Lecture # 3

Thermodynamics of Ideal Gas Mixtures and Separation

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1. Ideal Gas Mixtures
2. Entropy of mixing
3. Ideal separation work
4. Air separation for O_2 production
5. CO_2 separation from products and air.

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Ideal Gas Mixture

mass fraction $Y_i = m_i / m, \quad m = \sum_{i=1}^{N} m_i$ where mass of component is m_i

number of moles $n_i = m_i / \widetilde{M}_i$, where $\widetilde{M}_i$ is molecular weight, and mole fraction $X_i = n_i / n, \quad n = \sum_{i=1}^{N} n_i$

mass and mole fractions are related $X_i = \dfrac{\left(Y_i / \widetilde{M}_i\right)}{\left(\sum_{i=1}^{N}\left(Y_i / \widetilde{M}_i\right)\right)}, \quad Y_i = \dfrac{\left(X_i \widetilde{M}_i\right)}{\sum_{j=1}^{N}\left(X_j \widetilde{M}_j\right)}$

Equation of state: $p\forall = n\Re T$, for an ideal gas.

partial pressure: $p_i \forall = n_i \Re T$, $p_i = X_i p$ (all components occupy same total voume $\forall$)

partial volume: $\forall_i = \dfrac{n_i \Re T}{p}$, and $\forall_i / \forall = \dfrac{n_i}{n} = X_i$ (as if all components were at same p)

Component	Molecular weight M_i	Mole fraction X_i	Vol. fraction $\forall_i / \forall$	Partial pressure $p_i = X_i p$	Mass fraction
N_2	28.016	0.7803	0.7803	0.7803	0.7546
O_2	32.000	0.2099	0.2099	0.2099	0.2319
Ar	39.944	0.0098	0.0098	0.0098	0.0135

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Ideal Gas Mixture

for ideal mixture (and gases)

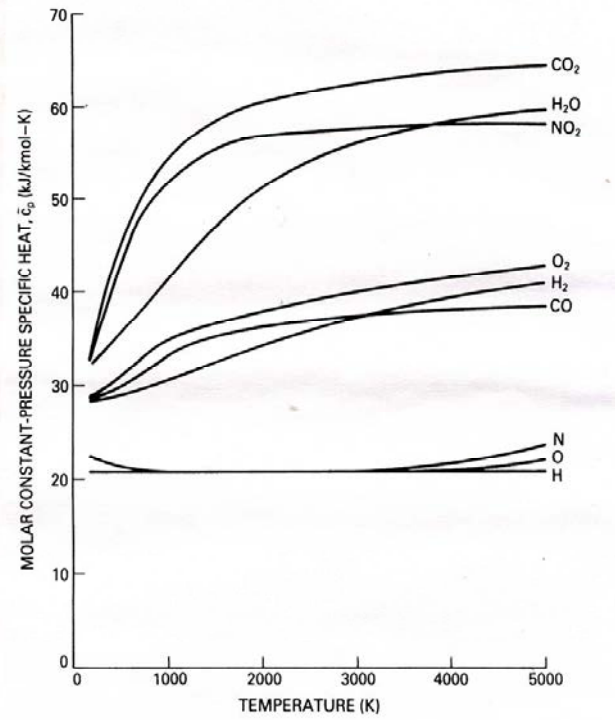
mixing does not affact the properties of individual components

(enthaply of mixing = 0)

Enthalpy of a mixture: $h = \sum_{i=1}^{N} Y_i \, h_i(T)$

$$\hat{h} = \sum_{i=1}^{N} X_i \, \hat{h}_i(T),$$

$$h_i = h_i^o + \int_{T^o}^{T} c_{p,i}(T)\,dT, \qquad \hat{h}_i = \hat{h}_i^o + \int_{T^o}^{T} \hat{c}_{p,i}(T)\,dT$$



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Entropy of a Mixture

entropy of ideal gas: $\hat{s}(T,p) = \hat{s}^o(T) - \Re\, \ell n \frac{p}{p^o}$,

$$\hat{s}^o(T) = \hat{s}^{oo} + \int_{T^o}^{T} \frac{\hat{c}_p(T)}{T} dT$$

Entropy of a mixture: $\hat{s}(T,p) = \sum_{i=1}^{N} X_i \hat{s}_i(T,p_i) = \sum_{i=1}^{N} X_i \left\{ \hat{s}_i^o(T) - \Re \ell n \frac{p_i}{p^o} \right\}$

$$= \underbrace{\sum_{i=1}^{N} X_i \hat{s}_i^o(T) - \Re\, \ell n \frac{p}{p^o}}_{\text{entropy before mixing}} - \Re \sum_{i=1}^{N} X_i\, \ell n X_i$$

