

Lecture 3 - Fundamental Eqs + Balances

1

Ideal gas

What is it? Particles with mass, no volume, interact by purely elastic collisions.

Empirically have: $PV = N k_B T = n RT$ R: gas const.

ii U only depends on T
particles don't interact

In simple case, appropriate to monatomic gases and to polyatomics over restricted T ranges, have

$$U = c N k_B T \quad c = \begin{cases} 3/2 & \text{monatomic} \\ 5/2 & \text{diatomic (rot)} \end{cases}$$

U as a variable suggests entropy representation

$$\frac{1}{T} = c \frac{N R}{U} = \frac{c R}{U} \quad \frac{P}{T} = \frac{N R}{V} = \frac{R}{v}$$

$$dS = \frac{c R}{U} dU + \frac{R}{v} dv \rightarrow$$

$$S(u, v) = c R \ln\left(\frac{U}{U^*}\right) + R \ln\left(\frac{v}{v^*}\right) + S_0, \quad S_0 = S(u^*, v^*)$$

- or

$$S(u, v, N) = N \left[R \ln \left[\left(\frac{U}{U^*} \right)^c \left(\frac{v}{v^*} \right) \left(\frac{N}{N^*} \right)^{(c+1)} \right] + S_0 \right]$$

Might be more intuitive to express in terms of T

$$S(T, v, N) = c N R \ln \frac{T}{T^*} + N R \ln \frac{v}{v^*} + N S_0$$

Could get μ by differentiation or by Gibbs-Duhem

(2)

~~Using stat. mech., can show that~~

$$S_0 = \frac{3}{2} k \left(\frac{5}{3} + \ln \frac{4\pi m}{3h^3} \right)$$

~~where m is the molecular mass and h Planck's constant.~~

Sackur-Tetrode eqn

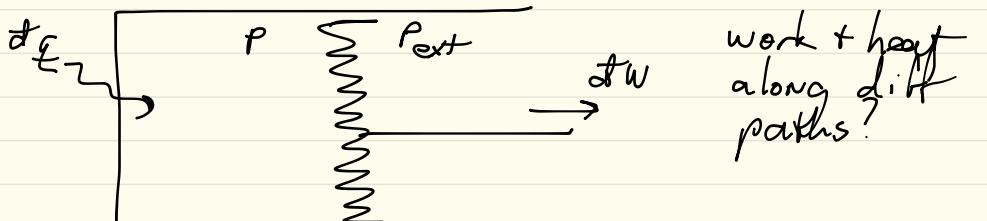
$$S(T, V, N) = cNR \ln \frac{T}{T_0} + NR \ln \frac{V}{Nv_0} + Ns_0$$

momentum DOFs position DOFs

$S = k \ln \Omega$. What are the "microstates" to count in an ideal gas?
 Each molecule specified by $\{\vec{r}, \vec{p}\}$ pair, position (scals w/V) and momentums (scals w/T)

The two EOS's above could have been inferred from gas kinetic theory + the Boltzmann distribution, and S from stat. mech.

Let's put the fundamental eq to work



$$\begin{aligned} dU &= TdS - Pdv \\ &= dQ^{\text{qs}} + dW^{\text{qs}} \end{aligned}$$

adiabatic QS work

① start from fund eq...

$$TdS = 0 \leftrightarrow dQ_{\text{gas}} = 0$$

$$s(u, v) = cR \ln\left(\frac{u}{u_0}\right) + R \ln\left(\frac{v}{v_0}\right)$$

$$W = \Delta U \quad u^c v = \text{const} \quad u = u_0 \left(\frac{v_0}{v}\right)^{1/c}$$

$$u - u_0 = \left[\left(\frac{v_0}{v}\right)^{1/c} - 1 \right] u_0$$

$T \downarrow$

$$\left[\left(\frac{v_0}{v}\right)^{1/c} - 1 \right] \cdot cRT_0$$

$$= c R (T - T_0)$$

reversible? Yes!

