P-chem Thermo   Fri.
    SDSU   2018-02-22   CHEM 343 SP19
                                    SAV 0041
                                    MF 2-2:50P, M.

Atkins Thermo 10th ed.   Ch. 3
& de Paula   Remember "Big Picture" is Chapter "0"
              Foundations, start p.2

Why do things happen?

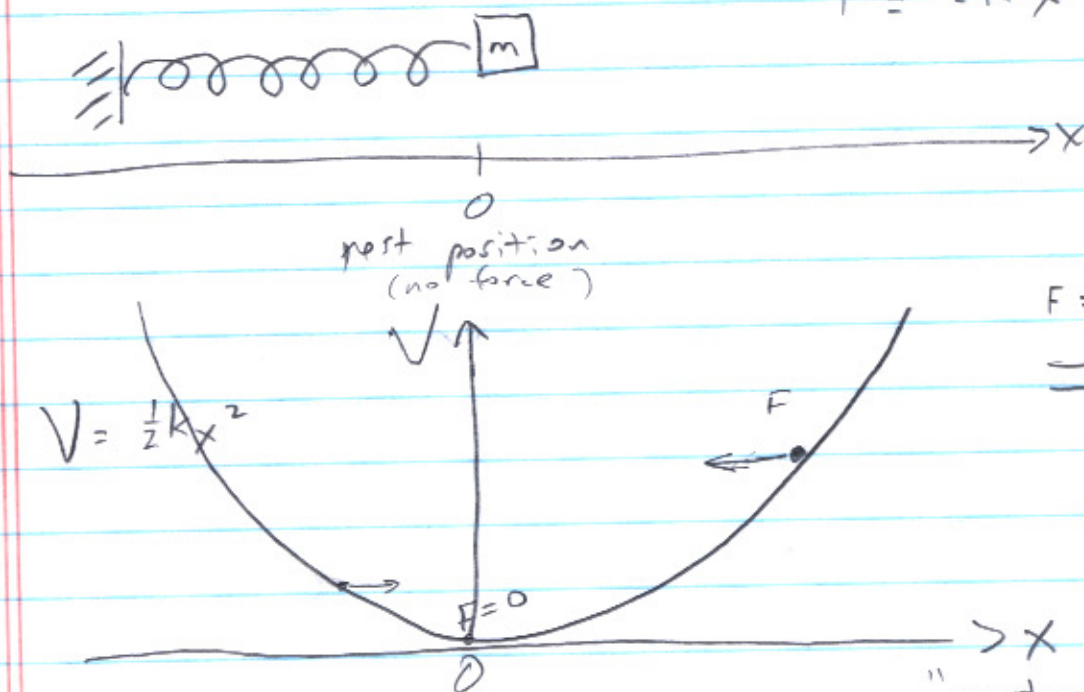Mechanical analogy   1-D, 1 particle system
    physics , Newtonian mechanics
         V   =   potential E
         K   =   kinetic energy
         E = V + K   conserved if no external
                                      forces

E.g. 1-D Hooke's law spring

                              F = -kx

$\exists$|rorororo|m|

———————————————————————————→X
              |
              0
         rest position
         (no force)

                                    Note:
                                  $F = -\dfrac{dV}{dX}$

$V = \frac{1}{2}kx^2$ F
                                  ←———•

              V=0
               0————————————————→X
               0   "spontaneous"

Force is always towards a lower V $\Delta V < 0$
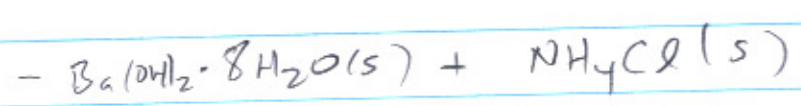
Can we do similar with state variables
(V, T, P, H etc.) and a thermodynamic
system?

Many spontaneous reactions & processes are exothermic
(most) ($\Delta U < 0$ or $\Delta H < 0$)

Some are not!

