Thermodynamics and Gases

Last time

- Kinetic Theory of Gases for simple (monatomic) gases
  - Atomic nature of matter
  - Demonstrate ideal gas law
  - Atomic kinetic energy = internal energy
  - Mean free path and velocity distributions
- From formula for E_{int}, can get specific heats
- Specific Heats of Simplest Gases
  - Constant Volume
  - Constant Pressure

Today

- Specific Heats for more complex gases
- Adiabatic Expansion
- Entropy

review

Internal Energy from Atomic Nature

- *pV=nRT* understood from atomic nature of matter
  - ◆ *pV=NkT* is equivalent form
  - ◆ Both are generally applicable (up to small van der Waals corrections) for all gases … *pV* μ kinetic energy of atoms
- Internal energy of the gas is a sum of all the energy forms (including kinetic energy) of the molecules
  - ◆ simplest is monatomic gas (one atom in the molecule, rotationally symmetric) -> energy all translational
  - ◆ real world: coefficient, 3/2, only applies to “noble gases”

monatomic gas

$$pV = NkT = nRT$$

$$\langle K_{atom} \rangle = \tfrac{3}{2} kT$$

$$E_{\text{int}} = N \langle K_{atom} \rangle = \tfrac{3}{2} NkT$$

$$E_{\text{int}} = \tfrac{3}{2} nRT$$

ANY gas

$$pV = NkT = nRT$$

$$\langle E_{atom} \rangle = \frac{C_V}{R} kT$$

$$E_{\text{int}} = N \langle E_{atom} \rangle = N \frac{C_V}{R} kT$$

$$E_{\text{int}} = nC_V T$$

review

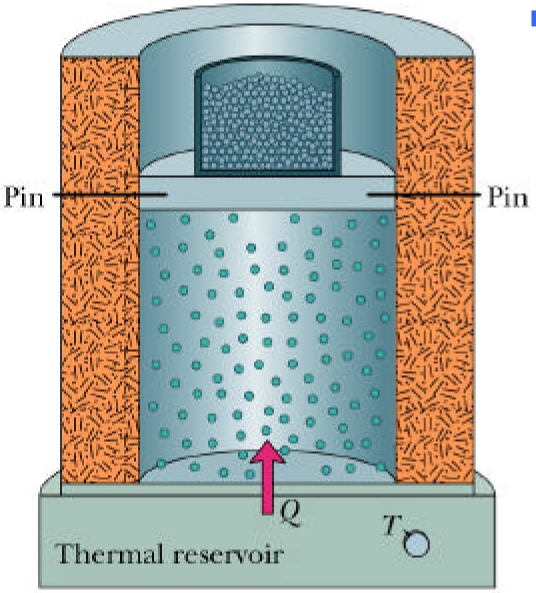
Specific Heat at Constant Volume (isochoric)

1st Law of Therm.

$$dE_{int} = dQ - dW$$

monatomic gas

$$E_{int} = \frac{3}{2} nRT$$



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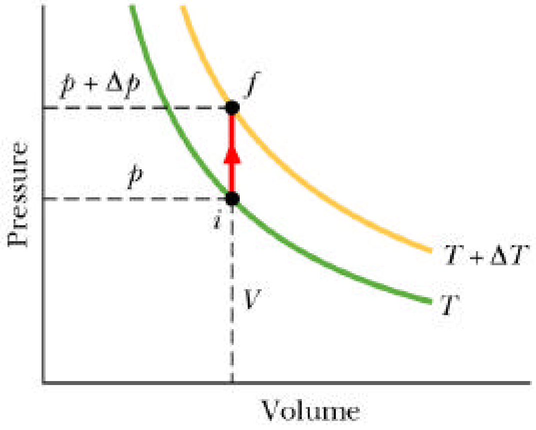


(b)

- **No change in volume implies no work done:**
  - $dW = 0$
- **Heat introduced proportional to temperature change when no work**
  - $Q\ ^{o}\ n\ C_V\ DT$
- **Since $dW=0$, then the heat added must equal the change in internal energy**
  - $DE_{int} = Q = n\ C_V\ DT$

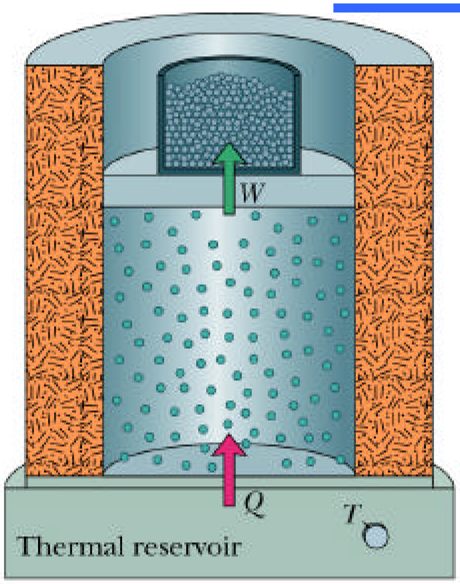
And we predict:
Monatomic (billiard ball) gases have $C_V=3R/2$

any gas

$$E_{int} = nC_V T$$

review

Specific Heat at Constant Pressure (isobaric process)



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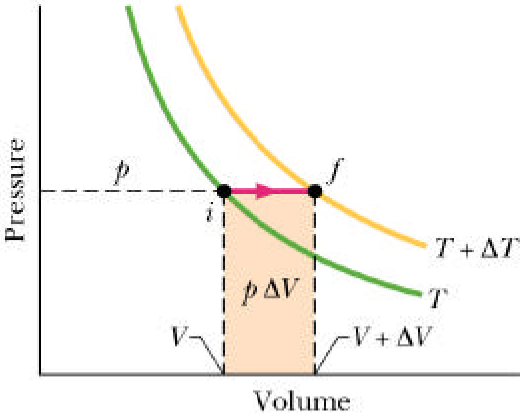


(b)

- For process shown (*n* fixed)
  - ◆ $Q \equiv n\,C_P\,\Delta T$
- Here, as expansion occurs,
  - ◆ work is done <u>and</u>
  - ◆ internal energy increases

$$Q = \Delta E_{int} + W$$

$$= nC_V\,\Delta T + p\,\Delta V$$

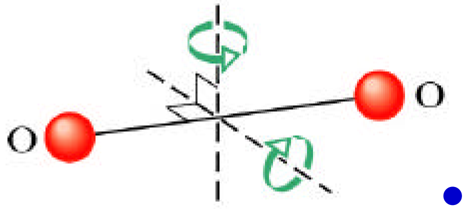
$$= nC_V\,\Delta T + nR\,\Delta T$$

$$Q = n\left(C_V + R\right)\Delta T$$

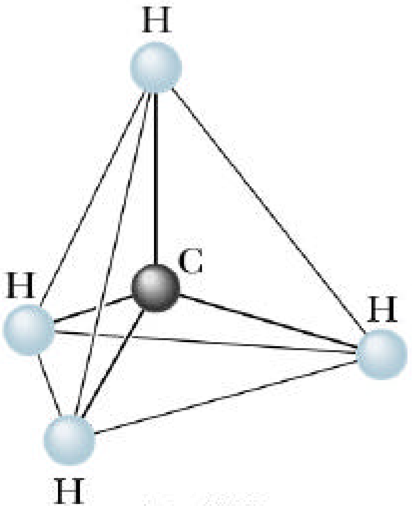
$$C_P = C_V + R$$

How about molecules that are <u>not</u> "monatomic"?