(4)

Alt approach: integrate $-PdV$

(2) $W = - \int P_{ad} dV$ what's $P_{ad}(V)$? integrate $P \propto V^{-\gamma}$

adiabat $s \text{ const} \rightarrow U^\gamma V = \text{const}$

$$U = cRT = cPV \rightarrow P^c V^{c+1} = \text{const}$$

$$P V^{\frac{c+1}{c}} = \text{const}$$

$$\gamma = \frac{c+1}{c}$$

$$P = P_0 \left(\frac{V_0}{V} \right)^\gamma \quad \text{adiabat}$$

$$W = - \int P_0 \left(\frac{V_0}{V} \right)^\gamma dV = \dots - \frac{RT_0}{1-\gamma} \left[\left(\frac{V}{V_0} \right)^{1-\gamma} - 1 \right]$$

same answer!

$$1-\gamma = -\frac{1}{c}$$

(3) Another alt approach, starting f. EOS.

$$S = \text{const} \rightarrow dS = 0 \rightarrow dU = dW_{ad} = -PdV$$

cos cos

$$U = c RT = c PV \rightarrow dU = c(PdV + VdP)$$

$$-PdU = c(PdV + VdP) \rightarrow$$

or just set $S \infty$
to + const.

$$(c+1) \frac{dU}{V} = -c \frac{dP}{P} \rightarrow P^c V^{c+1} = \text{const}$$

$$P V^\gamma = \text{const} \quad \text{adiabat}$$

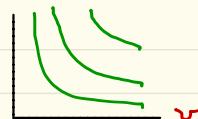
$$W_{ad} = - \int PdV \xrightarrow{\text{some work}} - \frac{RT_0}{1-\gamma} \left[\left(\frac{V}{V_0} \right)^{1-\gamma} - 1 \right]$$

$\hookrightarrow -P_0 V_0^\gamma \int V^{-\gamma} dV \quad \uparrow$

5

Fun with an ideal gas
isothermal expansion

^{not}
physical



$$T = \text{const} \rightarrow U = \text{const} \rightarrow PV = \text{constant} \quad (\text{NRT})$$

isotherms

$$\delta Q = -\delta W$$

$$S(u, v) = cR \ln\left(\frac{u}{u_0}\right) + R \ln\left(\frac{v}{v_0}\right)$$

$$\Delta S_{\text{sys}} = S_f - S_i = NR \ln\left(\frac{V}{V_0}\right)$$

entropy of system increases

$$Q_{\text{qs}} = T \Delta S = RT \ln\left(\frac{V}{V_0}\right)$$

$$\Delta U = 0 \rightarrow Q_{\text{qs}} = -W_{\text{qs}} = RT \ln\left(\frac{V}{V_0}\right)$$

heat flows to compensate work

- OR -

$$W_{\text{qs}} = - \int P dV = -RT \int \frac{dV}{V}$$

$$W_{\text{qs}} = -RT \ln\left(\frac{V}{V_0}\right)$$

expansion extracts work

reversible? YES!

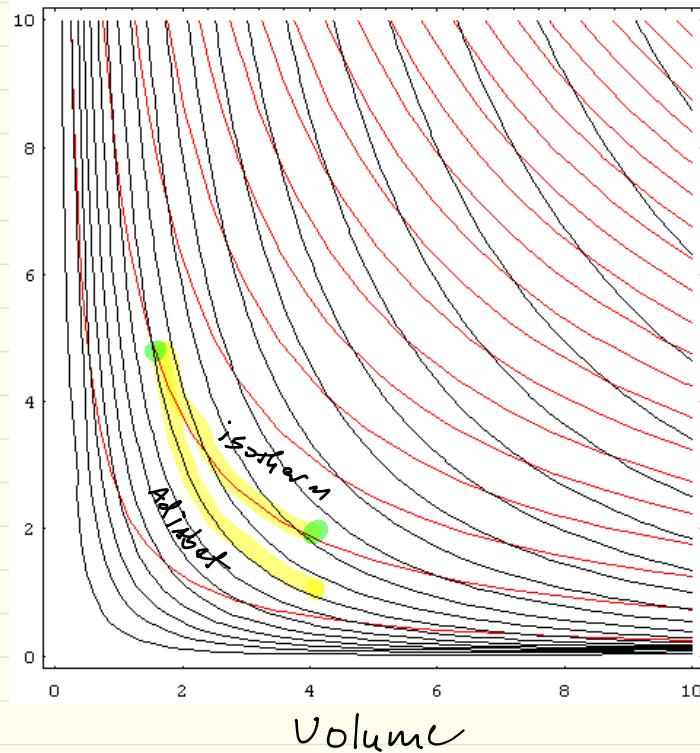
$$\Delta S_{\text{sur}} = Q_{\text{sur}}/T = -Q_{\text{qs}}/T$$

