# Hazardous Substances Policy – Control Measures

# Enhanced Good Chemical Practice for Work with Cryogenic Liquids

### Appendix 3 – Oxygen Depletion Calculations

## Assessment of Ventilation Requirements

The following guidance is based on that provided in British Compressed Gases Association Code of Practice 30.

The rate at which a room is ventilated is usually expressed in the number of air changes per hour.

In locations above ground level with no special ventilation openings, natural ventilation provides typically 1 change per hour. However, a lower value will apply where windows are sealed with tight seals. For underground rooms with small windows 0.4 changes per hour is assumed.

Mechanical ventilation is considered necessary where the ventilation requirement is for more than 2 changes per hour.

## Calculating the Potential Oxygen Depletion in a Room Due to Liquid Gas Filling and Spillage

Five cases are considered:

a) Evaporative loss from the storage tank,
b) filling losses which always occur when a dewar is being filled,
c) spillage of the contents of the dewar and
d) the 'next worst case' where the entire contents of the vessel are lost to the room immediately after the dewar is filled
e) the “worst case” where there is catastrophic failure of the full storage tank.

### a) Evaporative loss from storage tank

In order to allow for a deterioration in the insulation performance over the life of the tank it is prudent to double the manufacturer’s quoted evaporation rate.

$$\text{Reduced oxygen concentration, } C_\infty = \frac{Vr * 0.21 * n}{L + (Vr * n)}$$

where:

- $L$ = gas release $m^3/hr$
- $V_R$ = room volume $m^3$
- $n$ = air changes per hour
- * = multiply

## b) Filling

A value of 10% of the volume of the product in the dewar is used to estimate the losses to atmosphere during filling.

$$V_O = 0.21[V_R - [\frac{0.1 * V_D * f_g}{1000}]\ ]$$

where:

| | |
|---|---|
| 0.1 | = 10% volume loss during filling |
| $V_R$ | = room volume, $m^3$ |
| $V_D$ | = dewar capacity, litres |
| $f_g$ | = Liquid to gas expansion ratio. |
| 0.21 | = The normal concentration of oxygen in air, 21% |
| * | = multiply |

Resulting oxygen concentration, $C_{ox} = \frac{100 * V_o}{V_R}$

where:

| | |
|---|---|
| $V_o$ | = the volume of oxygen, $m^3$ |
| $V_R$ | = room volume, $m^3$ |
| * | = multiply |

## c) Spillage

For the spillage of the entire contents of a dewar:

$$V_O = 0.21[V_R - [\frac{V_D * f_g}{1000}]\ ]$$

Resulting oxygen concentration, $C_{ox} = \frac{100 * V_o}{V_R}$

where the symbols are as before.

## d) Filling and spillage together

The 'next worst case', where the entire contents of a dewar are lost to the room immediately after filling, equivalent to 110% of vessel contents to allow for the 10% filling losses prior to spillage:

$$V_O = 0.21[V_R - [\frac{1.1 * V_D * f_g}{1000}]\ ]$$

where:

| | |
|---|---|
| 1.1 | =110% volume loss during filling and spillage |
| $V_R$ | = room volume, $m^3$ |
| $V_D$ | = dewar capacity, litres |
| $f_g$ | = Liquid to gas expansion ratio. |
| 0.21 | = The normal concentration of oxygen in air, 21% |
| * | = multiply |

Resulting oxygen concentration, $C_{ox} = \frac{100 * V_o}{V_R}$

where:

| | |
|---|---|
| $V_o$ | = the volume of oxygen, $m^3$ |
| $V_R$ | = room volume, $m^3$ |

### e) Catastrophic failure of Storage Tank

For the release of the entire contents of a tank:

$$V_O = 0.21[V_R - [\frac{V_D * f_g}{1000}]\ ]$$

Resulting oxygen concentration, $C_{ox} = \frac{100 * V_o}{V_R}$

where the symbols are as before (except, $V_D$=tank capacity)

## Oxygen Depletion Example for Liquid Nitrogen

### Example:

A basement room contains two 25 litre and three 10 litre dewars.
Room dimension: 7 x 8 x 2.5 metres =140m$^3$,
5 litre dewar: loses 0.2 litres per day through evaporation
10 litre dewar: loses 0.15 litres per day through evaporation

(dewar manufacturers' quoted evaporation rates).

