Energy equation of state

recall: pressure equation of state

$$PV = NkT \quad \text{(ideal gas)}$$

intensive
variable = independent of system size

extensive variable: proportional to system size
$$N, V, M, E$$

$\Rightarrow$ often convert extensive $\Rightarrow$ intensive
energy/particle etc.

Here, we just state energy equation of state.
(It was historically determined empirically, and)
(later we will derive it from first principles.)

$$E = \frac{3}{2} NkT \quad \text{(ideal gas)}$$

For a van der Waals gas

$$E = \frac{3}{2} NkT - N\frac{N}{V}a$$

ex: Work done on ideal gas at constant temperature

→ work done on gas at constant T so that $V_1 \to V_2$, what is ΔE?

$$E = \frac{3}{2} NkT \implies \Delta E = 0 \text{ since } \Delta T = 0$$

(E independent of volume!)

→ calculate Q

(1) $\Delta E = Q + W = 0 \implies Q = -W$

(2) $Q = -W = \int P dV = \int_{V_1}^{V_2} \frac{NkT dV}{V} = NkT \log(V_2/V_1)$

Heat capacity & Enthalpy

heat capacity: energy transfer due to heating required
to create unit temperature rise

$$\text{heat capacity} = C = \frac{Q}{\Delta T} \quad \text{(general definition)}$$

→ value of C depends on <u>constraints</u>

$$C_V = \left(\frac{\partial E}{\partial T} \right)_{V,N} \longleftarrow \text{what is held fixed in}$$
partial derivative
(sometimes N omitted)

heat from process that is done at
constant volume

__ex__: What is C_v for an ideal gas?

$$C_v = \left(\frac{\partial E}{\partial T}\right)_{V,N} = \left(\frac{\partial}{\partial T} \frac{3}{2} NkT\right)_{V,N}$$

$$= \frac{3}{2} Nk$$

__note__: often see specific heat, c, which is independent
of amount of material (intensive!),
expressed in terms of moles, mass, etc

New state function: __enthalpy__

lets us talk about heat from process when
work is done at constant pressure

$$\boxed{H = E + PV}$$

We can use this to define C_p:

$$dE = dQ + dW \qquad \text{(always!)}$$

$$= dQ - PdV$$

__note__: $d(PV) = VdP + PdV$

$$dQ = dE + PdV = dE + (d(PV) - VdP)$$

constant pressure $\rightarrow dP = 0$

$$dQ = dE + d(PV)$$

$$dQ = d(E + PV) = dH$$

Thus, $\quad C_p = \left(\dfrac{\partial H}{\partial T}\right)_{P,N}$

ex: C_p for ideal gas

$$H = E + PV = \frac{3}{2} NkT + PV \qquad\qquad PV = NkT$$

$$= \frac{5}{2} NkT$$

$$\left(\frac{\partial H}{\partial T}\right)_{P,N} = \frac{5}{2} Nk$$

Note: $C_p > C_v$, why?

    unless we prevent it, system expands upon
      heating $\Rightarrow$ does work on surroundings

    Constant P $\Rightarrow$ energy to   +   energy to
                   increase T   do work

    Constant V $\Rightarrow$ energy to
                       increase T

ex : temperature after thermal contact

Two systems, A & B, brought into thermal contact, initially at T_A, T_B, what's final temperature?
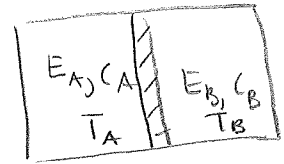
(assume C_A, C_B are independent of T)

(1) conservation of energy

$$\Delta E_A + \Delta E_B = 0$$

(2) $$C_A(T-T_A) + C_B(T-T_B) = 0$$

$$C_A T - T_A C_A + C_B T - C_B T_B = 0$$

$$\boxed{T = \frac{C_B T_B + C_A T_A}{C_A + C_B}}$$

2nd Law of Thermodynamics

- many processes we do not observe to occur, but are consistent with conservation of energy (1st law)

  ex : energy spontaneously moving from a cold body to hot one

⇒ there is another state function we must take into account, entropy

note: it is remarkable that 19th century
scientists realized that entropy
must exist even though they had
no way to measure it

Q: we often use heat to do work
burn fuel → make steam → turbine in $\vec{B}$ → make electricity
⌐ can we convert all energy to work?

NO!

HISTORICAL STATEMENTS

Kelvin-Planck 2nd law: impossible to make cylic process that
does nothing but convert energy to work
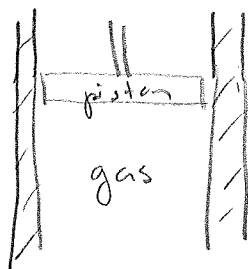
isothermal expansion → pushes piston
(gas does work, so it must lose energy)
$E = \frac{3}{2} NkT$ ← $\Delta T = 0$ ⇒ $\Delta E = 0$

$\Delta E = 0$ ⇒ $W = -Q$

absorbed energy completly converted
to work! why is this ok??

→ not a cyclic process!
macrostate differes at end
than in beginning

→ e.g. can't make an engine
out of it

<u>2nd law</u>:   No process is possible whose sole result is to
cool a colder body and heat a hotter one

Clausius

→ look different but are exactly the same statement

<u>2nd law</u>: there exists an additive state function, entropy,
that can never decrease in an isolated system

⇒ S is maximum for isolated system in equilibrium

⇒ additive $S = S_A + S_B$ total entropy of A, B
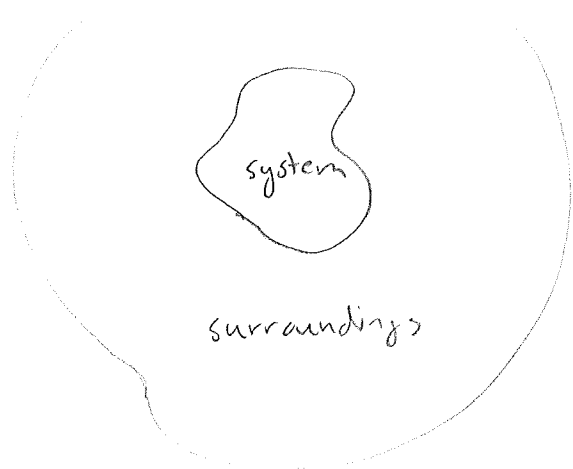
e.g. cup of coffee (system) in
this room (surroundings)

$\Delta S_{composite} \geq 0$ any process!

reversible process

if $\Delta S > 0$ ⇒ $\Delta S_{reverse} < 0$

⇒ $\Delta S = 0$ reversible process

We can relate S to temperature as follows:

$$\left(\frac{\partial S}{\partial E}\right)_{V,N} = \frac{1}{T}$$ ← definition T this way makes
it identical to ideal gas scale