$$= -\Delta S_{\text{sys}}$$

6

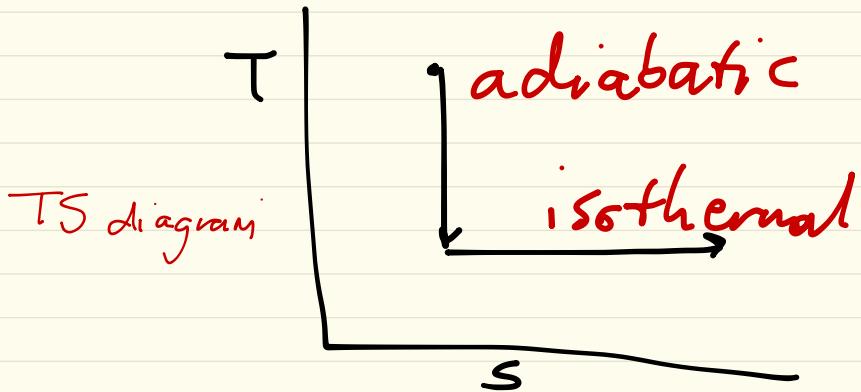
$$\left(\frac{\partial P_{ad}}{\partial V}\right) > \left(\frac{\partial P_{iso}}{\partial V}\right)$$

Pressure



red: isotherms

black: adiabats



Who does more work? adiabatic or isothermal?

$$V = 2V_0 \quad T_0 = 500 \text{ K} \quad N = 1 \quad c = \frac{3}{2} \rightarrow \gamma = \frac{5}{3}$$

$$W_{\text{iso}} = -500R \ln 2 \quad W_{\text{Ad}} = -500R (0.56) \\ -500R (0.69)$$

winner!

$$\Delta U_{\text{Ad}} = W_{\text{Ad}} = -\frac{NRT_0}{1-\gamma} \left[\left(\frac{V}{V_0} \right)^{1-\gamma} - 1 \right] = cNR(T-T_0)$$

$$\Rightarrow T = T_0 \cdot \left(\frac{1}{2} \right)^{\frac{1}{\gamma-1}} = 315 \text{ K} \quad T \text{ decreases}$$

$$\text{Can use this to show } \frac{T}{T_0} = \left(\frac{P}{P_0} \right)^{\frac{\gamma-1}{\gamma}}$$

$$P_{\text{ad}} = P_0 \left(\frac{1}{2} \right)^{5/3} \quad P_{\text{iso}} = P_0 \cdot \left(\frac{1}{2} \right)$$

No entropy change anywhere!

Example

Adiabatic free expansion

$$\delta W = 0 \quad \delta q = 0 \quad \Delta U = 0 \quad \Delta T = 0$$

$$\text{From fundamental eq} \quad \Delta S = N R \ln \frac{V}{V_0}$$

Exactly the same as isothermal, because end states the same. But, $\delta q = 0 \rightarrow \Delta S_{\text{sur}} = 0$

$$\Delta S_{\text{univ}} = \Delta S_{\text{sys}} > 0 ! \quad \text{irreversible}$$

(8)

Isothermal process + free expansion
 both start and end at the same place, but different w & q . What's the max w one can get?

