

Lecture 4 - Fundamental Engs

Chemical engineers concerned with stuff
that is

- a) not single component
- b) not ideal
- c) not single phase
- d) some combination of a, b, c

Need some representative fund engs.

- 1. ideal mixture
- 2. vdW fluid

ideal gas mixture

Would like $S(U, V, N_1, N_2, \dots)$

Assume additive behavior

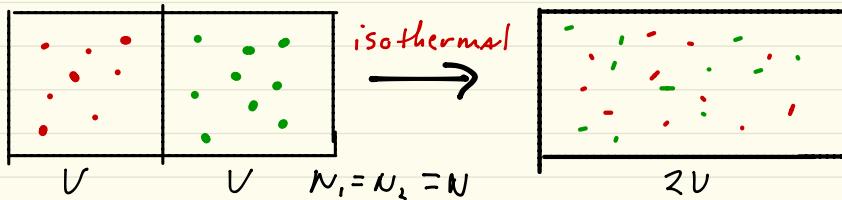
$$PV = RT \sum_i N_i = \sum_i P_i \quad U = RT \sum_i c_i N_i = \sum_i u_i$$

$$S(T, V, N) = c NR \ln \frac{T}{T_0} + NR \ln \frac{V}{Nv_0} + Ns_0$$

Assume - not enough eqns to derive

$$S = \sum_i N_i (s_{i0} + c_i R \ln \frac{T}{T_0} + R \ln \frac{V}{N_i v_0}) = \sum_i s_i$$

Could eliminate T from this, just messy



$$\Delta U = 0 \quad \Delta P = 0 \quad \Delta S = ?$$

$$S_e = N(s_{i0} + c_i R \ln \frac{T}{T_0} + R \ln \frac{V}{N_i v_0}) \quad \text{ditto } s_r$$

For mixture, helpful to rewrite $\text{mult by } \frac{N}{N}$

$$S = \sum_i N_i (s_{i0} + c_i R \ln \frac{T}{T_0}) + \sum_i N_i \left(R \ln \frac{V}{N_i v_0} \frac{N}{N} \right)$$

$$S = \sum_i N_i \left(S_{i,0} + c_i R \ln \frac{T}{T_0} \right) + N R \ln \frac{V}{N V_0} - R \sum_i N_i \ln \frac{n_i}{N}$$

mixture:

entropy of mixing

$$\begin{aligned} S_{\text{mix}} &= N \left(S_{e,0} + c_e R \ln \frac{T}{T_0} \right) + N \left(S_{r,0} + c_r R \ln \frac{T}{T_0} \right) \\ &\quad + 2 N R \ln \frac{2V}{2NV_0} - R \sum_i N_i \ln x_i \\ &= S_e + S_r - R \sum_i N_i \ln x_i \end{aligned}$$

$$\Delta S_{\text{mix}} = -R \sum_i N_i \ln x_i$$

Entropy to combine gases keeping density constant ^{total}

Written $-R \sum_i x_i \ln x_i$ on per mole basis

-Work necessary to "unmix"

What is the minimum work to separate a mixture of 50:50 mixture into one that is 90:10 + the other 10:90, @ const T + P?

$$\boxed{x_1 = x_2 = \frac{1}{2}} \rightarrow \boxed{\begin{aligned} x_1 &= 0.9 \\ x_2 &= 0.1 \end{aligned}} + \boxed{\begin{aligned} x_2 &\geq 0.9 \\ x_1 &> 0.1 \end{aligned}}$$

$$\Delta u + q_{rhs} + w_{rws} = 0 \quad T \text{ const} \rightarrow \Delta u = 0$$

$$w_{rws} = -q_{rhs}$$

$$\Delta S + \frac{q_{rhs}}{T_{rhs}} = 0$$

$$\begin{aligned} \Delta S &= s_f - s_i = \left(-\frac{1}{2} R (0.9 \ln 0.9 + 0.1 \ln 0.1) \right. \\ &\quad \left. - \frac{1}{2} R (0.1 \ln 0.1 + 0.9 \ln 0.9) \right) \\ &\quad + R (0.5 \ln 0.5 + 0.5 \ln 0.5) \end{aligned}$$

