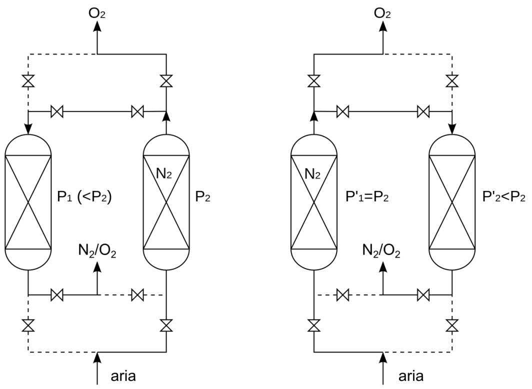
Chemical Engineering Thermodynamics
Quiz 3
January 31, 2019

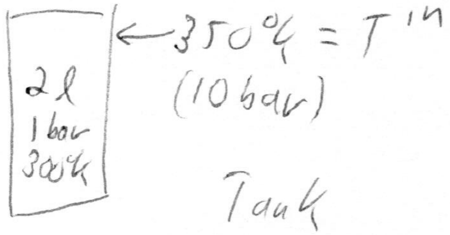


Pressure swing absorption (PSA) is used to separate gasses under non-cryogenic conditions. For example, this is used to separate oxygen from air in a semi-continuous process. Two tanks contain a zeolite (high surface area aluminosilicate) that preferentially absorbs nitrogen at high pressure. The zeolite has a selectivity of about 99% for nitrogen at 10 bar and 298°K. The selectivity drops quickly at lower pressure and all nitrogen is released at low pressure (1 bar).
a) The tank is filled with compressed air at a fixed flow rate.
b) After the tank pressurizes, the inlet and outlet have different air flow rates but the same flow rate of oxygen and the tank releases almost pure oxygen while the zeolite absorbs the nitrogen until it reaches capacity.
c) The tank pressure is released, desorbing nitrogen and the process starts again.
A second tank operates in counter sequence to ensure an almost continuous flow of oxygen.

The design criterion is to pressurize the first tank from atmospheric pressure to 10 bar in 30 seconds. The tank has a volume of 2 liters and the inlet air is at 350°K. The tank is initially at 1 bar and 300°K.
Three stages: a) fill, b) steady state, c) decompress

a) Determine the inlet flow rate to fill the tank to 10 bar in 30 s. First find the final temperature without assuming a rate. Assume no nitrogen has absorbed.
b) Assume you start with pure oxygen in the tank at 10 bar and 300°K and that all of the nitrogen is absorbed into the zeolite which holds 2 ml/g and the tank contains 2kg of zeolite, if the outlet is 0.1 mole/min what is the inlet rate, how long until the zeolite reaches capacity and what is the temperature if the absorption process is athermal ($\Delta H_{\text{absorption}} = 0$). The inlet is at 350°K.
c) For the desorption stage how long will it take to reach 1.5 bar? The outlet flow rate is 0.25 mole/min and there is no inlet flow. Assume the zeolite is releasing nitrogen at 0.1 mole/min during the process at the same temperature as the tank. What is the temperature when the tank reaches 1.5 bar. Assume that you start at 10 bar and 300°K.
d) How could you improve the process considering the temperature profiles for absorption and desorption in time and the counter sequence of the two tanks?

a) 10 bar 30 s $\dot{n} = ?$



$$n^i = \frac{P^i V}{RT^i} = \frac{0.1\,\text{MPa}\ 2{,}000\,\text{cm}^3}{8.31\,\frac{\text{MPa cm}^3}{\text{K mole}}\ 300\,\text{K}}$$

$$n^i = 0.0802\ \text{mole}$$

Tank In flow

$$d(nU) = H^{in}\,dn^{in}$$

$$\int d(nU) = \int H^{in}\,dn^{in}$$

$$U^f n^f - U n^i = H^{in}(n^f - n^i)$$

$$= (U^{in} + RT^{in})(n^f - n^i)$$

$$n^f(U^f - U^{in}) - n^i(U^i - U^{in}) = RT^{in}(n^f - n^i)$$

✓ ✓ ✓

$$n^f C_v (T^f - T^{in}) - n^i C_v (T^i - T^{in}) = RT^{in}(n^f - n^i)$$

— ✓ — ✓ ✓ ✓ ✓ ✓ ✓ ✓ ∅ ✓

2 unknowns 1 eqn & $n_f = \frac{P_f V}{RT_f}$

$$\frac{P_f V}{R} C_v\left(1 - \frac{T^{in}}{T_f}\right) - n^i C_v (T^i - T^{in}) = RT^{in}\left(\frac{P_f V}{RT_f} - n^i\right)$$