(*a*) **He**



(*b*) **O₂**



(*c*) **CH₄**

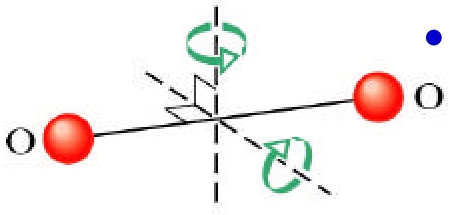
- We found that "sphere-like" molecules (single inert atoms) had $C_V = 3R/2$ … what about the rest?
  - Came from considerations of kinetic energy ($E_{int} = nC_VT$) deriving gas law
- Our single atoms had only one kind of available energy ®
  - Kinetic energy from translation in 3 dimensions
- More generally molecules can have other "degrees of freedom"
  - rotations
  - vibrations
  - ,,,
- Maxwell:

$$E_{int}^{molecule} = f\left(\tfrac{1}{2}kT\right)$$

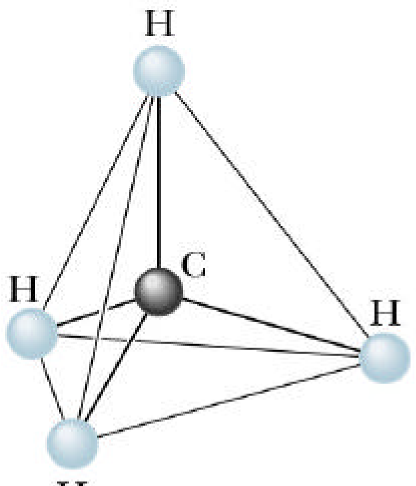
$$f = \#\ \text{deg of freedom}$$

Molecular Specific Heats

(*a*) **He**



(*b*) $\mathbf{O_2}$



(*c*) $\mathbf{CH_4}$

$$E_{int}^{molecule} = f\left(\tfrac{1}{2}kT\right)$$

$$f = \#\ \text{deg of freedom}$$

- f=different independent ways that molecule can contain and exchange energy
- Need enough thermal energy to “excite” the modes to be seen (Quantum Mechanics)
    - ◆ fig - H_2 gas C_V/R

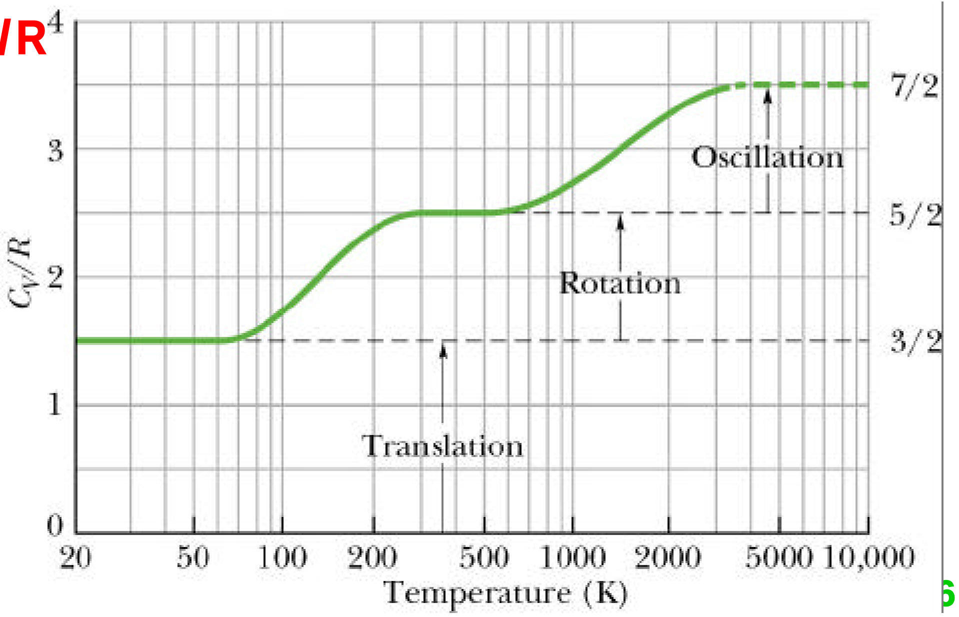
any gas

$$E_{int} = nf\left(\tfrac{1}{2}RT\right)$$

$$E_{int} = nC_VT$$

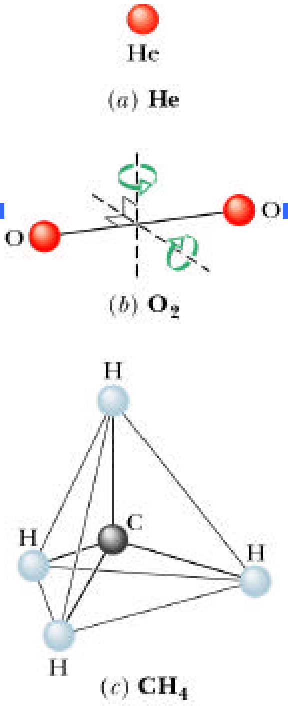
$$C_V = \tfrac{1}{2}Rf$$

$$C_P = R\left(\tfrac{f}{2} + 1\right)$$



Real Gas at low pressures

	f	C_v	C_p	$\gamma = C_p / C_v$
Translational Only	3	3R/2	5R/2	$\frac{5}{3} = 1.67$
+ Rotational diatomic	2	5R/2	7R/2	$\frac{7}{5} = 1.40$
+ Rotational polyatomic	1	3R	4R	$\frac{4}{3} = 1.33$