(when all gases were at p and their partial volme)

Entropy of Mixing: $(\Delta \hat{s})_g = \left(\hat{s}_{\text{after mixing}} - \hat{s}_{\text{before mixing}} \right) = -\Re \sum_{i=1}^{N} X_i \ell n X_i$ (always positive)

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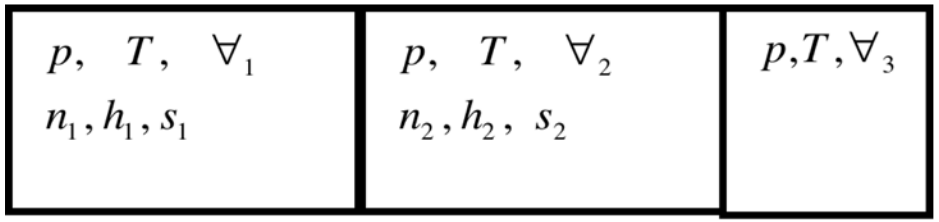
Spontaneous mixing of gases at same T and p



$$p,\ T,\ \sum \forall,\ p_i = X_i p,\ X_i = \forall_i / \forall$$
$$H = \sum n_i \hat{h}_i, S = \sum n_i \hat{s}_i (T, p_i) \quad ,$$

Entropy is generated as gases, with initial volumes $\forall_i$ but same (T, p) mix at constant T and "total" p. Following mixing $\forall = \sum_i \forall_i$.

Thus, during mixing, each component expands freely, lowering its pressure from p to $p_i = \forall_i / \sum \forall_i = X_i \forall$, without doing work.

The lost work, $T_o (\Delta \hat{s})_g$, is the "chemical potential" for doing work.

It is also the "chemical availability", more on that later.

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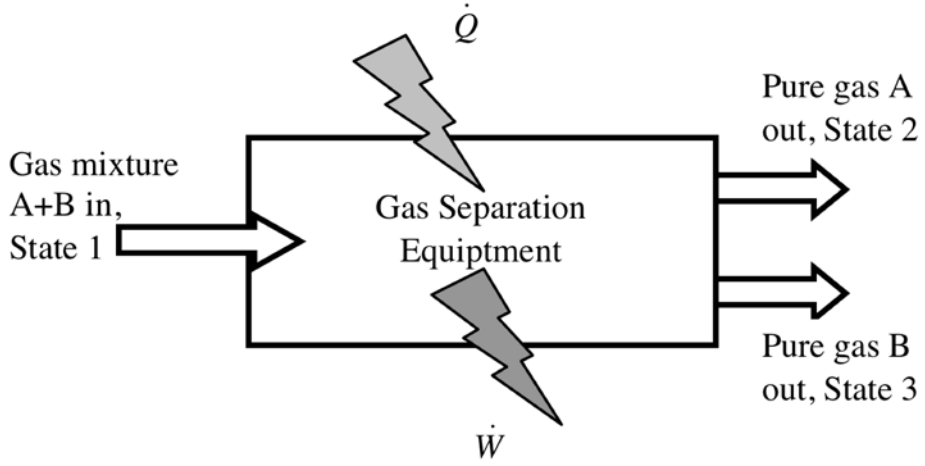
Ideal Work of Separation, steady continuous flow:



First Law: $\dot{Q} - \dot{W} + \dot{n}_1 \hat{h}_1 - \left(\dot{n}_a \hat{h}_{a2} + \dot{n}_b \hat{h}_{b3} \right) = 0$

Second Law: $\dfrac{\dot{Q}}{T_0} + \dot{n}_1 \hat{s}_1 - \left(\dot{n}_a \hat{s}_{a2} + \dot{n}_b \hat{s}_{b3} \right) + \dot{S}_g = 0$

$$-\dot{W} = \left[\dot{n}_a \left(\hat{h}_{a2} - T_0 \hat{s}_{a2} \right) + \dot{n}_b \left(\hat{h}_{b3} - T_0 \hat{s}_{b3} \right) \right] - \dot{n}_1 \left(\hat{h}_1 - T_0 \hat{s}_1 \right) + T_o \dot{S}_g$$

per one mole of original mixture, $w = \dot{W} / \dot{n}_1, \quad X_a = \dot{n}_a / \dot{n}_1, \quad X_b = \dot{n}_b / \dot{n}_1$

$$-\hat{w}_{\min} = X_a \left[\left(\hat{h}_{a2} - \hat{h}_{a1} \right) - T_0 \left(\hat{s}_{a2} - \hat{s}_{a1} \right) \right] + X_b \left[\left(\hat{h}_{b3} - \hat{h}_{b1} \right) - T_0 \left(\hat{s}_{b3} - \hat{s}_{b1} \right) \right]$$