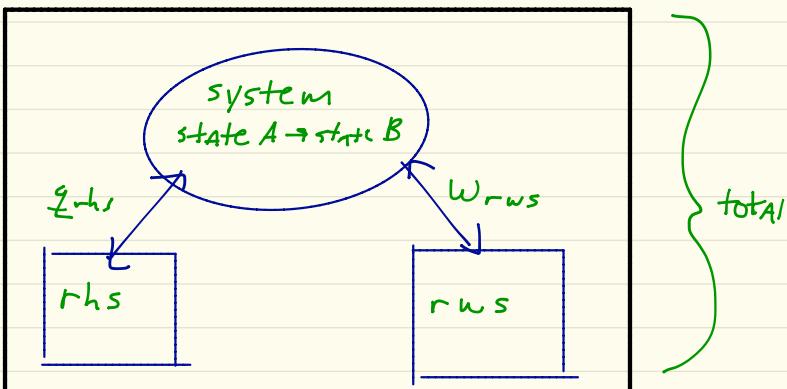
reversible work source - reservoir to which we can add or remove work reversibly. All processes w/i RHS are quasi-static and isentropic

reversible heat source - reservoir to which we can add or remove heat reversibly. All processes w/i RHS are quasi-static

RHS characterized by a heat capacity $C(T)$

$$dU_{rhs} = \cancel{dq}_{rhs} = C(T) dT$$

$$dS_{rhs} = \cancel{dq}_{rhs}/T = \frac{C(T)}{T} dT$$



What's the maximum work that can be done in taking the system from some state A to some other state B?

$$U(S^A, V^A, N_1^A, N_2^A, \dots) \rightarrow U(S^B, V^B, N_1^B, N_2^B, \dots)$$

one step, several, reversible, irreversible?

maximum work theorem:

The delivery of work is maximum and heat is minimum for an overall reversible process ($dS_{tot} = 0$). The work + heat are identical for every reversible process.

Consider infinitesimal change $A \rightarrow B$, so system energy change is dU .

Let $dW_{rhs} > 0$ for work done by system
 $dq_{rhs} > 0$ " heat taken from system

Energy conservation $\rightarrow dU + dq_{rhs} + dW_{rhs} = 0$

Entropy maximum $\rightarrow dS_{tot} = dS + dS_{rhs}$
 $= dS + dq_{rhs}/T_{rhs} \geq 0$

$$dq_{rhs} \geq -T_{rhs} dS$$

$$\begin{aligned} dW_{rhs} &= -(dU + dq_{rhs}) \\ &\leq -(dU - T_{rhs} dS) \end{aligned}$$

$$dW_{rhs} \leq T_{rhs} dS - dU$$

T_{rhs} , ΔU , ΔS are all specified, so right hand side is specified. ΔS is limit.

How to maximize ΔW_{rhs} ? Minimize Δq_{rhs} .
 Minimum is $\Delta q_{rhs} = -T_{rhs} \Delta S \rightarrow \boxed{\Delta S_{tot} = 0}$

Perhaps not surprising, but process that creates the most useful work is the one that overall creates no entropy. By construction, all such processes have same $q + w$.

In finite difference form, have

$\Delta S, \Delta U$
apply to system

energy cons: $\Delta U + q_{rhs} + w_{rhs} = 0$

reversible: $\Delta S_{tot} = \Delta S + \int \frac{dq_{rhs}}{T_{rhs}} = 0$

If we know $C_{rhs}(T) = \frac{dq_{rhs}}{dT}$, then

$$\Delta S_{tot} = \Delta S + \int \frac{C_{rhs}(T)}{T} dT = 0$$

If rhs is a reservoir with fixed $T +$ thus $C(T)$

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

Then $w_{rhs} = T_{rhs} \Delta S - \Delta U$

Example 1

maximum work from isothermal expansion of ideal gas?

$$\text{ideal gas } C = \frac{3}{2} \rightarrow \gamma = 5/3 \quad T_0 = 500\text{ K} \rightarrow T_i = 500\text{ K}$$

isothermal expansion $\rightarrow V_i = 2V_0$

energy balance: $\Delta U + \cancel{q_{rhs}} + w_{rhs} = 0 \quad w_{rhs} = -q_{rhs}$

entropy minimum: $\Delta S + \cancel{q_{rhs}}/T_{rhs} = 0 \quad q_{rhs} = -T_{rhs} \Delta S$

$$\Delta S = R \ln \left(\frac{V_i}{V_0} \right) = R \ln 2$$

$$w_{rhs} = T_{rhs} \Delta S = 500 R \ln 2$$

exactly what we got by integrating $-PdV$!!