(a) He

(b) O_2

(c) CH_4

- **Empirical check**

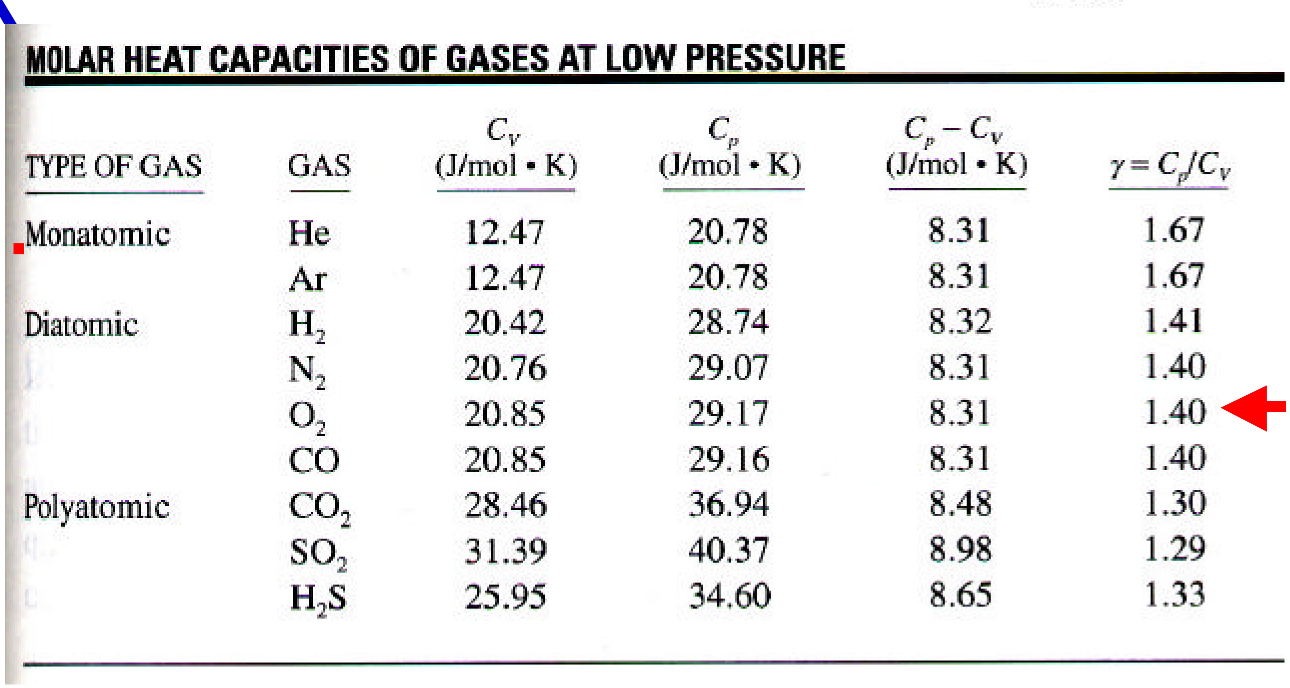
any gas

f = # active d.f.

$$C_V = \tfrac{1}{2} R f$$

$$C_P = R\left(\tfrac{f}{2} + 1\right)$$

$$\gamma \equiv \frac{C_p}{C_V} = 1 + \frac{2}{f}$$

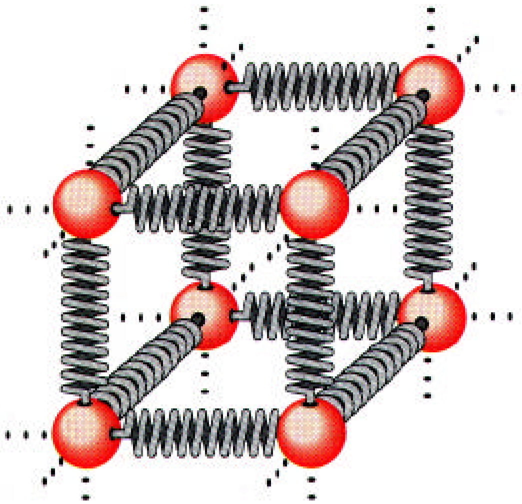


MOLAR HEAT CAPACITIES OF GASES AT LOW PRESSURE

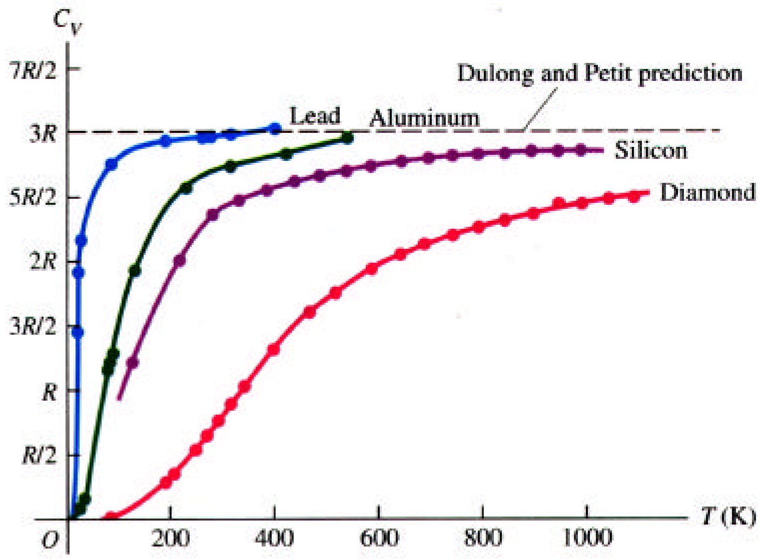
TYPE OF GAS	GAS	C_V (J/mol • K)	C_p (J/mol • K)	$C_p - C_V$ (J/mol • K)	$\gamma = C_p/C_V$
Monatomic	He	12.47	20.78	8.31	1.67
	Ar	12.47	20.78	8.31	1.67
Diatomic	H_2	20.42	28.74	8.32	1.41
	N_2	20.76	29.07	8.31	1.40
	O_2	20.85	29.17	8.31	1.40
	CO	20.85	29.16	8.31	1.40
Polyatomic	CO_2	28.46	36.94	8.48	1.30
	SO_2	31.39	40.37	8.98	1.29
	H_2S	25.95	34.60	8.65	1.33

Aside: How about Solids?