For "least" minimum work, (1) out streams must be in thermal equilibrium with environment,

$$T_1 = T_2 = T_3 = T_0, \quad \frac{\hat{w}_{\min}}{\Re T_0} = X_a \ell n \left(X_a \frac{p_1}{p_{a2}} \right) + X_b \ell n \left(X_b \frac{p_1}{p_{b3}} \right)$$

and (2) out stream must be in mechanical equilibrium with environment,

$$p_1 = p_2 = p_3 = p_0, \quad \frac{\hat{w}_{\min}}{\Re T_0} = X_a \ell n X_a + X_b \ell n X_b = \sum_N X_i \ell n X_i$$

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For a mixture with "two" components, X_1 and $(1\text{-}X_1)$,

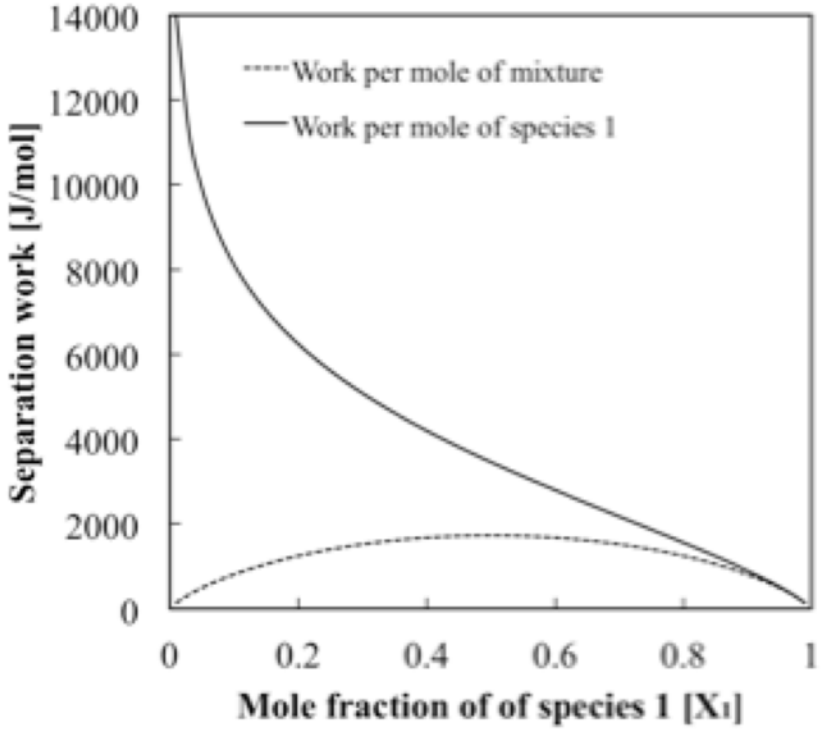
minimum work per mole of mixture:

$$\hat{w}_{mole\,of\,mixture} = -\Re T_o \left(X_1 \ell n X_1 + (1 - X_1) \ell n (1 - X_1) \right)$$

work per mole of component 1 is:

$$\hat{w}_{mole\,of\,X_1} = \frac{\hat{w}_{mole\,of\,mixture}}{X_1} = -\Re T_o \left(\ell n X_1 + \frac{(1 - X_1)}{X_1} \ell n (1 - X_1) \right)$$

Work of separation, at T = 300 K.



EXAMPLE: Production of argon by separating it from air:

Air contains 0.9% argon, and 99.1% of nitrogen and oxygen, by volume,

that is: $X_{Ar} = 0.009$ and $X_{O_2+N_2} = 0.991$.

$$\hat{w}_{mole\text{-}mixture} = -\Re T_o \left(X_1 \ell n X_1 + (1 - X_1) \ell n (1 - X_1) \right) \approx -\Re T_o \, X_1 \ell n X_1$$

Substituting, at 25°C, we get -0.127 MJ/kmol of air, or –14.3 MJ/kmol of argon.