Example 2

maximum work if our rhs is only @ 400 K ?

exactly same analysis $\Rightarrow w_{rhs} = 400 R \ln 2 < 500 R \ln 2$

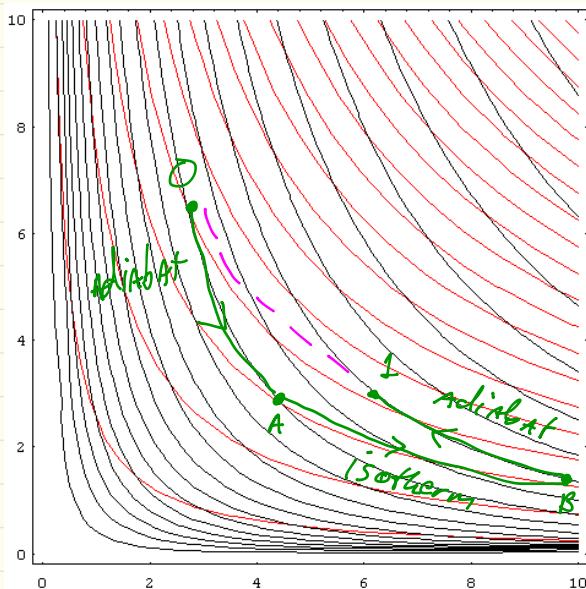
Begs the question how?? Have to find overall reversible path.

What's reversible? Adiabatic steps + isothermal steps w/ no T gradient.

Suggests • Adiabatic expansion to T_{rhs}

• Isothermal expansion to some TBD volume

• Adiabatic compression to final V + T .



$$O \rightarrow A \quad T_0 = 500 \text{ K} \quad T_A = 400 \text{ K}$$

$$\text{Adiabatic } \Delta U = -w_{\text{rev}} = cR(400 - 500) = -100cR$$

$$\Delta S = 0$$

Adiabat of an ideal gas: $T V^{\gamma-1} = \text{const}$

$$V_A = V_0 \left(\frac{T_0}{T_A} \right)^{1/\gamma-1} = V_0 \left(\frac{500}{400} \right)^{3/2} = V_0 \left(\frac{5}{4} \right)^{3/2}$$

$$B \rightarrow 1 \quad T_B = 400 \text{ K} \quad T_1 = 500 \text{ K}$$

exact opposite calculation

$$\Delta U = 100cR = -w_{\text{rev}} \quad \Delta S = 0$$

$$V_B = V_1 \left(\frac{T_1}{T_B} \right)^{1/\gamma-1} = 2V_0 \left(\frac{5}{4} \right)^{3/2} = 2V_A$$

aren't ideal gases nice?

(13)

$$A \rightarrow B \quad T_A = T_B = 400\text{ K} \quad \Delta U = 0$$

$$\text{isothermal work } w_{\text{rms}} = R T \ln \frac{V_B}{V_A} = R \cdot 400 \ln 2$$

$$\mathcal{E}_{\text{rhs}} = -R \cdot 400 \ln 2$$

$$\Delta S = \frac{\mathcal{E}}{T} = R \ln 2$$

Add 'em up!

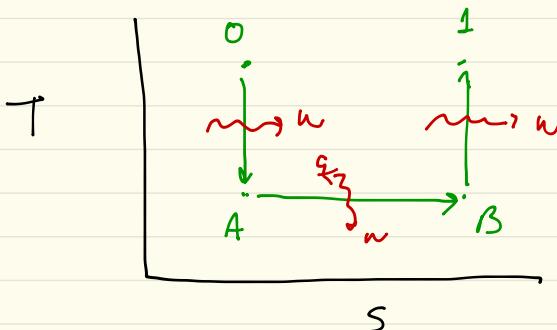
$$w_{\text{rms}} = 100c_R + 400R \ln 2 - 100c_R = \underline{400R \ln 2} \quad !!$$

$$\mathcal{E}_{\text{rhs}} = -400R \ln 2$$

$$\Delta U = -100c_R + 0 + 100c_R = 0$$

$$\Delta S = 0 + R \ln 2 + 0 = R \ln 2$$

Could have got more work if we had stopped @ 400K



Looks different on a "TS" diagram. Note $w =$
area under TS curve.