- **Generally expect $C_V = fR/2$**
- **While gases are <u>unbound</u>, solids have atoms bound to adjacent atoms**
  - **no net translations in 3D space but**
  - **there <u>does</u> exist**
    - **Vibrational kinetic energy -- 3 deg of freedom**
    - **potential energy (of binding) -- 3 deg of freedom**



- **Recall table 19-3: many solids tend to have molar heat capacity C ~ 25 J/mol-K**
- **Naively expect $f=6$ and $C_V=3R$ ~3(8.31 J/mol-K)**
- **This value approached in most solids as temperatures rise**



Adiabatic Expansion of Gas

- **Adiabatic = no heat enters or leaves system (gas) … *Q=0***
- **But temperature changes as gas does work**

$$pV = nRT \qquad pdV + Vdp = nRdT$$

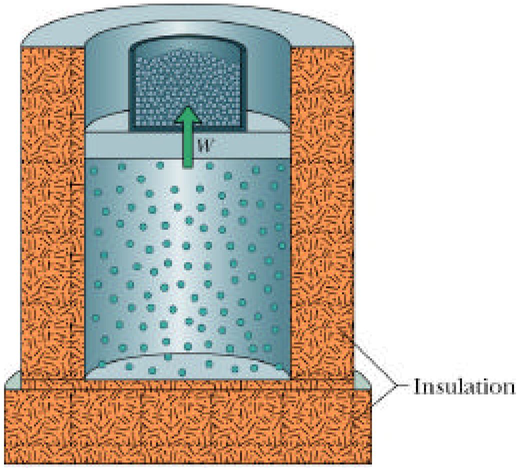
$$ndT = \frac{pdV + Vdp}{R} = \frac{pdV + Vdp}{(C_P - C_V)}$$

$$dE_{int} = dQ - dW$$

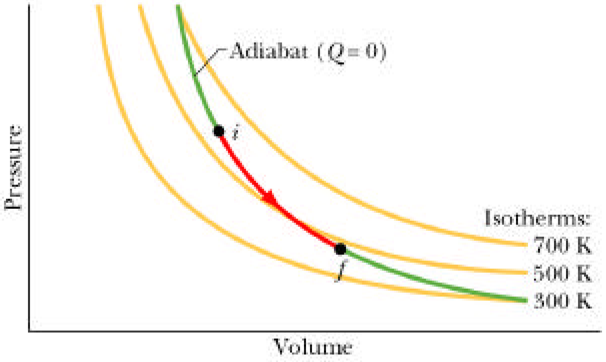
$$dE_{int} = -dW$$

$$nC_V dT = -pdV$$

$$ndT = -\frac{pdV}{C_V}$$



(a)



(b)

$$\frac{pdV + Vdp}{c_P - c_V} = -\frac{pdV}{c_V}$$

Adiabatic Expansion - algebra

$$\frac{pdV + Vdp}{c_P - c_V} = -\frac{pdV}{c_V}$$

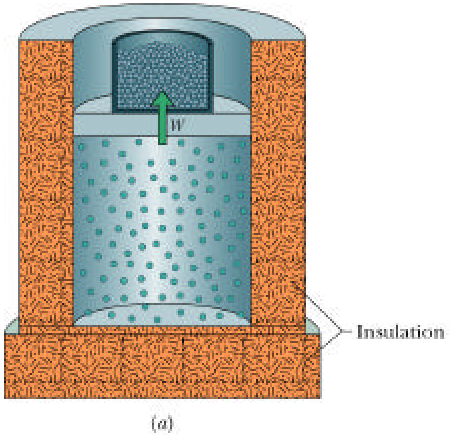
$$pdV\left[\frac{1}{c_P - c_V} + \frac{1}{c_V}\right] = -\frac{Vdp}{c_P - c_V}$$

$$pdV\left[\frac{c_P}{c_V\,(\cancel{c_P - c_V})}\right] = -\frac{Vdp}{\cancel{c_P - c_V}}$$

$$Vdp + \frac{c_P}{c_V}pdV = 0$$

$$\frac{dp}{p} + g\frac{dV}{V} = 0 \qquad g = \frac{C_P}{C_V}$$

Differential equation states that fractional change in pressure plus g times fractional change in volume must equal zero in any <u>adiabatic expansion</u>



Adiabatic Expansion - calculus

$$\frac{dp}{p} + \gamma \frac{dV}{V} = 0 \qquad \gamma = \frac{C_P}{C_V}$$

$$pV^{\gamma} = const$$

$$\ln p + \gamma \ln V = \text{const.}$$

$$\left(\frac{nRT}{V}\right) V^{\gamma} = const$$

$$\ln(pV^{\gamma}) = \text{const.}$$

$$\boxed{T_1 V_1^{\gamma - 1} = T_2 V_2^{\gamma - 1}}$$

$$\boxed{p_1 V_1^{\gamma} = p_2 V_2^{\gamma}}$$

$$\gamma = \frac{C_p}{C_V} = 1 + \frac{R}{C_V}$$

$$\gamma = \frac{(\frac{f}{2} + 1)R}{\frac{f}{2} R} = 1 + \frac{2}{f}$$

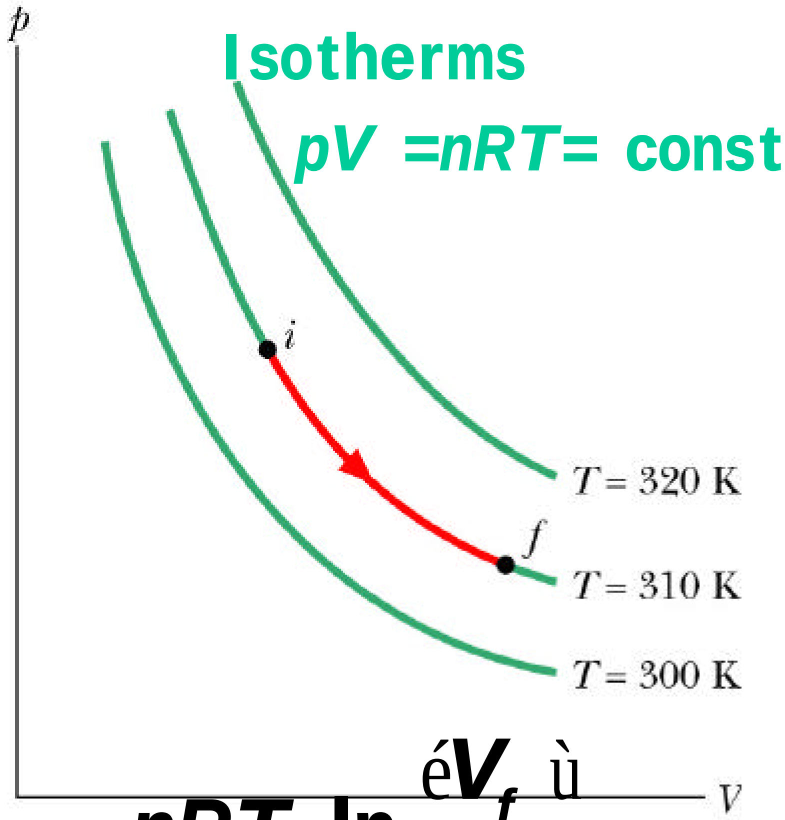
- Conclude that adiabatic change (no heat enter or leave) requires new relations among parameters
  - ratio (γ) spec. heats important
  - Ideal gas law also still true

review

Gases: Isothermal Expansion

$$pV = nRT$$

- Units
  - ◆ $R = 8.31\ J/(mol\text{-}K) = kN_A$
- Work (constant temperature) done obtained from integral in p-V (see sample prob 20-1)