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Work Done in an Air Separation Unit:

@1 atm and 25 C. mole fractions are 0.21 of O_2 and 0.79 of N_2.

$$\hat{w}_{mole\text{-}mixture} = -\Re T_o \left(X_1 \ell n X_1 + (1 - X_1) \ell n (1 - X_1) \right), \Re = 8.314 \text{ kJ/kmol.K}$$

Minimum work per kmol of air is –1.273 MJ/kmol of air.

OR 1.611 MJ/kmol of N_2, OR 6.061 MJ/kmol of O_2

(Available technology consumes ~ 30 MJ/kmol of O_2)

Second law efficiency of separation is low: 10-30%.

Enthalpy of reaction of methane (LHV) ~ 800 MJ/kmol methane

(with 50% efficiency, work is ~ 400 MJ/kmol methane)

2 moles of oxygen are required for each mole of methane:

Separation energy penalty in oxy-combustion of gas

$$\text{(in \%) is } \frac{2.0 \times 6.06}{(\eta_{II} = 0.2) \times 400} \approx 15\% \text{ of original energy}$$

Need better air separation technology

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Direct Air Capture (DAC)

Work for separating CO_2 from air with 500 ppm:

Take: $X_{CO_2} \sim 0.0005$ and $X_{O_2+N_2} = 0.9995$.

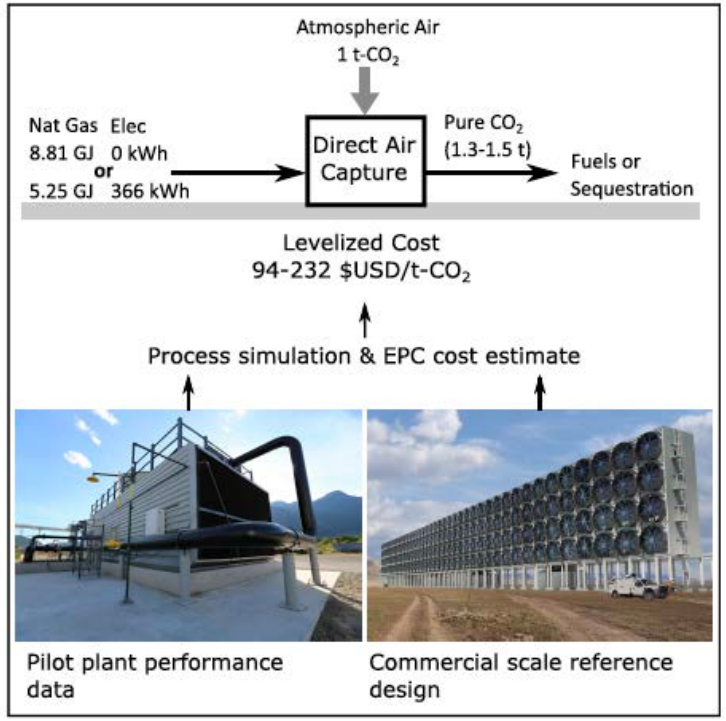
$\hat{w}_{unitCO_2} \approx -\Re T_o \ \ell n X_1, \Re = 8.314$ kJ/kmol.K

At 25°C, we get 18.415 MJ/kmol CO_2 or 0.418.5 MJ/kg CO_2

Recent paper (Keith et al., Joule, 2, 2018. Company: Carbon Engineering) claims 8.8 GJ_{th}/ton CO_2 (from methane burning). Assuming 50% efficiency, equivalent work is 4.4 MJ_e/kg CO_2.

It seems that the second law efficiency of this technology is ~ 10%

This is not unreasonable since it accounts for the process inefficiencies (plenty, will be discussed later), the work of sucking all this air as well compressing CO_2 to storage conditions (~ 150 bar!).



Keith et al., Joule, 2, 2018

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$$C_6H_6 + 7.5\left(O_2 + 3.76N_2\right) \Rightarrow 6CO_2 + 3H_2O + 7.5x3.76N_2$$

Ideal Work for CO_2 Separation from combustion products (post combustion capture):

The concentrations are: $X_{CO_2} = 0.16$ and $X_{H_2O+N_2} = 0.84$. At T_0~300K,

$$w_{\min} = \Re T_o\left(X_1 \ell n X_1 + (1 - X_1)\ell n(1 - X_1)\right) = 1.107 \text{ MJ/Kmol mix}$$

$$= 6.92 \text{ MJ/Kmol } CO_2 = 0.16 \text{ MJ/kg } CO_2$$

Also: the work is 41.1 MJ/kmol of benzene.