### Normal Evaporation Losses

Evaporation is a continuous process, hence the increase in nitrogen concentration ($C_\infty$) can be calculated over a long period using:

$$C_\infty = \frac{Vr * 0.21 * n}{L + (Vr * n)}$$

where:

- $C_t$ = gas concentration
- $L$ = gas evaporation rate m$^3$/hr
- $V_R$ = room volume m$^3$
- $n$ = air changes per hour
- * =multiply

Whilst manufacturers will quote the evaporation rate for their dewar, it is prudent to double it when calculating the rate of nitrogen release. *L.* This allows for a deterioration in the insulation performance over the life of the dewar. The nitrogen gas factor of 683 at 15°C has to be used to calculate the volume of gaseous nitrogen released through evaporation, as the dewar manufacturer's figures relate to the volume of liquid nitrogen lost.

Thus:

$$L = \frac{2 * 683 * (2 * 0.2 + 3 * 0.15)}{24 * 1000} = 0.048 m^3 / h$$

Assume there is an average of 0.4 air changes per hour in the room. The oxygen concentration increase is, therefore:

$$C_{ox} = \frac{140 * 0.21 * 0.4}{0.048 + 140 * 0.4} = 0.2098 = 20.98\%$$

Thus, in this case, evaporation from the five dewars in the circumstances described would reduce the oxygen concentration by some 0.02%.

In this example, normal nitrogen evaporation from the dewars has only a small effect in increasing the nitrogen concentration, and thus reducing the oxygen concentration, in the room. If, however, far more dewars were stored in the same room used in the above example, or if a much smaller room was used for the five dewars mentioned, then the nitrogen concentration would increase by a much higher larger factor. If $C_{ox}$in such a case was calculated to be 0.20 (i.e. 20%), then forced ventilation would be recommended, since this would reduce the oxygen concentration in the room by 1%, which is at the level where the safety margin has been virtually used up.

## Losses due to Filling

First calculate the volume of oxygen in the room, $V_O$.

Using:

$$V_O = 0.21[V_R - [\frac{0.1 * V_D * f_g}{1000}]\ ]$$

The same dewars and room size are used (140m$^3$), but here the largest nitrogen release is during the filling of the largest (25 litre) dewar and again the nitrogen factor of 683 must be used to convert liquid to gaseous nitrogen.

Thus:

$$V_O = 0.21[140 - [\frac{0.1 * 25 * 683}{1000}]\ ] = 29.04 m^3$$

The resulting oxygen concentration in the room ($C_{ox}$) can then be calculated: Using:

$$C_{ox} = \frac{100 * V_o}{V_R}$$

Thus:

$$C_{ox} = \frac{100 * 29.04}{140} = 20.7\%$$

Clearly, this is acceptable. As a guide it is recommended that the combined effect of normal evaporation and filling processes should give rise to alarm if the oxygen level falls to 19.5%.

## Losses Due to Filling and Spillage

Following the same process as above, calculate the volume of oxygen in the room $V_O$) as a result of the spillage of the entire contents following filling.
Using:

$$V_O = 0.21[V_R - [\frac{1.1 * V_D * f_g}{1000}]\ ]$$

Again we have a 140m$^3$ room and again the largest release is from the 25 litre dewar.

Thus:

$$V_O = 0.21[140 - [\frac{1.1 * 25 * 683}{1000}]\ ] = 2505 m^3$$

Then calculate the resulting room oxygen concentration (Cox) after the spillage:

Using:

Schedule 3.12

$$C_{ox} = \frac{100 * V_o}{V_R}$$

Thus:

$$C_{ox} = \frac{100 * 25.5}{140} = 18.2\%$$

This is just above the level (set at 18%) at which oxygen monitors are usually set to give an emergency alarm, leading to immediate evacuation.

In this example, it is recommended an oxygen monitor be fitted with two levels of alarm:

- 19.5% should lead to urgent investigation and corrective action
- 18.5% should cause immediate evacuation - assuming that this level results from spillage.