Example 3

14

In these examples assumed T of rhs (or system) were constant. Wouldn't have to:

$$q_{rhs} = \int_{T_c}^{T_f} C_{rhs}(T) dT$$

$$q_{sys} = \int C_{sys}(T) dT$$

It's 5°C outside and I have a 1 kg bucket of 90°C water ($C_v = 75 \text{ J/mol K}$). How much work could I get out of cooling the water to ambient?

$$\Delta U_{ice} + q_{rhs} + w_{rhs} = 0 \quad (\text{Assume } H_2O \text{ does no P_r work in cooling down})$$

$$\Delta U_{ice} = \int_{T_0}^{T_f} C_v dT = -80 \text{ C}_v$$

$$\Delta S_{ice} + q_{rhs}/T_{rhs} = 0$$

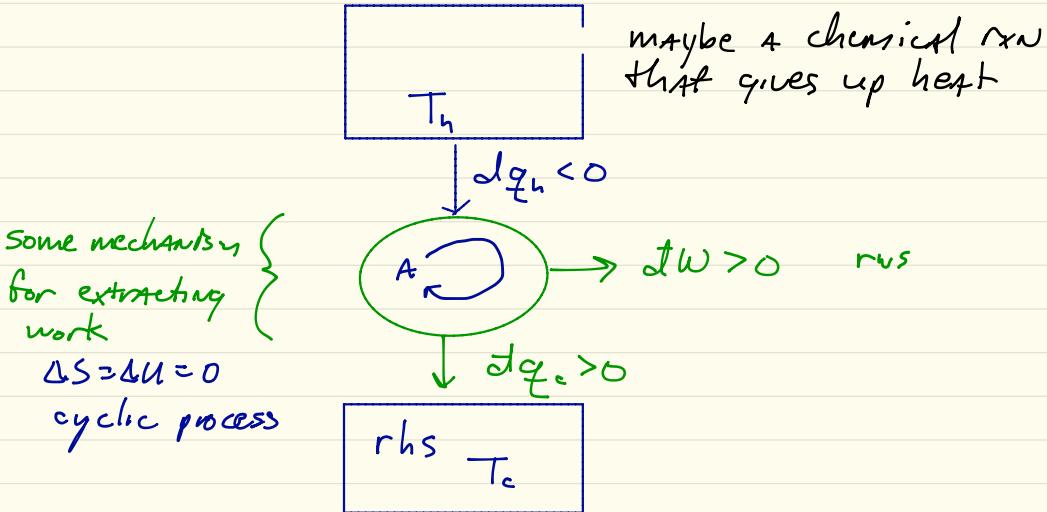
$$\Delta S_{ice} = \int \frac{C_v}{T} dT = C_v \ln T \Big|_{363}^{273} = C_v \ln \frac{273}{363} = -0.28 \text{ C}_v$$

$$q_{hi} = 278(0.28) \text{ C}_v$$

$$\begin{aligned} w_{rhs} &= -(\Delta U + q_{rhs}) = (80 - 0.28(278)) \text{ C}_v \\ &= 2.16 \text{ C}_v \end{aligned}$$

Good level-in too ...

thermodynamic engine



Focus on work associated with heat rejection,
so assume $dW_u = 0$ (it just adds to work at
the end anyway).

$$dS_{\text{tot}} = dS_h + dS_c = \frac{dq_h}{T_h} + \frac{dq_c}{T_c} \geq 0$$

2nd law

$$dq_c \geq -dq_h \left(\frac{T_c}{T_h} \right)$$

$$dw = -dq_h - dq_c \leq (-dq_h) \left(1 - \frac{T_c}{T_h} \right)$$

$$\frac{dw}{(-dq_h)} \leq 1 - \frac{T_c}{T_h}$$

E_e

If only we had
a lot of $T_c = 0$
Around!