The enthalpy of reaction of benzene is 3171 MJ/kmol.

Taking 40% efficient cycle, the "useful" work produced is 1268.4 MJ/kmol of benzene.

There is a penalty of 3.25% for the separation of CO_2 at T =27C.

Actual separation processes require more work (5-10 time) due to irreversibility.

Thus, efficiency penalty can be as large as 32.5% of the original work.

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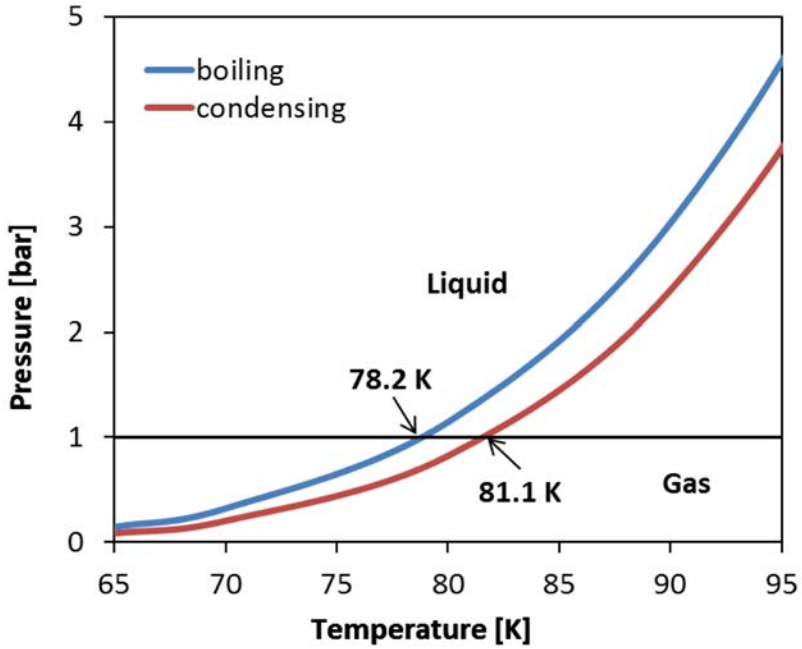
Air Liquefaction

(used extensively in air separation,
and could be a good large scale storage option)

At atmospheric pressure, the boiling/condensation temperature of oxygen is 90 K (-183 C) and of nitrogen is 77 K (-196 C) (nitrogen is more volatile than oxygen as it evaporates at lower temperature).

When air is cooled at atm. pressure, it remains gas till 81.6 K. and completely liquefy at 79 K (inverse when heated)



