

# 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  $\mu$  by differentiation or by Gibbs-Duhem

Using stat. mech., can show that

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

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 (scalars w/  $V$ ) and momentums (scalars w/  $T$ )

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

2

## Fun with an ideal gas isothermal expansion

not physical



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

$$\delta W = - \int P dV = -NRT \int \frac{dV}{V}$$

$$W_{\text{iso}} = -NRT \ln(V/V_0)$$

expansion extracts work

$$\Delta U = 0 \rightarrow Q_{\text{iso}} = -W_{\text{iso}} = NRT \ln(V/V_0) \quad \text{heat flows to compensate work}$$

From fundamental eq above,

$$\Delta S_{\text{sys}} = S_f - S_i = N R \ln(V/V_0)$$

entropy of system increases

## Adiabatic expansion

$$S = \text{const} \rightarrow dS = 0 \rightarrow dU = \delta W_{\text{ad}} = -P dV$$

$$U = cNRT = cPV \rightarrow dU = c(PdV + Vdp)$$

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

or just set S eqn to a const.

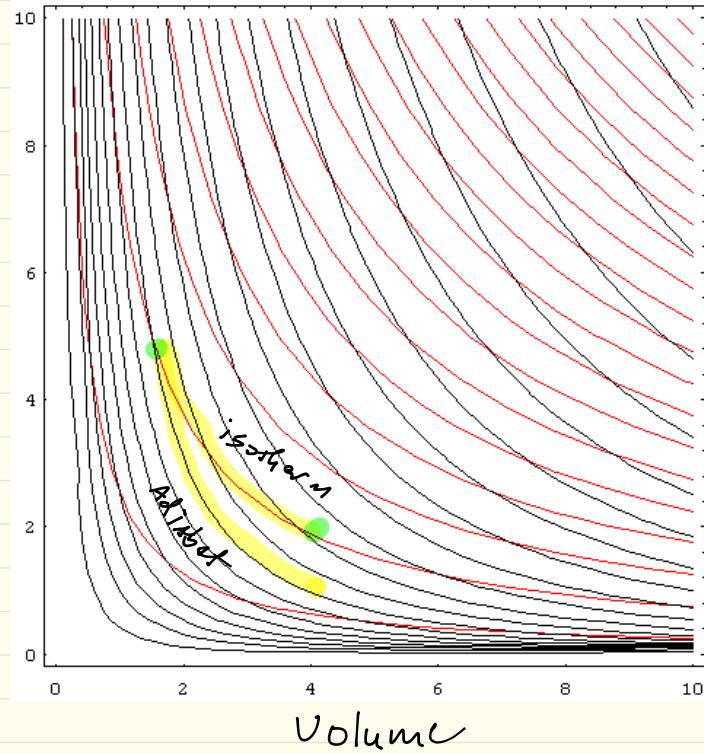
$$(c+1) \frac{dU}{V} = -c \frac{dp}{P} \rightarrow P^c V^{c+1} = \text{const}$$

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

$$W_{\text{ad}} = - \int P dV \xrightarrow[\text{work}]{\text{some}} - \frac{NRT_0}{1-\gamma} \left[ \left( \frac{V}{V_0} \right)^{1-\gamma} - 1 \right]$$

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

Pressure



red: isotherms

black: adiabats

(3)

Who does more work?

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

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

winner!

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

$$\Rightarrow T = T_0 \cdot \left( \frac{1}{2}^{2/3} \right) = 315 \text{ K} \quad T \text{ decreases}$$

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

$$P_{\text{ad}} = P_0 \left( \frac{1}{2} \right)^{5/3} \quad P_{1,50} = P_0 \cdot \left( \frac{1}{2} \right)$$

No entropy change anywhere!

Adiabatic free expansion

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

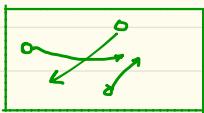
$$\text{From fundamental eq} \quad \Delta S = N R \ln \frac{V}{V_0}$$

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

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

## 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 · volume<sup>2</sup> = energy · volume

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

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

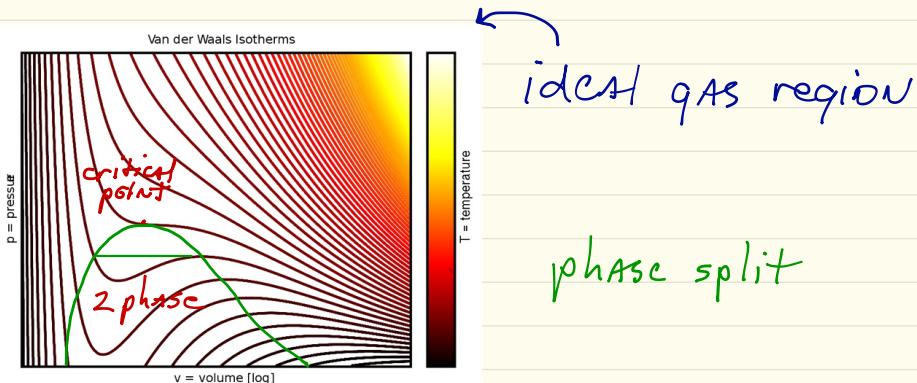
$$\text{compare } PV = RT$$

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

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

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

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



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  $\text{vdW}$  is

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

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

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

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.

