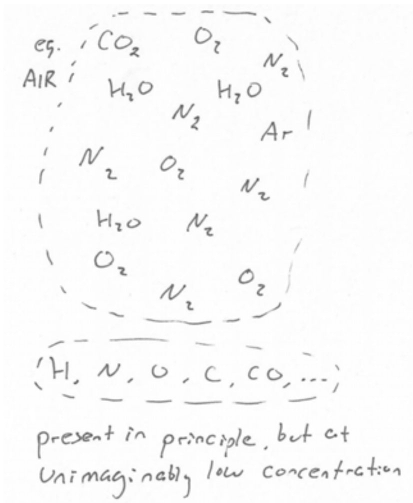
3.020 Lecture 13

Prof. Rafael Jaramillo

1 Gas mixtures: Homogeneous, multicomponent systems



- Phase = Gas
- Components = N_2, O_2, Ar, CO_2, H_2O, ...
- Elements = N, O, Ar, C, H, ...

---

2 Dalton's law of partial pressures

In a gas mixture, each component contributes a partial pressure to the total pressure in proportion to its mole fraction
e.g. 2 component $P = P_1 + P_2$ and $P_i = P\ \frac{n_i}{n_{TOT}} = P\ X_i$

mole fraction

---

3 Reactions can change: components & phase

but not elements

ex. reaction that changes components but not phase

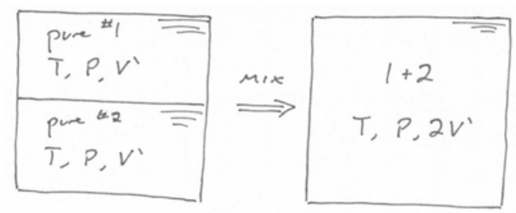
$$\frac{1}{2}N_2(g) + \frac{1}{2}O_2(g) = NO_2(g)$$

ex. reaction that changes components and phase

$$H_2(g) + \frac{1}{2}O_2(g) = H_2O(l)$$

---

4 Ideal gas mixtures (a.k.a solutions)



Ideal gas molecules don't interact

$$\Downarrow$$

Each component acts as if it undergoes isothermal expansion

$$\Delta G_i^{'} = n_i RT \ln(\frac{P_i}{P})$$

$$G_i = G_i^o + RT \ln(\frac{P_i}{P^o})$$

(G_i^o, P^o) = some standard state. e.g. 1 atm

---

5 Notation

G_i = molar, intensive property = $G_i^{'}/n_i$, "Gibbs free energy per mole of i"
$G_i^{'}$ = extensive property of component i
G_i^o = molar Gibbs free energy of component i in its standard state
Standard state for gases: Pure gas at standard pressure $P^o = 1\ bar$ and same temperature as the system in question

---

6 Chemical potential and ideal gas mixtures

$$dG^{'} = -S^{'}dT + V^{'}dP + \sum_i \mu_i dn_i \quad \Longrightarrow \quad \mu_i = \frac{\partial G^{'}}{\partial n_i}_{T,P,n_{j\neq i}}$$

using result from board 4

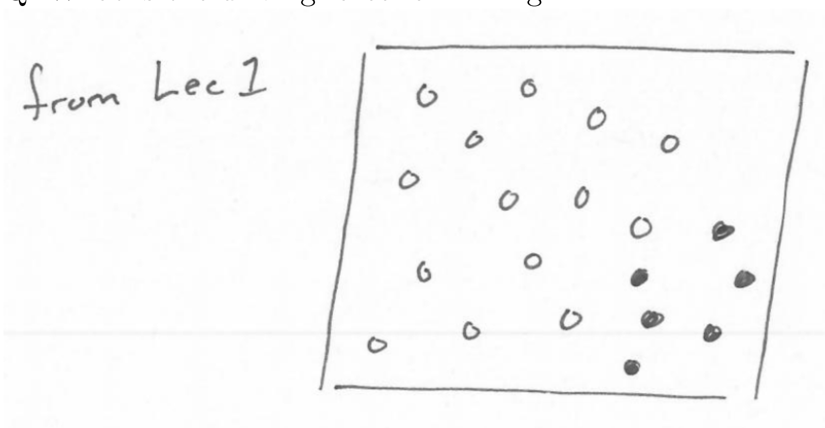
$$\mu_i = \mu_i^o + RT \ln(\frac{P_i}{P^o})$$

μ_i : chemical potential at component i;
μ_i^o : relative to standard state;
$RT\ln(\frac{P_i}{P^o})$: at temp. T and partial pressure P_i

---

Q. Do ideal gases mix spontaneously ?

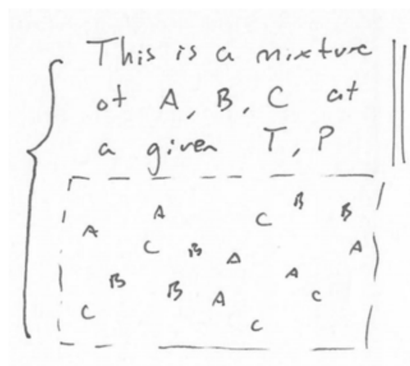
Q. What is the driving force for mixing ?



---

7 Balancing chemical reactions

ex. gas phase reaction $A + B = 2C$



- reax. balance

  $$O = 2C - A - B = V_c C + V_A A + V_B B$$

  defines stoichiometric coeffs. V_i

- $V_i' s$ come from conservation of atoms

  constraints on $dn_i' s$

- Constraints on $dn_i' s$

$$\underbrace{\frac{dn_A}{V_A} = \frac{dn_B}{V_B} = \frac{dn_C}{V_C}} = d\xi, \quad \xi = \textbf{reax. extent}$$

$$\underbrace{M - 1 \quad \textbf{equations in M variables}}$$

reduces to 1 independent variable

ex. $dn_A = \frac{V_A}{V_C}\, dn_C, \quad dn_B = dn_A$

using either one of n_A, n_B, or n_C as indep. var.

---

8 Coupled reactions

e.g.

$$HNH_3 + 5O_2 = 4NO + 6H_2O \tag{1}$$

$$HNH_3 = 2N_2 + 6H_2 \tag{2}$$

$$2N_2 + 3O_2 = 4NO \tag{3}$$

$$6H_2 + 3O_2 = 6H_2O \tag{4}$$

$$(1) = (2) + (3) + (4)$$

- Overall change in state variables is the sum of changes between intermediate states
  e.g. $\Delta G^{[1]} = \Delta G^{[2]} + \Delta G^{[3]} + \Delta G^{[4]}$
- Each reaction will obey its own equilibrium balance (next time)