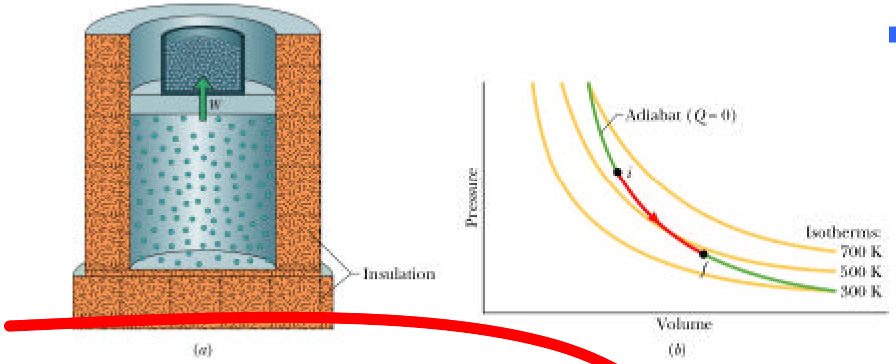


Isotherms

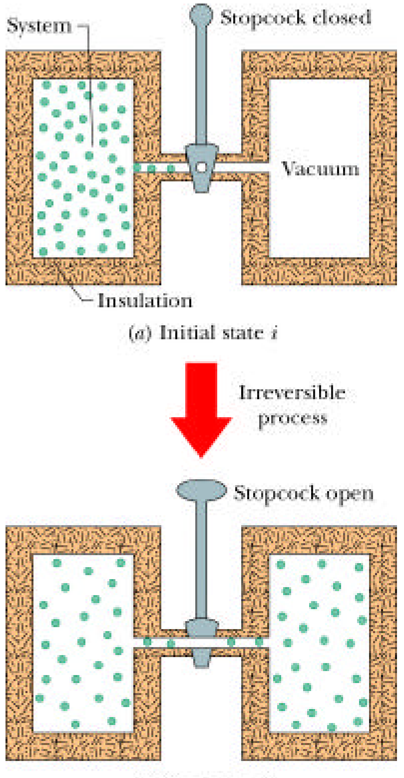
$pV = nRT =$ const

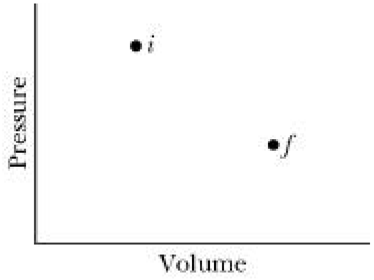
$$W = \int_{V_i}^{V_f} p\, dV = \int_{V_i}^{V_f} \frac{nRT}{V}\, dV = nRT \ln\left[\frac{V_f}{V_i}\right]$$

Reversibility



- All these (isothermal, isobaric, isochoric, adiabatic) are reversible processes
  - each point on P,V diagram is a possible state … state can be changed in any direction along a curve
- Contrast free expansion of gas
  - not reversible
  - $T_f=T_i$
  - $p_fV_f=p_iV_i$
  - but *f* state cannot return to *i* state





Sample Problem 20-9a

- **Recall sample problem 20-2, <u>isothermal</u> expansion of 1 mole O_2 at 310K & p_i=*2.0* atm from *12* liters to *19* liters gave P_f = *1.26* atm & *W=Q=1180 J*.**
- **Now <u>adiabatic expansion</u> of same sample.**
  - ◆ **Final pressure?**
  - ◆ **How much work done?**

$$p_2 = p_1\left(\frac{V_1}{V_2}\right)^{\gamma}$$

$$p_2 = 2.0\left(\frac{12}{19}\right)^{1.40}$$

$$p_2 = 1.05 \text{ atm}$$

$$T_2 = T_1\left(\frac{V_1}{V_2}\right)^{\gamma-1}$$

$$T_2 = 310\left(\frac{12}{19}\right)^{0.40}$$

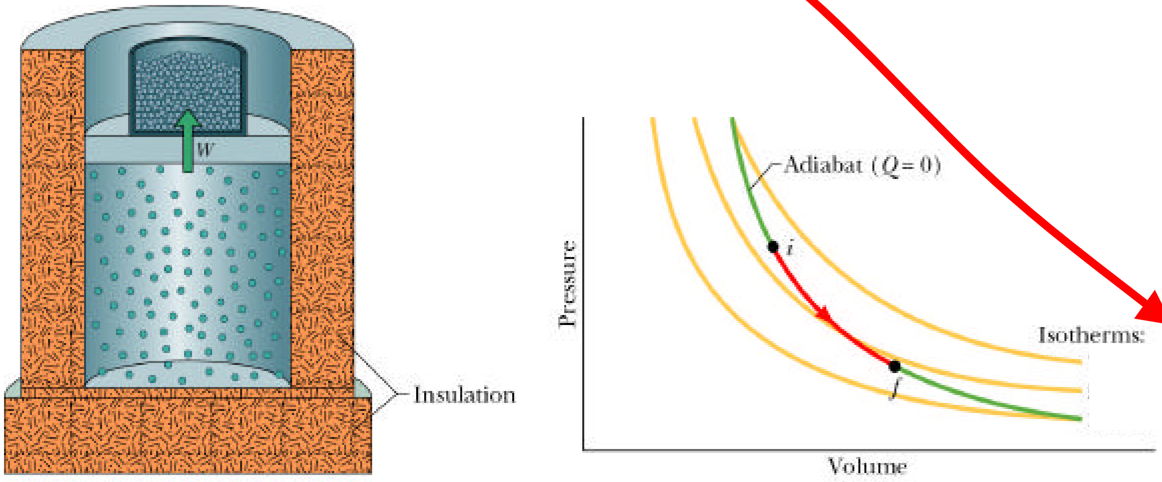
$$T_2 = 258\text{K}$$

$$\Delta T = -52.0\text{K}$$

$$Q = 0$$

$$W = -\Delta E_{\text{int}} = -nC_V\,\Delta T = -(1)(20.85)(-52.0)$$

$$W = 1085 \text{ Joules}$$

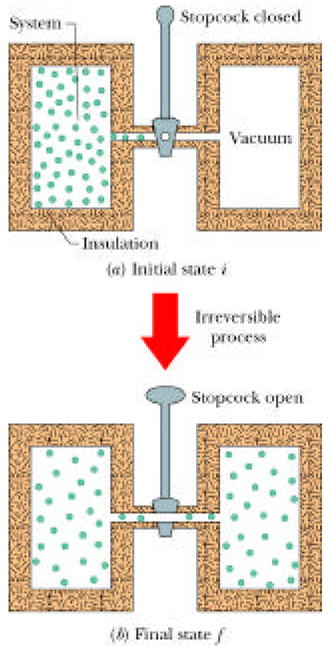


(a) (b)

