$\dot{m} = (q_{net})A/\Delta H_v \qquad \Delta H_v = \text{heat of vaporization}$$

$$= (q_{(net)})\pi D Z/\Delta H_v$$

$$= (103,450)\pi(15)(9.05)/3.943\times10^5 = 111.9 \text{ kg/s}$$

At the NBP of benzene, the vapor density is 2.755 kg/m^3. Thus

$$\dot{m}_v = \dot{m}/\rho = 111.9/2.755 = 40.65 \text{ m}^3/\text{s}$$

The vent area needed for this volumetric flow rate can be determined by use of an orifice equation of the form

$$A = \frac{\dot{m}}{0.61[(2)\Delta p\,\rho]^{1/2}} \qquad \Delta p = 250 \text{ Pa}$$

$$= \frac{111.9}{(0.61)[(2)(250)(2.755)]^{1/2}} = 4.94 \text{ m}^2$$

The area for the vent is much too large for the tank. Therefore a weak seam roof <u>should be specified</u>

Answer

Several assumptions were made in the solution of this problem and need to be verified. First, the convective flux is only 9% of the total heat flux. Even if it were changed ± 100%, the overall result would only be changed slightly. Thus, an exact calculation of the heat transfer coefficient would not change the final conclusion.

There is some resistance to heat transfer through the walls of the tank. For a tank wall of 0.0125 m, the temperature gradient is

$$\Delta T = q_{(net)}\,t_w/k_w = (103,450)(0.0125)/45 = 28.7^\circ\text{C}$$

This will have a negligible effect on the results, and thus this assumption is acceptable. However, there is also a thermal resistance with the film on the inside of the tank. Typical heat transfer coefficients are on the order of several thousand W/m^2·K. Assuming a value of

2-20 (continued, 3)

2,000 $W/m^2 \cdot K$, the ΔT across the film is

$$\Delta T = q_{(net)}/h = 103{,}450/2000 = 51.7\,^{\circ}C$$

The combination of these two resistances only reduces the convective flux rate by approximately 6%. This change would have negligible effect on the final answer.

As a footnote, the NFPA Fire Protection Handbook and API 650 all reommend the following equation for the net heat flux to a tank subjected to an external fire:

$$q_{(net)} = 43{,}200\, A^{0.82}$$

where $q_{(net)}$ is in watts and A is the wetted area in m^2. For this problem

$$q_{(net)} = 43{,}200\,[\pi D_L Z]^{0.82} = 43{,}200\,[\pi(15)(9.05)]^{0.82}$$
$$= 6.19 \times 10^6 \text{ W}$$

from this

$$\dot{m}_V = q_{(net)}/\Delta H_v \rho$$
$$= 6.19 \times 10^6/(3.943 \times 10^5)(2.755) = 5.6 \text{ m}^3/\text{s}$$

The major difference in results is that the heat flux in the problem statement applies to a fire that completely surrounds the tank. Generally fires are seldom large enough to surround large tanks. In addition a soot layer builds up on the cool tank walls which further restricts the heat transfer. Thus, the total heat flux is reduced substantially. However, the venting rate even under these conditions will be large and a tank with a weak roof seam would be recommended.