What we have essentially shown is that it is impossible to convert some amount of heat into an equivalent amount of work. The maximum amount of work is given by

$$W_{\max} = q \left(1 - \frac{T_c}{T_h}\right)$$

refrigerator

run everything
the other
direction

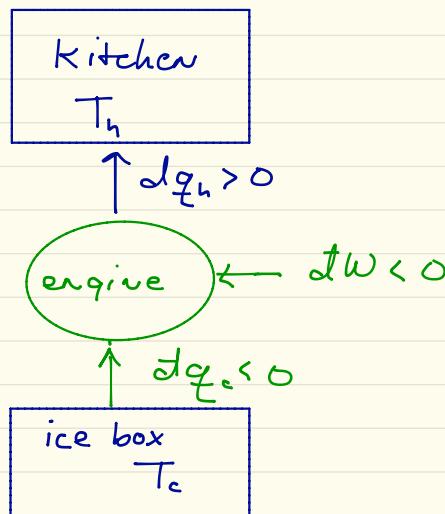


Figure of merit now $\frac{-\Delta q_c}{-\Delta W}$, coefficient of performance

$$\Delta W = -\Delta q_h - \Delta q_c \leq (-\Delta q_c) \left(1 - \frac{T_h}{T_c}\right)$$

$$COP = \left(\frac{-\Delta q_c}{-\Delta W}\right) \leq \frac{T_c}{T_h - T_c}$$

As $T_c \rightarrow 0$, $-\Delta W \rightarrow \infty$!!

Note COP can be > 1 ; it takes less than $A J$ of work to move $A J$ of heat! COP of a refrigerator ~ 2 or so depending on actual operation.

Another fundamental eq

ideal gas mixture

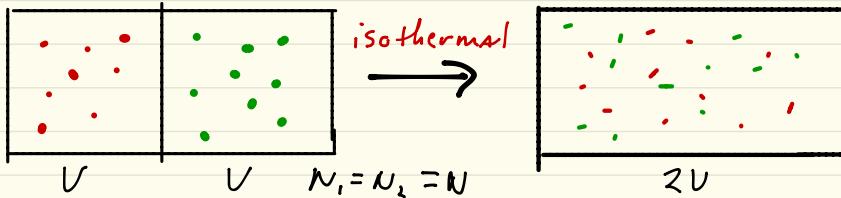
Would like $S(U, V, N_1, N_2, \dots)$

Assume additive behavior

$$PV = RT \sum_i N_i = \sum_i P_i \quad U = RT \sum_i c_i N_i = \sum_i U_i \quad \text{Assume - not enough eqns to derive}$$

$$S = \sum_i N_i (S_{i,0} + c_i R \ln \frac{T}{T_0} + R \ln \frac{V}{N_i v_0}) = \sum_i S_i$$

Could eliminate T from this, just messy



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

$$S_g = N \left(S_{i,0} + c_i R \ln \frac{T}{T_0} + R \ln \frac{V}{N_i v_0} \right) \text{ ditto } S_r$$

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

$$S = \sum_i n_i \left(S_{i,0} + c_i R \ln \frac{T}{T_0} \right) + \sum_i n_i \left(R \ln \frac{V}{n_i v_0} \frac{N}{N} \right)$$

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

mixture:

entropy of mixing

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

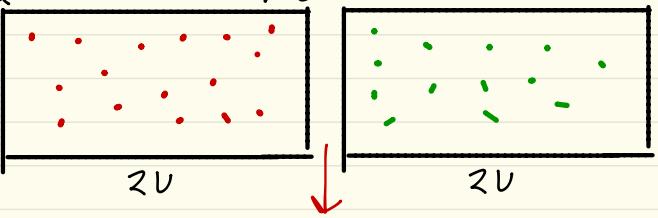
$$\Delta S_{\text{mix}} = -R \sum_i N_i \ln x_i$$

Entropy to combine gases keeping density constant

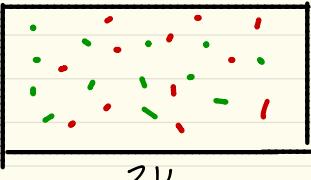
Written $-R \sum_i x_i \ln x_i$ on per mole basis