Contrast Gas Expansions (sample 20-2 & 20-9)

All involve expansion of gas at 2 atm, 310K, and 12liters to a volume 19liters in different ways

Free Expansion



Variable	*Isothermal*	*Adiabatic*	*Free*
P_1	2.0 atm	2.0 atm	2.0 atm
V_1	12 L	12 L	12 L
T_1	310 K	310 K	310 K
P_2	1.26 atm	1.05 atm	1.26 atm
V_2	19 L	19 L	19 L
T_2	310 K	258 K	310 K
W	1180 J	1085 J	0 J

reversible

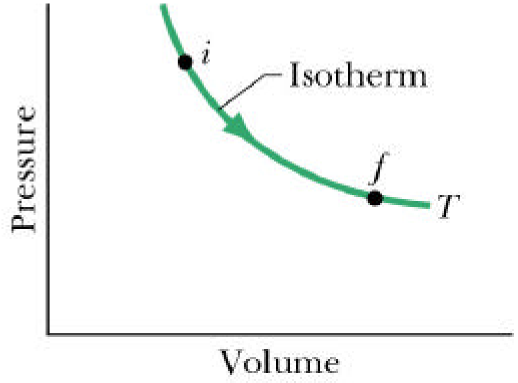
irreversible

- **Check you get the answers for these**
- **Big difference for <u>irreversible</u>: ENTROPY**

Entropy Definition

$$\Delta S = S_f - S_i \equiv \int_i^f \frac{dQ}{T}$$

$$= \frac{\Delta Q}{T} \quad \text{for } T \text{ fixed}$$

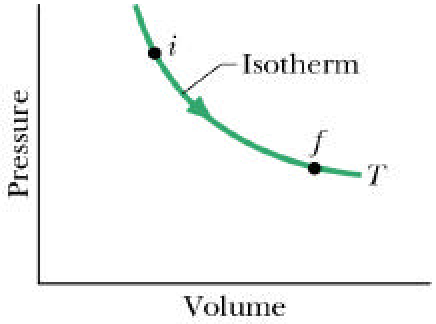


- **precise quantitative definition measuring heat flow energy at specific temperature (*S*=*Q*/*T*, units *J*/*K*)**
  - ◆ **Sign convention: heat added (DQ>0), then entropy increases (DS>0)**
- **simplest underlying concept underlying thermodynamics:**
  - ◆ **Closed system … total entropy change zero or positive**
- **Reversible process: an entropy increase is compensated by an entropy decrease in another part of system … entropy recoverable**
- **Irreversible: entropy increases and cannot be recovered**
- **can calculate entropy change for irreversible process by connecting initial & final states with (series of) reversible processes**

Second Law of Thermodynamics

- Simplest (and simplistic) expression: “Heat energy always flows from hotter bodies to cooler bodies”
  - intuitively obvious
- Take a more complete statement (though more abstract) with concept of <u>entropy</u>
  - “In any <u>closed system</u>, the entropy always <u>increases</u> for irreversible processes and is <u>constant</u> for reversible processes.” <u>Entropy never decreases in closed systems, and typically increases in real processes</u>!
  - Heat flow from hot to cold is a consequence.
  - Found to be provide experimentally correct predictions in wide array of circumstances
  - Has a physical interpretation in terms of the system’s <u>order</u>
  - Provides an understanding of where our sense of the “arrow of time” arises.

Reversibility: isothermal expansion of gas

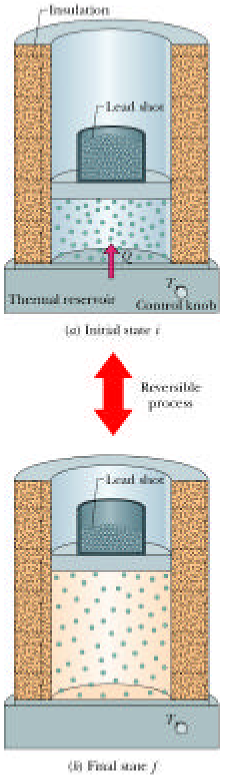


$$\Delta S = \frac{Q}{T} = \frac{W}{T} = \int \frac{pdV}{T} = \frac{nRT}{T}\int_{V_i}^{V_f} \frac{dV}{V}$$

$$\Delta S^{gas}_{expansion} = +nR \ln \frac{V_f}{V_i}$$

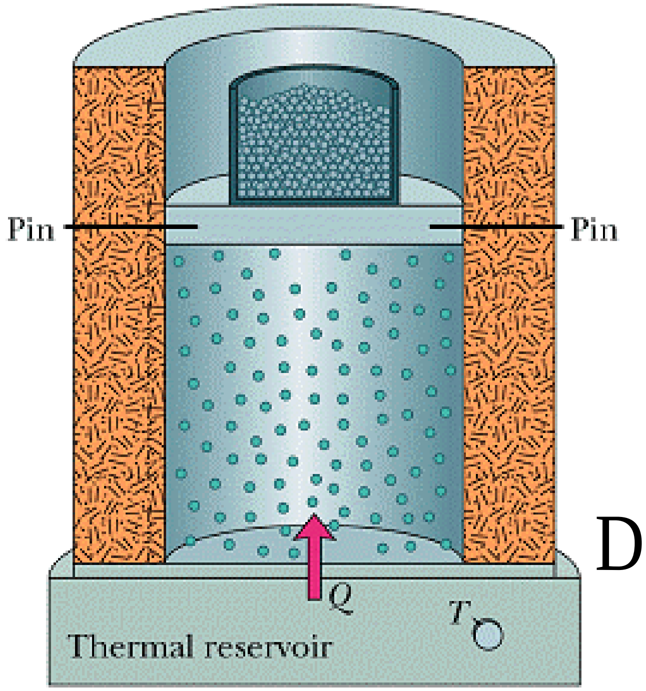
- Entropy increase of the gas during expansion occurs as a consequence of heat (Q) into gas at temp T
- An equal and opposite decrease in the entropy of the reservoir occurs at the same time
- If the gas is isothermally compressed, the gas entropy decreases and the reservoir entropy increases

$$\Delta S^{gas}_{compression} = -nR \ln \frac{V_f}{V_i}$$



reversible isothermal expansion

Isochoric temperature change of gas



- **Add heat with doing work by increasing reservoir temp**
- **Temperature change of gas in contact with temp reservoir is also <u>reversible</u>**

$$\Delta S = \frac{\Delta Q}{T} = \int \frac{\Delta E_{int}}{T} = nC_V \int_{T_i}^{T_f} \frac{dT}{T}$$

$$\Delta S_{T_i \rightarrow T_f} = +nC_V \ln \frac{T_f}{T_i}$$

$$\Delta S_{T_f \rightarrow T_i} = +nC_V \ln \frac{T_i}{T_f} = -\Delta S_{T_i \rightarrow T_f}$$