- Evaporation/boiling (above T_b)

- $Ba(OH)_2 \cdot 8H_2O(s) + NH_4Cl(s)$

- Dissolving NH_4Cl in H_2O

- Mixing/diffusion (sometimes no change in U or H)

So, we need something else!
U or H is not enough

In cases above, always more dispersal of energy
("randomness" or "disorder") in products
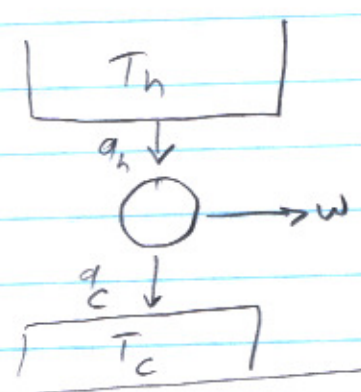
not well defined!

Heat engine
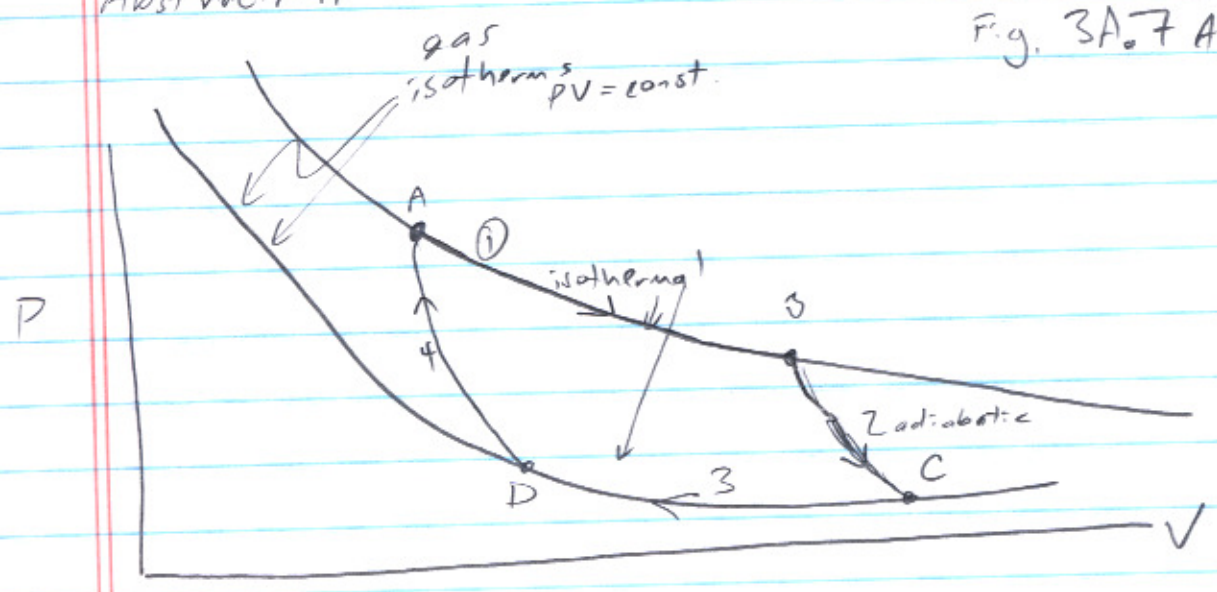
1900s industrial revolution

1816   stirling engine

www.animatedengines.com/vstirling.html

heat removed from T_h q_h

heat rejected at T_c q_c

    work done w

Abstraction — Carnot cycle   PV diagram

Fig. 3A.7 Atkins

gas
isotherms $PV = const.$

Max

efficiency $\eta = \dfrac{\text{work out}}{\text{heat in}} = \dfrac{|w|}{|q_h|}$

can show that this equals $\eta = 1 - \dfrac{T_c}{T_h} = \dfrac{T_h - T_c}{T_h}$

(absolute T's !)

How to maximize efficiency?
- go slow, minimize frictional losses, stay close to equilibrium at all times
- do it as a <u>reversible</u> process

(That's built into the eqns for η at top of page)

Could we ever get $\eta = 1$? would need reversible and $T_c = 0$
i.e. NO cold reservoir. Possible?

<u>No</u> that is the Kelvin statement of the 2nd law.