~~$\frac{P_f V}{R} C_v (T_f - T^{in}) - n^i C_v T_f (T^i - T^{in}) = RT^{in}\left(\frac{P_f V}{R} - n^i T_f\right)$~~

$$T_f\left(\frac{P_f V C_v}{R} - n^i C_v (T^i - T^{in}) + RT^{in} n^i\right)$$

$$= RT^{in}\frac{P_f V}{R} + \frac{P_f V C_v T^{in}}{R}$$

$$T_f = \left(\frac{T^{in} P_f V}{R}(R + C_v)\right) \Big/ \left(C_v\left(\frac{P_f V}{R} - n^i (T^i - T^{in})\right) + RT^{in} n^i\right)$$

$$n_f = \frac{P^f V}{R T^f}$$

$$\overset{\circ}{n} = \left(\frac{n_f - n_i}{30\ s} \right)$$

$$T_f = \frac{\dfrac{350\,°K\ 1.0\,MPa\,2000\,cm^3}{\cancel{8.31}\ \frac{MPa\,cm^3}{K\,mole}}\ \dfrac{7}{2}\ \cancel{8.31}\ \frac{MPa\,cm^3}{K\,mole}}{8.31\ \cancel{\frac{mole}{MPa}}\ \dfrac{5}{2} \left(\dfrac{1.0\,MPa\ 2000\,cm^3}{8.31\ \frac{MPa\,cm^3}{K\,mole}} - 0.0802\,mole\,(300\,°K - 350\,°K) + 8.31\ \frac{cm^3\,MPa}{mole\,°K}\ 350\,°K\ 0.0802\,mole \right)}$$

$$= \frac{2{,}450{,}000\ MPa\,K\,cm^3}{5000\ MPa\,cm^3 + 83.3\ MPa\,cm^3 + 233\ MPa\,cm^3}$$

$$\boxed{T_f = 460\,°K \quad (188\,°C)}$$

$$n_f = \frac{1\,MPa\ 2000\,cm^3}{8.31\ \frac{MPa\,cm^3}{mole\,°K}\ 460} = 0.523\ mole$$

$$\overset{\circ}{n} = \frac{n_f - n_i}{30\,s} = 0.0148\ mole/s = 0.886\ \frac{mole}{min}$$

(b) ③

$\mathring{n}^{in}$

300°K
10 bar
Zeolite 2 ml/g × 2000 g = 4000 ml N_2

↓ 0.1 mole/min O_2 + Argon
$\mathring{n}^{out}$

Air 78% N_2
21% O_2
1% Argon

$$\mathring{n}^{out} = 0.22\,\mathring{n}^{in}$$

$$\boxed{\mathring{n}^{in} = \frac{0.1\ \text{mole/min}}{0.22} = 0.455\ \text{mole/min}}$$

2 ml N_2 at 10 bar 300°K

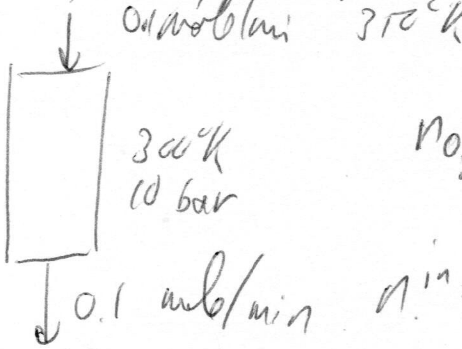
$$n = \left(\frac{PV}{RT}\right) = \frac{1.0\ \text{MPa}\ 4000\ \text{cm}^3}{8.31\ \frac{\text{MPa cm}^3}{\text{mole °K}}\ 300} = 1.60\ \text{mole } N_2$$

$$\mathring{n}^{in}_{N_2} = 0.455\ \frac{\text{mol}}{\text{min}}\ 0.78 = 0.355\ \text{mol/min}$$

$$\boxed{t = \frac{\text{Capacity}}{\text{Needed}}\ \text{in} = \frac{1.60\ \text{mole}}{0.355\ \text{mole/min}} = 4.51\ \text{min}}$$

④

Consider the Oxygen [illegible]



$n_{O_2} = \frac{1.0 MPa \; 2000 cm^3}{RT} = 0.802$ mole

$n^{in} = n^{out}$

$$d(nU) = H^{in} dn^{in} - H^{out} dn^{out}$$

$$n\,dU = (H^{in} - H)\left(\frac{dn}{dt}\right) dt$$

$$n\,C_v dT = (T^{in} - T)\,C_p \left(\frac{dn}{dt}\right) dt$$

~~$T = T^{in} +$~~

$$\frac{dT}{(T^{in} - T)} = \frac{C_p}{n C_v}\left(\frac{dn}{dt}\right) dt$$

$$x = T^{in} - T$$

$$dx = -dT$$

$$-\ln\left(\frac{T^{in} - T^f}{T^{in} - T^i}\right) = \frac{C_p}{n C_v}\left(\frac{dn}{dt}\right) t$$

$$T = T^{in} - (T^{in} - T^i)\exp\left(-\frac{C_p}{n C_v}\left(\frac{dn}{dt}\right) t\right)$$

$$= 350°K - 50°K \exp\left(-\frac{7}{5(0.802 \text{ mole})} \, 0.1 \frac{\text{mole}}{\text{min}} \; 4.51 \text{ min}\right)$$