Know that processes have a natural direction determined by entropy, know how to calculate equilibrium states.

Practical we want to take advantage of these spontaneous changes to do something useful, do work or move heat. How well can we do this?

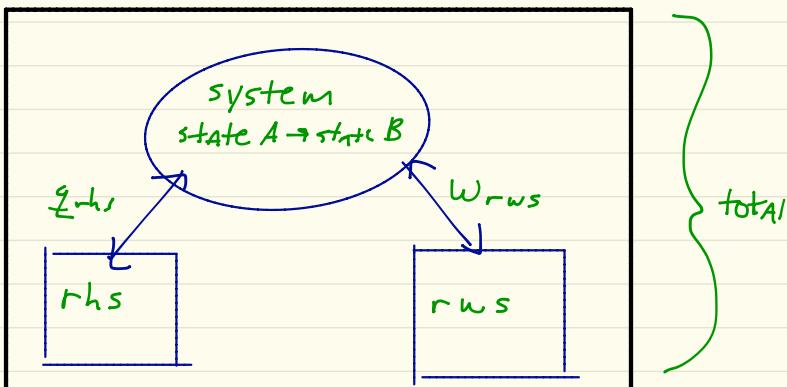
reversible work source - reservoir to which we can add or remove work reversibly. All processes w/i RWS are quasi-static and isentropic

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  $C(T)$

$$dU_{rhs} = \underline{dq_{rhs}} = C(T) dT$$

$$dS_{rhs} = \underline{dq_{rhs}} / T = \frac{C(T)}{T} dT$$



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

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

isothermal, adiabatic, ...?

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

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

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

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

$T_{rhs}$ ,  $\Delta U$ ,  $\Delta S$  are all specified, so right hand side is specified.  $\Delta S$  is limit.

How to maximize  $\Delta W_{rhs}$ ? Minimize  $\Delta q_{rhs}$ .  
 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  $w_{rhs} = T_{rhs} \Delta S - \Delta U$

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

$$V_0 \rightarrow V_i = 2V_0$$

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

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

$$\Delta S = R \ln(V_i/V_0) = R \ln 2$$

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

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

maximum work if our rhs is only @ 400 K?

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

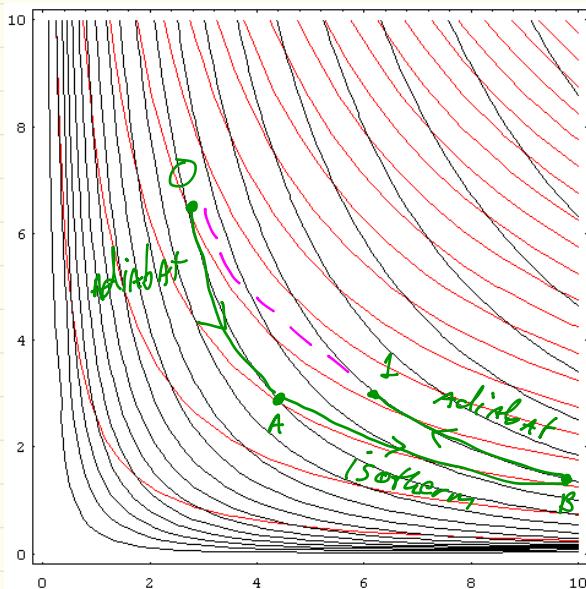
Beats the question how?? Have to find overall reversible path.

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  $V + T$ .

1)



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

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

$$\Delta S = 0$$

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?

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

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

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

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

Add 'em up!

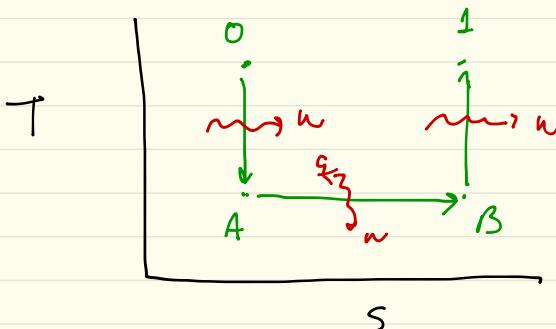
$$w_{\text{rms}} = 100c_R + 400R \ln 2 - 100c_R = \underline{400R \ln 2} \quad !!$$