Proof? It's a law, a summary statement of what we observe in physical world

How to quantify how "bad" it is?

entropy $\boxed{dS = \dfrac{dq_{rev}}{T}}$ 3A.1 p.115

Clausius inequality $\qquad dw - dw_{rev} \geq 0$

$$dS \geq \frac{dq}{T}$$

$\hookrightarrow \qquad dS \geq 0 \qquad$ isolated system

OR $\qquad \Delta S_{univ} = \Delta S_{sys} + \Delta S_{surr} \geq 0$

Overall, system plus surroundings, entropy is NOT conserved. (not always - it is if rev.)

Example problem

3A.10 (a) $\quad N_2 \quad 14\,g \quad\quad 298\,K$, 1.00 bar initially

(See also illustration 3A.7)

doubles volume $\quad\quad\quad V_2 = 2V_1$

(i) isothermal reversible process

Find
$\Delta S_{sys} \quad \Delta S_{tot}$
ΔS_{surr}

$$dS_{sys} = \frac{d\,q_{rev}}{T} \quad\quad \text{isothermal} \quad \Delta S_{sys} = \frac{q_{rev}}{T}$$

Need q_{rev} $\quad\quad$ isothermal, ideal gas

$$\Delta U = 0 \quad \text{for ideal gas, isothermal}$$

↑

$\left[\begin{array}{l} \text{why? See kinetic theory section 1B, B} \quad \text{also foundations} \\ \quad\quad \text{intermolec. forces} = 0 \text{ between particles} \\ \quad\quad\quad E = V + K = K \text{ (kinetic only)} \\ \quad\quad e.g. \quad E = \frac{3}{2}RT \text{ monatomic ideal gas} \end{array}\right]$

$$\Delta U = 0 = q + w \quad\quad q = -w$$

$$q_{rev} = -w_{rev} \quad\leftarrow \text{we can calculate this!}$$

$$d\,w_{rev} = -P\,dV \quad\quad (\text{Eq. 2A.8a})$$

ideal $\quad P = \frac{nRT}{V} \quad\quad w_{rev} = -\int \frac{nRT}{V}\,dV = -nRT\int_{V_1}^{V_2} \frac{dV}{V}$

$$w_{rev} = -nRT \ln\left(\frac{V_2}{V_1}\right) \quad\quad q_{rev} = nRT \ln\left(\frac{V_2}{V_1}\right)$$

3A.10(a) (in)...

N_2 14g   0.50mol

$$\Delta S = \frac{q_{rev}}{T} = \frac{1}{T} \cdot nRT \ln\left(\frac{V_2}{V_1}\right) = nR \ln\left(\frac{V_2}{V_1}\right) \qquad \text{Eq. 3A.16}$$

$$\Delta S_{sys} = (0.50 mol)\left(8.31 \frac{J}{K \cdot mol}\right) \ln\left(\frac{2V_1}{V_1}\right)$$

$$(0.500 mol)\left(8.31 \frac{J}{mol \cdot K}\right) \ln(2) = 28 \frac{J}{K} = \Delta S_{sys}$$

(note S has same units as R $\frac{energy}{Temp}$)

what about ΔS_{surr} ?

Note, the surroundings are a "special" case,
not like a normal system

For surr $$dS_{surr} = \frac{dq_{sur}}{T_{sur}} \qquad \text{Eq. 3A.3a}$$

Isothermal $$\Delta S_{surr} = \frac{q_{surr}}{T_{surr}} \qquad \begin{array}{l} q_{surr} = -q_{sys} \\ T_{surr} = T_{sys} \; \left(\begin{array}{l}iso-\\thermal\end{array}\right) \end{array}$$

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

$$-2.8 \frac{J}{K} = \Delta S_{surr}$$

$$\Delta S_{total(univ.)} = \Delta S_{sys} + \Delta S_{surr} = 0$$

(reversible process)

3A.10 (a)

(ii) Same expansion $V_2 = 2V_1$ but $P_{ex} = 0$

system: <u>same</u> initial & final state

$V_2 = 2V_1$, isothermal

Since S is a state function ΔS is <u>same</u> as (i)!

i.e. $\underline{\Delta S_{sys} = 2.8 \frac{J}{K}}$

surroundings ?   what is q_{surr} ?