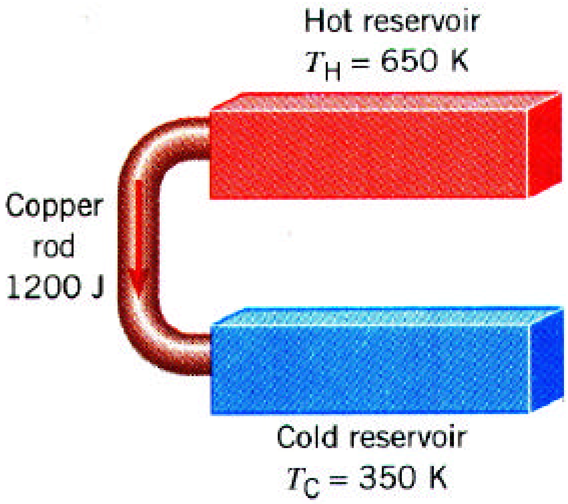
Entropy (more)

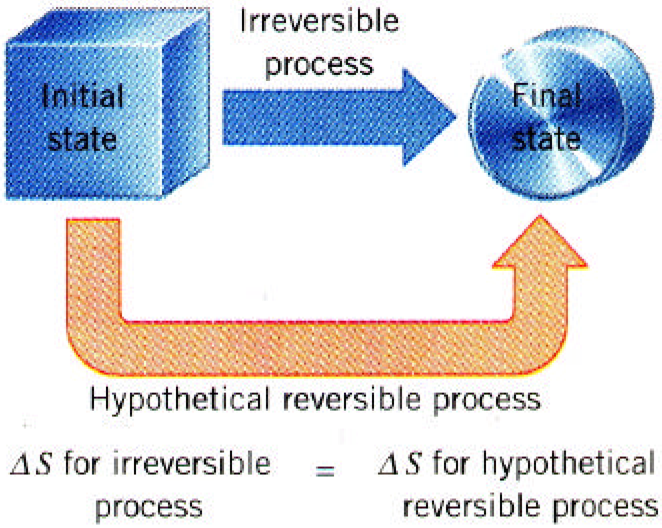
- Entropy is a physical measurable property of a system (like T,V, p,…) that is calculable in terms of the others
  - ◆ "state function"
- How does one calculate entropy change when the net entropy increases? (in an irreversible process like free expansion of a gas)
- Answer: Calculate entropy change for irreversible process by connecting initial & final states with (imagined series of) reversible processes. Examples
  - ◆ Simple heat flow between two solids.
  - ◆ Free expansion.

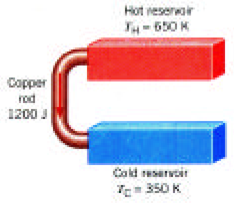
Entropy Change in Irreversible Process

$$\Delta S_{t=0} = \frac{\Delta Q_{t=0}}{350} - \frac{\Delta Q_{t=0}}{650} > 0$$

- **Note that entropy will increase so long as heat flows from hot body to cold body. The reverse (cold to hot) is not possible from 2^{nd} Law.**
- **Simple heat flow from hot body to cold is irreversible**
- **Calculate entropy change in irreversible process: connect initial & final states with series of pretend reversible processes**

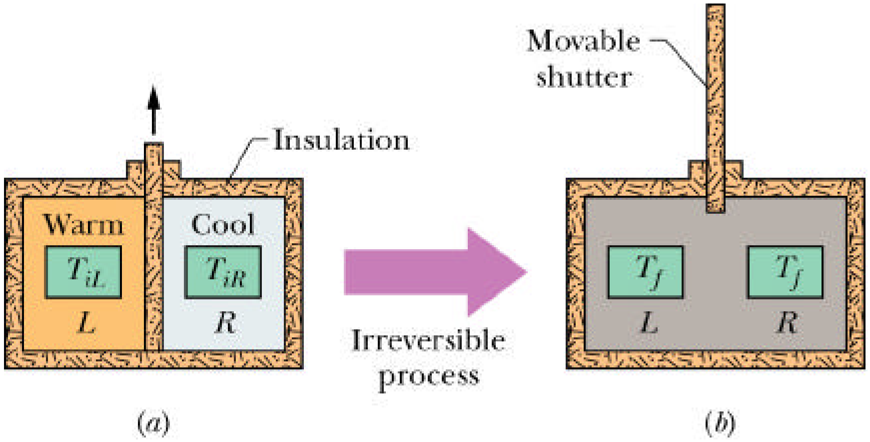


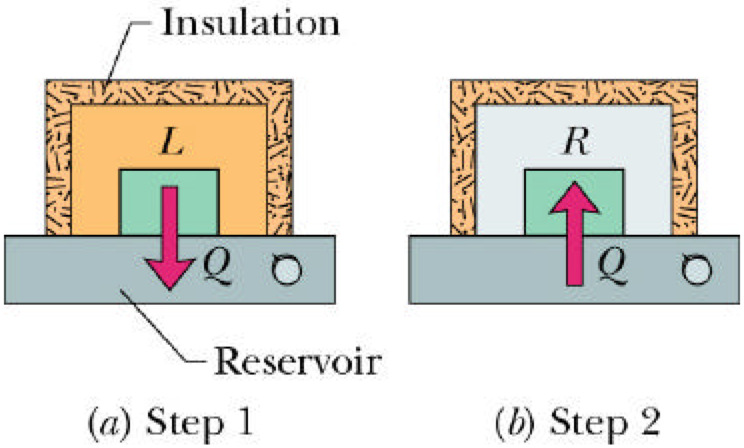




Entropy change: solids

- **Net entropy change of any process of a closed system is either zero (reversible) or greater than zero (irreversible)**
  - ◆ **Example <u>sample problem 21-2</u>: 2 equal mass (m) solids at different temps … equilibrium when both at final temperature T_f … what is entropy chg?**





