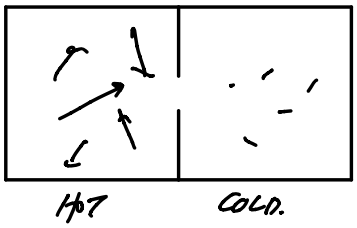
HEAT CAPACITY AND ENTHALPY, 10/7/19

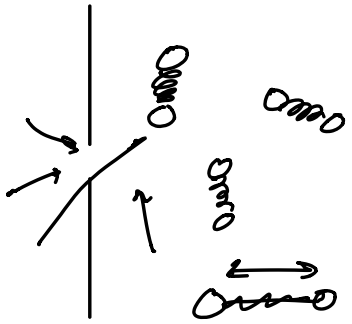
WE LEFT OFF BY DISCOVERING A LINK BETWEEN MICROSCOPIC DESCRIPTIONS OF STATES AND ENTROPY SOMETHING WE CAN MEASURE. HOW DO WE LEARN ABOUT BONDS?

THINK BACK TO IDEAL GAS:



ALL OF THE HEAT GOES TO INCREASING TEMPERATURE.

BUT WHAT IF WE HAVE MORE INTERESTING SYSTEM.?



IMAGINE WE LINK OUR IDEAL GAS TO A NON-IDEAL GAS CONSISTING OF SPRINGS.

A LOT OF ENERGY WILL GO TO RANDOM MOVEMENT OF PARTICLES ($\langle v^2 \rangle \propto T$).

SOME WILL GO TO REARRANGING INTERNAL BONDS.

WE CAN MEASURE THIS BY ASKING HOW MUCH ENERGY INPUT IT TAKES TO INCREASE TEMPERATURE: THE HEAT CAPACITY (C_p)

$\frac{\delta q}{dT} = C_p$. HOW MUCH HEAT MUST BE APPLIED TO INCREASE T?

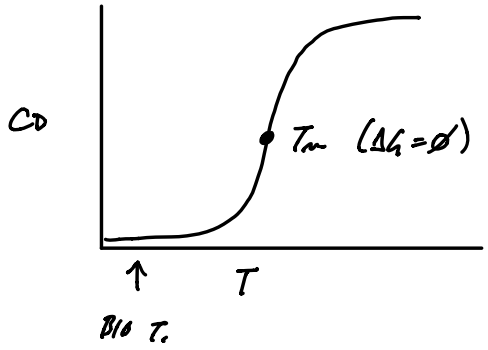
FOR SMALL C_p, ALL HEAT GOES TO INCREASING T. FOR LARGE C_p, "SOMETHING" IN SYSTEM ABSORBS EXCESS ENERGY.

$$\delta q = C_p dT$$

IF SYSTEM IS NOT DOING WORK, CHANGE IN HEAT REPORTS ON CHANGE IN ENTHALPY.

$$dH = \delta q + \cancel{dw} = C_p dT$$

IN FIRST LECTURE, WE TALKED ABOUT EXPERIMENT WHERE WE MELTED A PROTEIN TO LEARN ABOUT HOW IT WAS PUT TOGETHER:



WHAT WE REALLY CARE ABOUT IS BIOLOGICAL T.

HOW DO WE GET THERE?

$$G = H - TS$$

ln(PROB OF STATE) = BONDS AND STUFF − ENTROPY
(LOG NUMBER OF MICROSTATES)

$$G(T) = H(T) - TS(T)$$

LET'S DO H FIRST:

$$dH = C_p dT$$

$$\int_{H_r}^{H} dH = \int_{T_{r,H}}^{T} C_p dT$$

$$H - H_r = C_p (T - T_{r,H})$$

$$H(T) = C_p (T - T_{r,H}) + H_r$$

(1) H IS A LINEAR FUNCTION OF TEMPERATURE

(2) IF WE KNOW C_p AND THE ENTHALPY AT A REFERENCE TEMPERATURE, WE CAN CALCULATE ENTHALPY OF STATE AT ANY TEMPERATURE.

WHAT ABOUT S?

$$\frac{\delta q_r}{T} = dS \qquad \delta q = C_p dT$$

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

$$\int_{T_{s,R}}^{T} \frac{C_p dT}{T} = \int_{S_R}^{S} dS \qquad \int \frac{1}{x} = \ln(x)$$

$$C_p [\ln(T) - \ln(T_{s,R})] = S - S_R$$

$$C_p \ln\left(T / T_{s,R}\right) = S - S_R$$

$$S(T) = C_p \ln\left(T / T_{s,R}\right) + S_R$$

(1) S IS A LOGARITHMIC FUNCTION OF TEMPERATURE.

(2) IF WE KNOW C_p AND THE ENTROPY AT A REFERENCE TEMPERATURE, WE CAN CALCULATE ENTROPY OF STATE AT ANY TEMPERATURE.

$$G_T(T) = C_p(T - T_{rH}) + H_r - T\left[C_p \ln(T/T_{rS}) + S_r\right]$$

THIS IS FOR ONE STATE. WE ARE ALMOST ALWAYS COMPARING TWO STATES (I.E. F AND U). SO USUALLY WRITE IN Δ FORM:

$$\begin{aligned} \Delta G(T) &= \Delta H(T) - T\Delta S(T) \\ \Delta H(T) &= \Delta C_p(T - T_{rH}) + \Delta H_r \\ \Delta S(T) &= \Delta C_p \ln\left(T/T_{rS}\right) + \Delta S_r \end{aligned}$$

WITH THIS, WE CAN EXPERIMENTALLY ACCESS FREE ENERGY, ENTHALPY, AND ENTROPY AT BIOLOGICAL TEMPERATURE.

KEY POINTS:

- HEAT CAPACITY (C_p) MEASURES HOW EFFECTIVE HEAT IS AT INCREASING TEMPERATURE.
- C_p IS DETERMINED BY ABILITY OF BONDS ETC. TO ABSORB ENERGY AS OPPOSED TO KINETIC ENERGY OF EACH MOLECULE GOING UP. ($T\uparrow$)
- EXPRESSION FOR $\Delta G(T) = \Delta H(T) - T\Delta S(T)$ ALLOWS US TO MEASURE THERMODYNAMICS AT HIGH TEMP AND THEN CALCULATE THERMO AT LOW TEMP.