$q_{surr} = - q_{sys}$ what is q_{sys}

$q_{sys} = - w_{sys}$ what is w_{sys} ?

Constant P_{ex} expansion

$dw = -P_{ex} dV$ $w = -P_{ex} \Delta V$

$P_{ex} = 0$, $w = 0$, $q = 0$ } system

So, $q_{surr} = 0$, So $\Delta S_{surr} = 0$

$\Delta S_{univ} = \Delta S_{sys} + \Delta S_{surr} = 2.8 + 0 = +2.8 \frac{J}{K}$

irreversible process

Atkins Pr. 3B.2

Find $S_m^\ominus$ of lead at 25°C from C_p data

$$dS_{sys} = \frac{dq_{rev}}{T}$$

For heating $dq = CdT$ if constant P $dq = C_p dT$

$$dS = \frac{C_p dT}{T}$$

Can do if

— C_p is const.

$$dS = \int_{T_1}^{T_2} \frac{C_p dT}{T}$$

$$\Delta S = C_p \ln\left(\frac{T_2}{T_1}\right)$$
$$= n C_{p,m} \ln\left(\frac{T_2}{T_1}\right)$$

- We have functional form for $C_p(T)$ e.g. Table 2B.1

$$C = a + bT + \frac{c}{T^2}$$

- We have data, (C_p, T) numerically integrate

T/K	$C_{p,m}/(JK^{-1}mol^{-1})$
10	2.8
15	7.0
20	10.8
25	14.1
30	16.5
50	21.4
70	23.3
100	24.5
150	25.3
200	25.8
250	26.2
298	26.6

get $\frac{C_p}{T}$ vs T, plot, integrate

$0 \rightarrow 298 \text{ K}$

What about 0 K ?

Data, theory (Debye, Einstein, etc)
show $C_p \sim T^3$ at very low T

So $\dfrac{C_p}{T} \to 0$ as $T \to 0$

Add one data point on $T = 0K$

$$C_p/T = 0 \; J/mol\cdot K$$

what is S_m° at $0K$

third law $\qquad\qquad S_m^\circ = 0$

— crystal must be perfect —

If not, S_m° can be nonzero at $0K$

Sometimes can use statistical interp of S,

$S = k \ln W$, to estimate the "residual" molar
entropy

```matlab
% MATLAB script for Problem 38.2, Atkins and de Paula P-Chem Thermo

clear

% Data given in problem.  Cp in J/(mol K), T in K
Cpdata=[2.8,7.0,10.8,14.1,16.5,21.4,23.3,24.5,25.3,25.8,26.2,26.6];
Tdata=[10,15,20,25,30,50,70,100,150,200,250,298];

% Interesting to plot Cp by itself, then also Cp/T, the entropy integrand
% For the integrand, we manually add the data point for 0K, Cp/T -> 0
% In MATLAB, the . operator will make division do element by element
CpoverT=[0,Cpdata./Tdata];
% Also have to add to the xaxis (T)
T=[0,Tdata];

%   To create the figure, we can do it first manually/interactive, then
%   use the drop down menu to have it generate the code
%   Auto-generated by MATLAB on 22-Feb-2019 11:06:35
% Create figure
figure1 = figure;
% Comment out the line below if you want the figure to pop up
set(figure1, 'Visible', 'off');
% Create axes
axes1 = axes('Parent',figure1);
hold(axes1,'on');
% Create plot
plot(T,CpoverT,'Marker','o');
% Create ylabel
ylabel({'Cp/T/(J/K)'});
% Create xlabel
xlabel({'T/K'});
box(axes1,'on');

print('CpoverTplot.png','-dpng')

% Now, finally, after all that, we use the MATLAB trapezoidal integration
% routine to generate the output value.

Q=trapz(T,CpoverT);

disp('Estimated molar entropy of lead at 298 K, in J/(mol K):')
disp(Q)
```

Atkins Pr. 3B.2, Cp/T of Pb