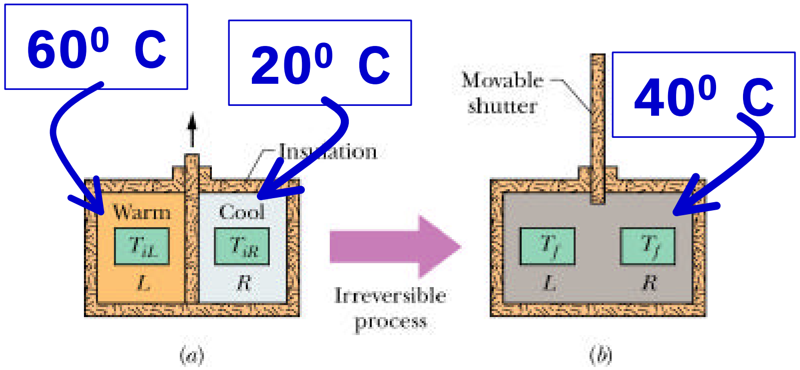
$$\Delta S = \int_i^f \frac{dQ}{T} = mc \int_{T_i}^{T_f} \frac{dT}{T} = mc \ln \frac{T_f}{T_i}$$

$$\Delta S_{rev} = \Delta S_L + \Delta S_R = mc \left[\ln \frac{T_f}{T_{iL}} + \ln \frac{T_f}{T_{iR}} \right]$$

$$\Delta S_{rev} = mc \ln \frac{T_f^{\,2}}{T_{iL} T_{iR}}$$

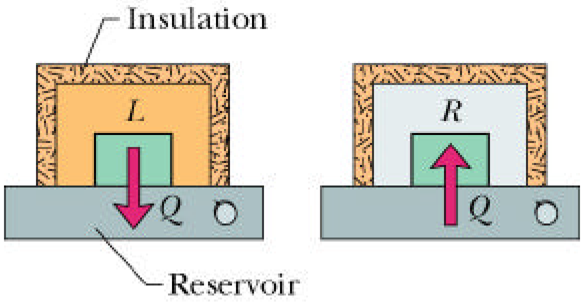
$$\Delta S_{rev} = \Delta S_{irrev}$$

Sample Problem 21-2



$$\Delta S = \Delta S_L + \Delta S_R$$

$$= mc\left[\ln\frac{T_f}{T_{iL}} + \ln\frac{T_f}{T_{iR}}\right]$$



(a) Step 1 (b) Step 2

- **m= 1.5 kg**
- **c= 386 J/kg-K**

$$\Delta S_{rev} = mc\ln\frac{T_f^{\,2}}{T_{iL}T_{iR}}$$

$$\Delta S_{rev} = \Delta S_{irrev}$$

Equal masses:

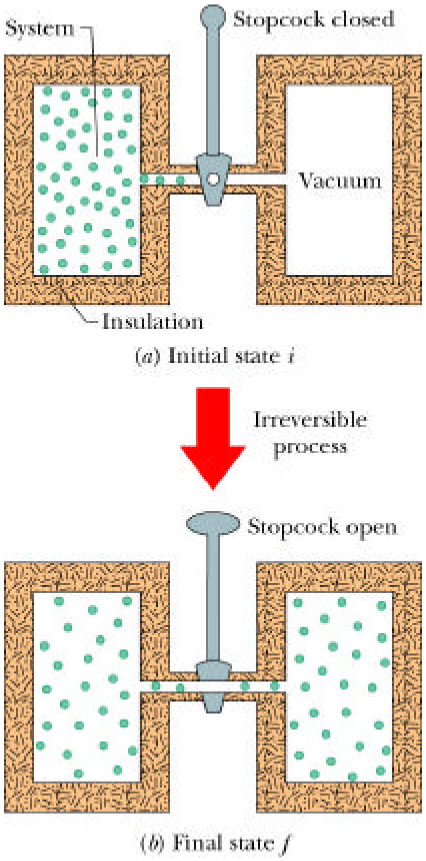
$$T_f = \tfrac{1}{2}\left[T_{iL} + T_{iR}\right] = 40^0 C$$

$$\Delta S = (1.5\,\mathrm{kg})(386\,\mathrm{J/kg\cdot K})\ln\left(\frac{313^2}{(293)(333)}\right)$$

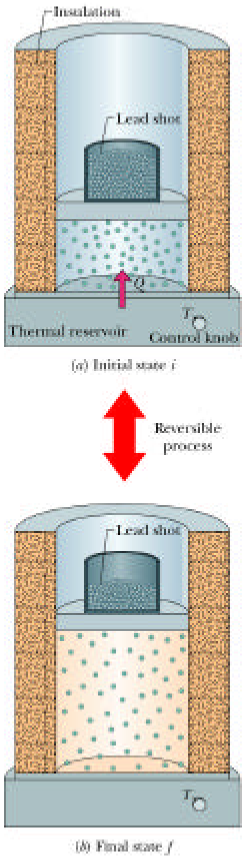
$$\Delta S = 2.37\ \mathrm{J/K}$$

- **Same net entropy increase for the two masses**
  - **Lost in irreversible process**
  - **Stored in reservoir for reversible process**

Entropy increase of free expansion of gas



irreversible in a closed system



reversible isothermal equivalent

$$\Delta S = \frac{Q}{T} = \frac{W}{T} = \frac{nRT}{T} \ln \frac{V_f}{V_i}$$

$$\Delta S = nR \ln \frac{V_f}{V_i}$$

- **Derived previously for isothermal expansion of the gas**
- **Since,in the two processes (reversible and irreversible), the gases have same initial states and same final states**
    - ◆ **the entropy change of the gas is the same for <u>both processes</u>**
- **<u>Note that free expansion process is irreversible</u>**
- **Note that net entropy of <u>closed</u> system in isothermal expansion is zero**

2nd Law of Thermodynamics: gases

- **Net entropy change of any process of a closed system is either zero (reversible) or greater than zero (irreversible)**
  - discussion section 21-2
- **Entropy is a state function; depends only on parameters of the system: calculate general change for gas**

$$\boxed{\Delta S \geq 0}$$

$$dQ = dE_{\text{int}} + dW$$

$$dQ = nC_V dT + pdV$$

$$\Delta S_{i \to f} = S_f - S_i$$

$$= \int_i^f \frac{dQ}{T}$$

$$\Delta S_{rev} = \Delta S_{irrev}$$

entropy change for ideal gas

$$\Delta S = \int_i^f \frac{dQ}{T} = nC_V \int_{T_i}^{T_f} \frac{dT}{T} + nR \int_{V_i}^{V_f} \frac{dV}{V}$$

$$\Delta S = nC_V \ln \frac{T_f}{T_i} + nR \ln \frac{V_f}{V_i}$$

Thermodynamics and Gases

Today

- Specific Heats of Simplest Gases
  - Constant Volume (isochoric)
  - Constant Pressure (isobaric)
- Specific Heats more generally
- Adiabatic Expansion
- Reversible and Irreversible Processes
- Entropy

Next

- More on Entropy
- Uses in engines, heat pumps, refrigerators
- Origin of Entropy