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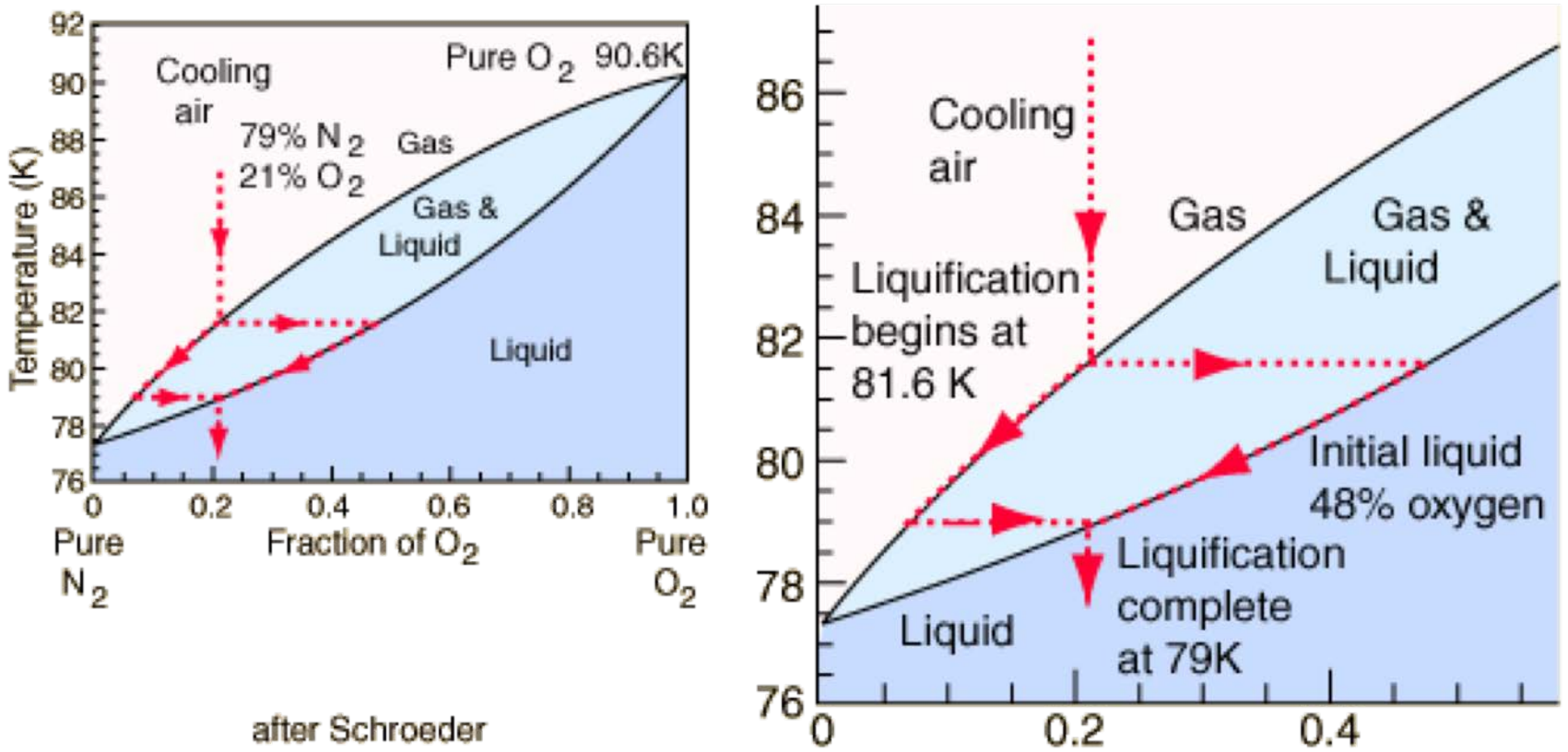
Air Liquefaction Process



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Ref: http://hyperphysics.phy-astr.gsu.edu/hbase/thermo/liqair.html

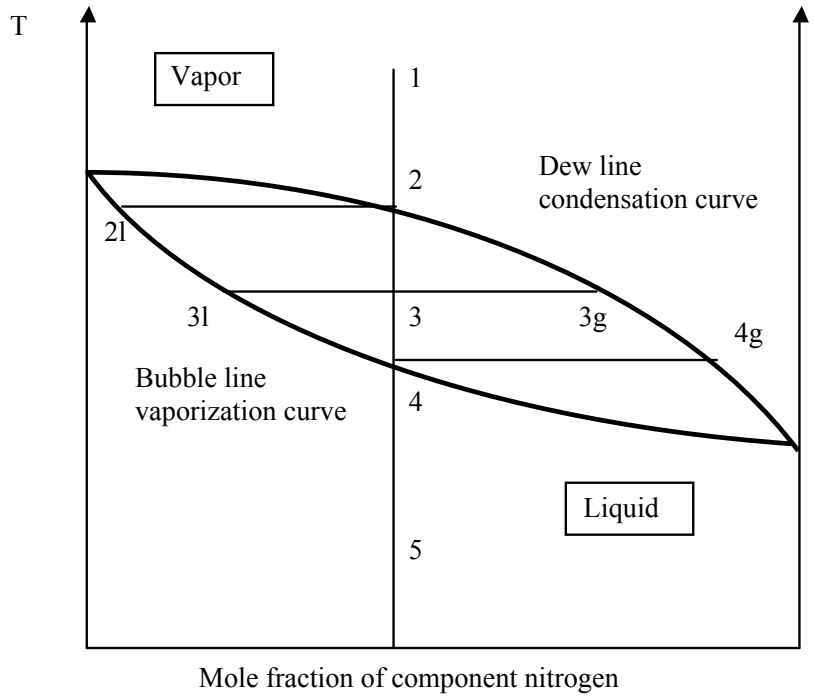
Introduction to binary mixture phase diagram

When cooling a mixture starting at 1, we see the following:

2 is where condensation starts, with 2l being the liquid mixture composition of the first element to condense, it is mostly oxygen

@ 3, 3l is the liquid mixture composition (still mostly oxygen) and 3g is the gas mixture composition (mostly nitrogen).

4 is the last gas element, 4g is that gas mixture composition (left after condensation), it is mostly nitrogen.



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