-Work necessary to "unmix"

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

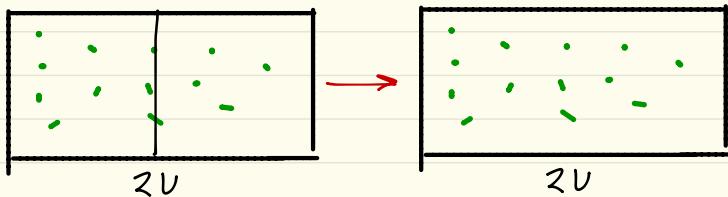


$$\Delta S_{\text{mix}} = 0 !$$



$$S_{\text{mix}} = \dots + 2NR \ln \frac{2V}{2NV} + 2NR \ln 2 = S_e + S_r$$

20



$$\Delta S = 0 !!$$

Gibbs' "paradox"

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

Another example, jumping ahead. The fundamental eqn of a mixture of ideal gases is

$$S = c R \ln\left(\frac{T}{T_0}\right) - R \ln\left(\frac{P}{P_0}\right) - R \sum_j x_j \ln x_j + \sum_j x_j s_{ij}$$

(we'll derive this later)

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?

$$\boxed{x_1 = x_2 = 1/2} \rightarrow \boxed{\begin{array}{l} x_1 = 0.9 \\ x_2 = 0.1 \end{array}} + \boxed{\begin{array}{l} x_2 = 0.9 \\ x_1 = 0.1 \end{array}}$$

$$\Delta u + \underline{q}_{rhs} + w_{rws} = 0$$

$T \text{ const} \rightarrow \Delta u = 0$

$$w_{rws} = -\underline{q}_{rhs}$$

$$\Delta S + \frac{\underline{q}_{rhs}}{T_{rhs}} = 0$$

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

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

$$\underline{q}_{rhs} = -T_{rhs} \Delta S = T_{rhs} R (0.37)$$

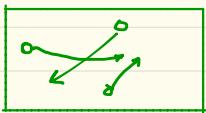
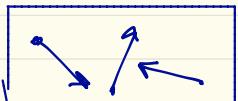
$$w_{rws} = -T_{rhs} R (0.37)$$

work becomes heat

how? membrane, centrifuge, absorption ...

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

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

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

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

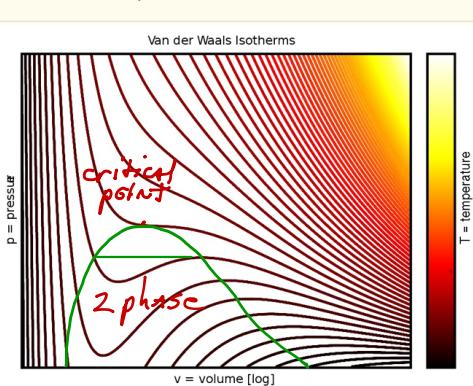
reduces to ideal gas as $V \rightarrow \infty$

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

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

23

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

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

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

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

24

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)

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

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

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

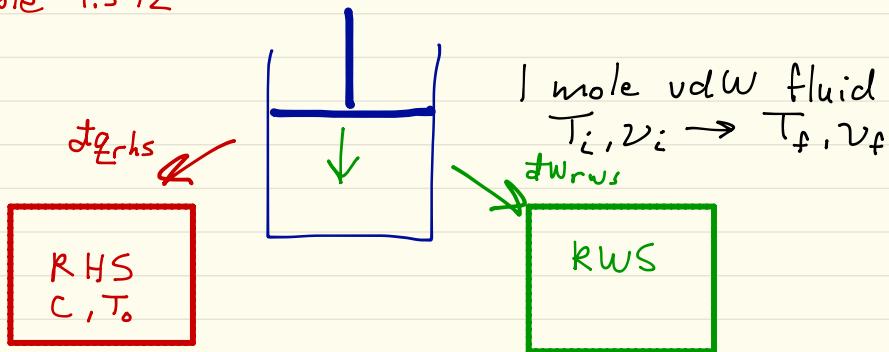
$$\text{ideal gAS } PV^\gamma = \text{const.}$$

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?