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

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

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

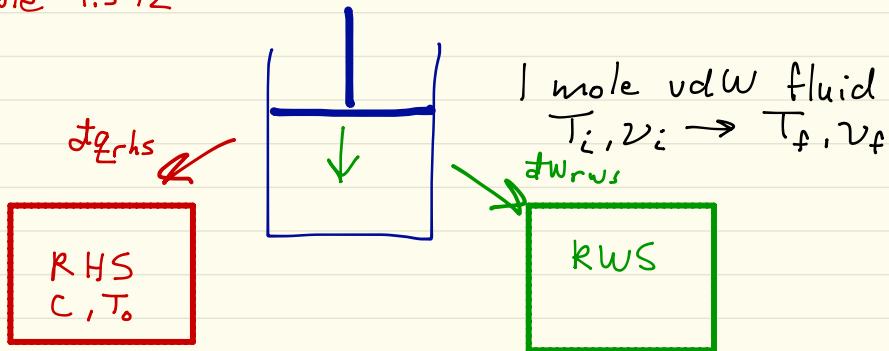
Could have got more work if we had stopped @ 400K



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

13

## Example 4.5-12



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

Recall for vdW fluid:

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

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

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

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

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

$$\dot{q}_{rhs} = \int C dT = C(T - T_0)$$

For maximum work

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

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

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

How?

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

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

(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?

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

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

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

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

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

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

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

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

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

work becomes heat

how? membrane, centrifuge, absorption ...

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?

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

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

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

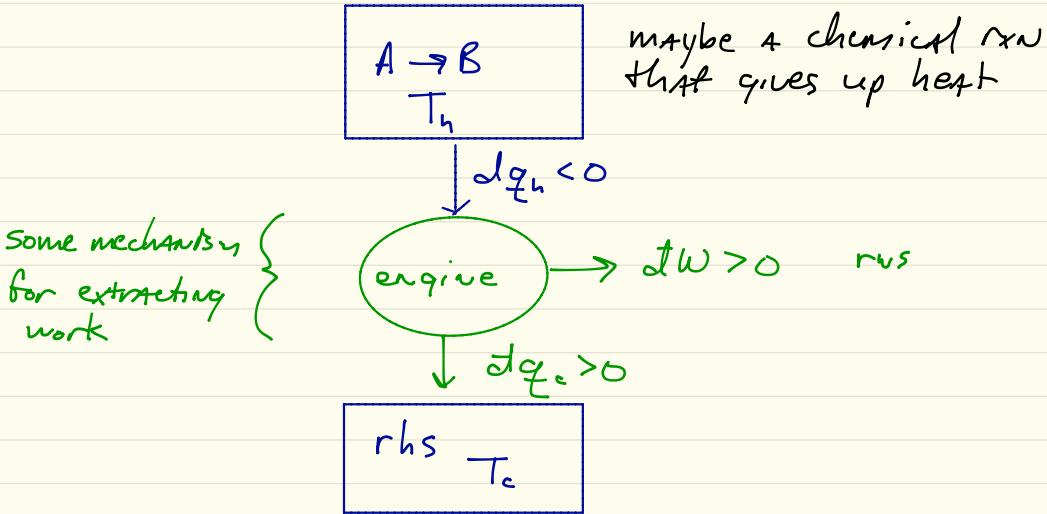
$$\Delta S_{ice} = \int \frac{C_v}{T} dT = C_v \ln T \Big|_{363}^{278} = C_v \ln \frac{278}{363} = -0.28 \text{ C}_v$$

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

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

Good level-in too ...

# thermodynamic engine



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

$$dS_{\text{tot}} = dS_h + dS_c = \frac{\delta q_h}{T_h} + \frac{\delta q_c}{T_c} \geq 0$$

2nd Law

$$\delta q_c \geq -\delta q_h \left( \frac{T_c}{T_h} \right)$$

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

$$\frac{\delta w}{(-\delta q_h)} \leq 1 - \frac{T_c}{T_h}$$

$E_e$

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

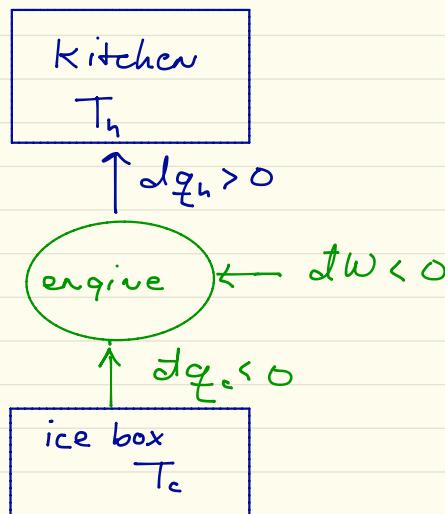


Figure of merit now  $\frac{-\Delta q_c}{\Delta W}$ , coefficient of performance

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

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

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  $\sim 2$  or so depending on actual operation.