$$R (\ln 0.5 - 0.9 \ln 0.9 - 0.1 \ln 0.1) = -0.37 R$$

$$q_{rhs} = -T_{rhs} \Delta S = T_{rhs} R (0.37)$$

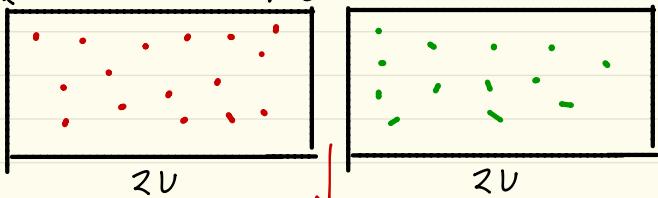
$$w_{rws} = -T_{rhs} R (0.37)$$

how? membrane, centrifuge, absorption ...

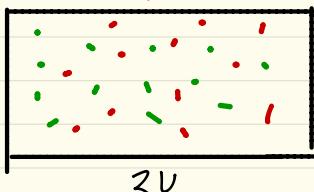
work becoming heat

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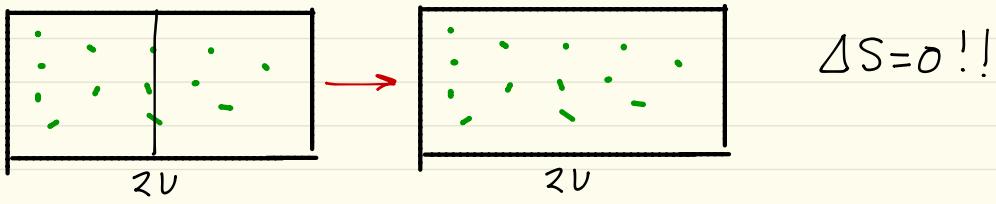
Compare: $S_g = \dots + N R \ln \frac{2V}{Nv}$ $S_r = \dots +$



$$\Delta S_{\text{mix}} = 0 !$$



$$S_{\text{mix}} = \dots + 2 N R \ln \frac{2V}{2Nv_s} + 2 N R \ln 2 = S_g + S_r$$



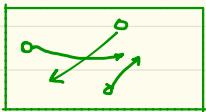
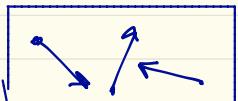
$$\Delta S = 0 !!$$

Gibbs' "paradox"

μ view: 50:50 vastly dominates all else. If green are indistinguishable, opening door doesn't add any more M states.

VAN DER WAALS fluid

Ideal gas assumes molecules have no volume and do not interact energetically, so they never condense



$$V \rightarrow V - Nb \quad b \text{ size molecule}$$

$$P \rightarrow P - \frac{a}{V^2}$$

Pressure reduced by attractions btwn molecules. Attractions go as density of molecule-molecule pairs $\frac{1}{V^2}$

$$P = \frac{RT}{V} \rightarrow \boxed{\frac{RT}{V-b} - \frac{a}{V^2}}$$

vdW eqn 1873
Nobel prize 1910

a, b constants different for each real gas
qualitatively realistic, not quantitative

b : units of volume $\sim 50 \text{ \AA}^3$ Ar

a : units pressure · volume² = energy · volume

$$\text{Ar} \sim 0.1 \text{ J m}^3/\text{mol}^2 \sim 2.2 \text{ eV \AA}^3$$

$$\text{isotherms } (P + \frac{a}{V^2})(V-b) = RT$$

$$\text{compare } PV = RT$$

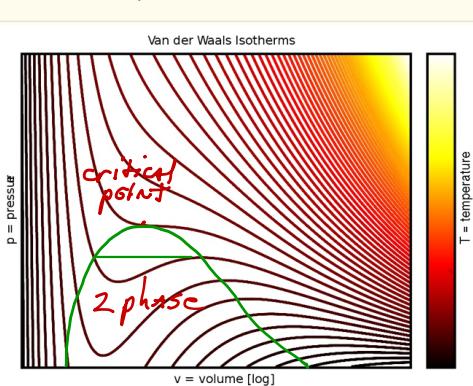
reduces to ideal gas as $V \rightarrow \infty$

Called a "cubic" EOS because of dependence on v :

$$v^3 - \left(b + \frac{RT}{P}\right)v^2 + \frac{a}{P}v - \frac{ab}{P} = 0$$

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Given $T, P \rightarrow$ multiple v roots
 Given $T, v \rightarrow$ single roots
 P, v



ideal gas region

phase split

fluid region - at least it condenses!