$$T = 327°K$$

Consider N_2

$$n_{N_2} = t\left(\frac{dn}{dt}\right)_{N_2} = (4.5\ \text{min})\left(3.55\ \frac{\text{mole}}{\text{min}}\right)_{N_2}$$

$$= 16.0\ \text{mole}\ N_2$$
@ 350°K

Add 16 mole N_2 @ 350°K
to
0.802 mole O_2 @ 327°K

$$dU_{N_2} = Q_{N_2} = -Q_{O_2} = dU_{O_2}$$

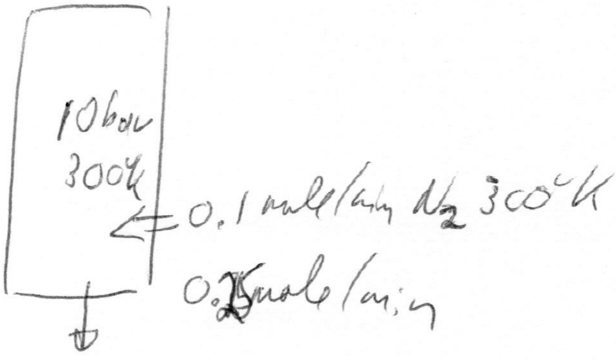
$$n_{N_2}\cancel{C_{V_{N_2}}}(T_f - T_{\substack{N_2\\i}}) = -\cancel{C_{V_{O_2}}}(T_f - T_{\substack{O_2\\i}})\,n_{O_2}$$

$$T_f = \frac{n_{N_2}T_{N_2} + T_{O_2}n_{O_2}}{n_{N_2} + n_{O_2}}$$

$$T_f = \frac{16.0\ \text{mole}\ (350°\text{K}) + 0.802\ \text{mole}\ (327°\text{K})}{(16.0 + 0.802)\ \text{mole}}$$

$$T_f = 349\ °\text{K}$$

c)



$$n_i = \frac{1.0\,MPa\ 2000\,cm^3}{R(300\,°K)} = 0.802\ mole$$

$P_f = 1.5$ bar $t = ?$

$$\overset{Tank}{d(nU)} = H^{\overset{in}{\cancel{out}}}dn^{in} - H^{out}dn^{out}$$

$$\left(\frac{dn}{dt}\right)^{in} = 0.1\ mole/min\ N_2 \qquad \left(\frac{dn}{dt}\right)^{out} = 0.25\ \frac{mole}{min}$$

$$\left(\frac{dn}{dt}\right)_{tank} = 0.15\ \frac{mol}{min}$$

$$H^{in} = H^{out} = H^{tank}$$

~~$U\left(0.15\frac{mol}{n}\right)dt = H\left(0.15\frac{mol}{min}\right)dt$~~

$$U\left(\frac{dn}{dt}\right)_{tank}dt + n\,dU = H\underbrace{\left(\left(\frac{dn}{dt}\right)^{in} - \left(\frac{dn}{dt}\right)^{out}\right)}_{\left(\frac{dn}{dt}\right)_{tank}}dt$$

$$n\,dU = (H - U)\left(\frac{dn}{dt}\right)^{tank}dt$$

$$\begin{matrix} dU & & H-U \\ \downarrow & & \\ C_v\,dT & & RT \end{matrix}$$

$$\frac{n}{dn} = \frac{R}{C_v}\ \frac{T}{dT} \qquad \frac{dn}{n} = \frac{C_v}{R}\ \frac{dT}{T}$$

$$\ln\frac{n}{n_i} = \frac{C_v}{R}\ln\frac{T}{T_i}$$

$$n = n_i - \left(\frac{dn}{dt}\right) t$$

$$\frac{n}{n_i} = 1 - \frac{\left(\frac{dn}{dt}\right)}{n_i} t$$

$$\ln\frac{T}{T_i} = \frac{R}{C_p} \ln\frac{P}{P_i} \quad \text{(ex. 2.15)}$$

$$n = n_i \exp\left(\frac{C_v}{C_p} \ln\frac{P}{P_i}\right)$$

$$t = \frac{(n_i - n)}{(dn/dt)} = \frac{n_i\left(1 - \exp\left(\frac{C_v}{C_p} \ln\frac{P}{P_i}\right)\right)}{(dn/dt)}$$

$$t = \frac{0.802\,\text{mol}\left(1 - \exp\left(\frac{5}{7} \ln\left(\frac{1.5\,\text{bar}}{10\,\text{bar}}\right)\right)\right)}{0.15\,\text{mol/min}}$$

$$\boxed{t = 3.97\ \text{min}}$$

$$T = T_i \exp\left(\frac{R}{C_p} \ln\frac{P}{P_i}\right)$$

$$= 300\text{K} \exp\left(\frac{2}{7} \ln\frac{1.5\,\text{bar}}{10\,\text{bar}}\right)$$

$$\boxed{T = 174^\circ\text{K}}$$

d) Significant Cooling occurs on desorption & de Compression Part(c)

Significant Heating occurs on compression Part (a)

A heat exchanger could transfer this heat to the other tank & would improve the process efficiency