Simplest EOS that gives us two phases.

This is one EOS; we need another to be able to construct fundamental eq.

Simplest possible consistent with vdW is

$$u = cRT - \frac{a}{v} \quad \text{internal energy reduced by attraction b/w molecules}$$

$$\text{Get } \frac{1}{T} = \frac{cR}{u + \frac{a}{v}} \quad \frac{P}{T} = \frac{R}{v-b} - \frac{acR}{uv^2 + av}$$

$$ds = \left(\frac{1}{T}\right)du + \left(\frac{P}{T}\right)dv$$

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Integrating (yech!) gives

$$S = S_0 + R \ln\left(\frac{v-b}{v^0-b}\right) + C R \ln\left(\frac{u+a/v}{u^0+a/v^0}\right)$$

Compare ideal gAS

$$S(u, v) = C R \ln\left(\frac{u}{u^0}\right) + R \ln\left(\frac{v}{v^0}\right) + S_0$$

Note similar appearance of volume & energy terms, from mechanical view.

vdW Adiabats (S constant)

$$(v-b)\left(u+\frac{a}{v}\right)^c = \text{const}$$

$$\text{Some algebra gives } u + \frac{a}{v} = c(P + \frac{a}{v^2})(v-b)$$

$$\text{Adiabat } (P + \frac{a}{v^2})(v-b)^\gamma = \text{const} \quad \gamma = \frac{C+1}{C}$$

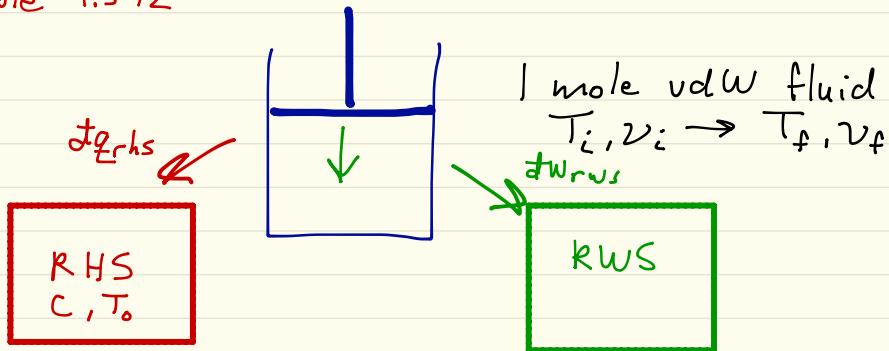
$$\text{ideal gAS } PV^\gamma = \text{const.}$$

Can do same sort of calculations as with ideal gAS. Eg isothermal expansion:

$$W_{iso} = - \int P dV = -N \int \left(\frac{RT}{v-b} - \frac{a}{v^2} \right) dv$$

On homework will compare ideal + vdW cases.

Example 4.5-12



What is maximum work delivered? What is the final temperature?

Recall for vdW fluid:

$$U = cRT - \frac{a}{v}$$

$$\Delta U_{\text{vdW}} = cR(T - T_i) - a \left(\frac{1}{v_f} - \frac{1}{v_i} \right)$$

(you'll show that in HW 3) $S = R \ln \left[(cRT)^c (v-b) \right] + s_0$

$$\Delta S_{\text{vdW}} = R \ln \left[\left(\frac{T}{T_i} \right)^c \left(\frac{v_f - b}{v_i - b} \right) \right]$$

$$\Delta S_{\text{rhs}} = \int \frac{C}{T} dT = C \ln \left(\frac{T}{T_0} \right)$$

$$q_{\text{rhs}} = \int C dT = C(T - T_0)$$

For maximum work

$$\Delta S + \Delta S_{\text{rhs}} = C \ln \left(\frac{T}{T_0} \right) + R \ln \left[\left(\frac{T}{T_i} \right)^c \left(\frac{v_f - b}{v_i - b} \right) \right] = 0$$

Solve for $T = \left[\left(\frac{v_i - b}{v_f - b} \right)^R T_i^R T_0^c \right]^{1/c(R+1)}$

$$W_{\text{max}} = -(\Delta U + q_{\text{rhs}}) = a \left(\frac{1}{v_f} - \frac{1}{v_i} \right) - cR(T - T_i) - C(T - T_0)$$

How?