<u>Today</u>

I.   Last Time

II. The Coffee Cup Calorimeter

III. Fuel Cells as an Example of Gibbs Free Energy

IV. A Extremum Principle for the Free Energy

I.   Nathalie discussed the various free free energies:

$U = U(S, V, N)$, $dU = TdS - PdV + \mu dN$

$H = U + PV$, which satisfies $dH = dU + PdV + VdP = TdS + VdP$, and hence is a function $H = H(S, P)$.

$F = U - TS$, then $F = F(T, V, N)$.

$G = U - TS + PV$, then $G = G(T, P, N)$. Suppose we had this one:

$dG = dU - TdS - SdT + PdV + VdP = -SdT + VdP + \mu dN$, then

$$\left(\frac{\partial G}{\partial P} \right)_{T,N} = V, \quad S = -\left(\frac{\partial G}{\partial T} \right)_{P,N}, \quad \mu = \left(\frac{\partial G}{\partial N} \right)_{T,P}$$

II. How do we get Enthalpies? I want to answer this because we are going to build a lot of discussion of free energies on top of the measurement of enthalpies.

Fix the number of particles, fix the environmental pressure

$$dH = d(U + PV) = dU + PdV + VdP = TdS + VdP = TdS = Q.$$

Measuring enthalpies amounts to measuring heats, and we do this with a calorimeter. Let's take the simplest example, a so-called coffee cup calorimeter: make a solution with one chemical and a 2nd solution with another, by mixing these a chemical reaction can proceed and give h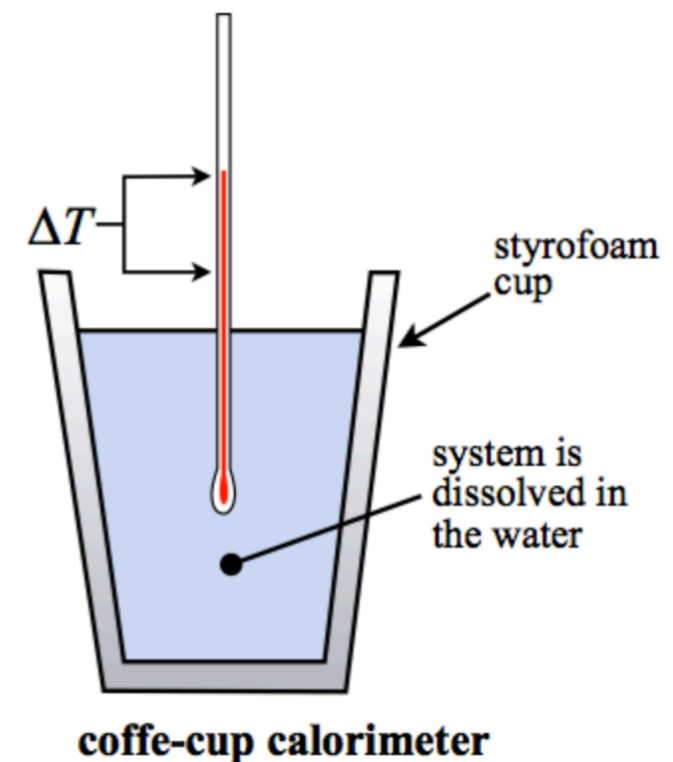eat up to the water. By stirring the reaction with a Thermometer and measuring the change in Temperature we can tell the amount of heat given Up to th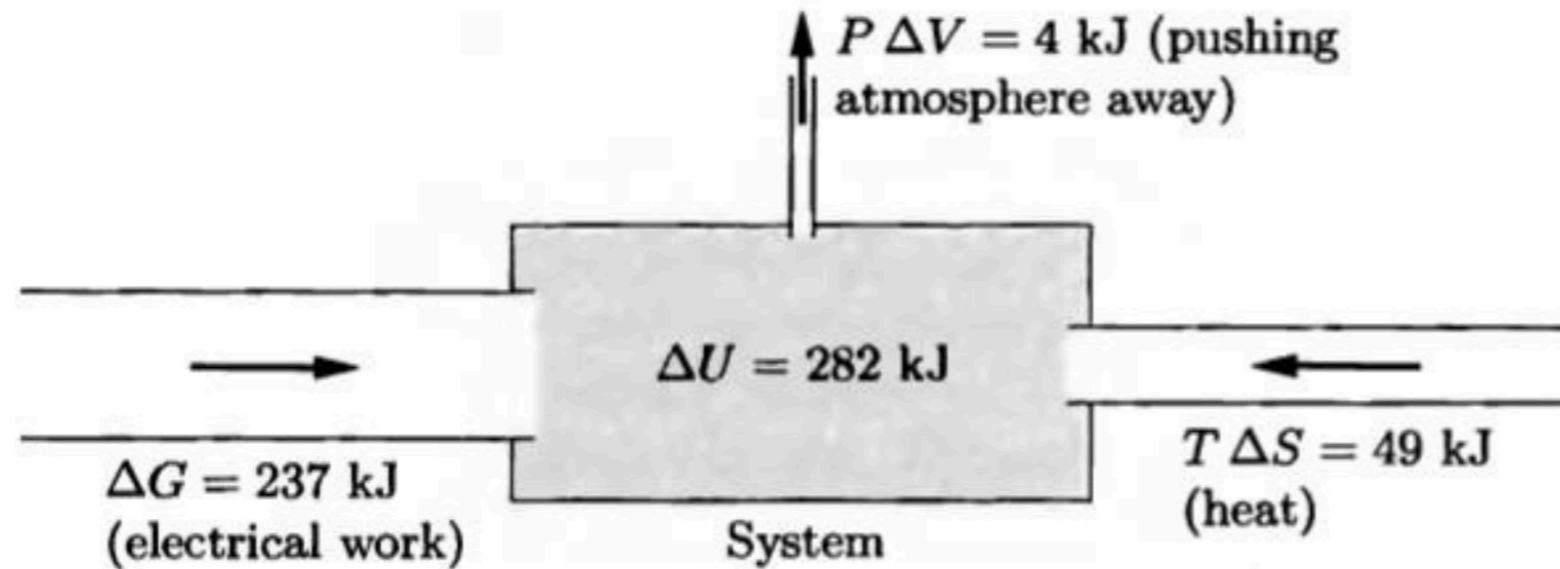e water. We can even calibrate the Calorimeter constant and compensate for any energy into the environment. This provides a measure of the change in enthalpy.

coffe-cup calorimeter

II. Combining this with Hess' law says that the changes in intermediate steps add up to the total change for a reaction:

$$\Delta H_{rxn} = \Delta H_1 + \Delta H_2 + \cdots + \Delta H_n.$$

$P \Delta V = 4$ kJ (pushing atmosphere away)

$\Delta U = 282$ kJ

$\Delta G = 237$ kJ (electrical work)

System

$T \Delta S = 49$ kJ (heat)

III. Let's see how we can use the Gibbs' free energy in the context of a Hydrogen fuel cell. We can measure the energy investment at room temperature and atmospheric pressure and find

$$\Delta H = 286 \text{ kJ}.$$

Running this in reverse we can get that much energy out of combining H_2 and O_2 gasses. Measuring the entropies gives $S_{H_2O} = 70$J/K, $S_{H_2} = 131$J/K, and $S_{O_2} = 205$J/K.

III. Running this in reverse we can get that much energy out of combining H_2 and O_2 gasses. Measuring the entropies gives $S_{H_2O} = 70J/K$, $S_{H_2} = 131J/K$, and $S_{O_2} = 205J/K$. The entropy piece is then

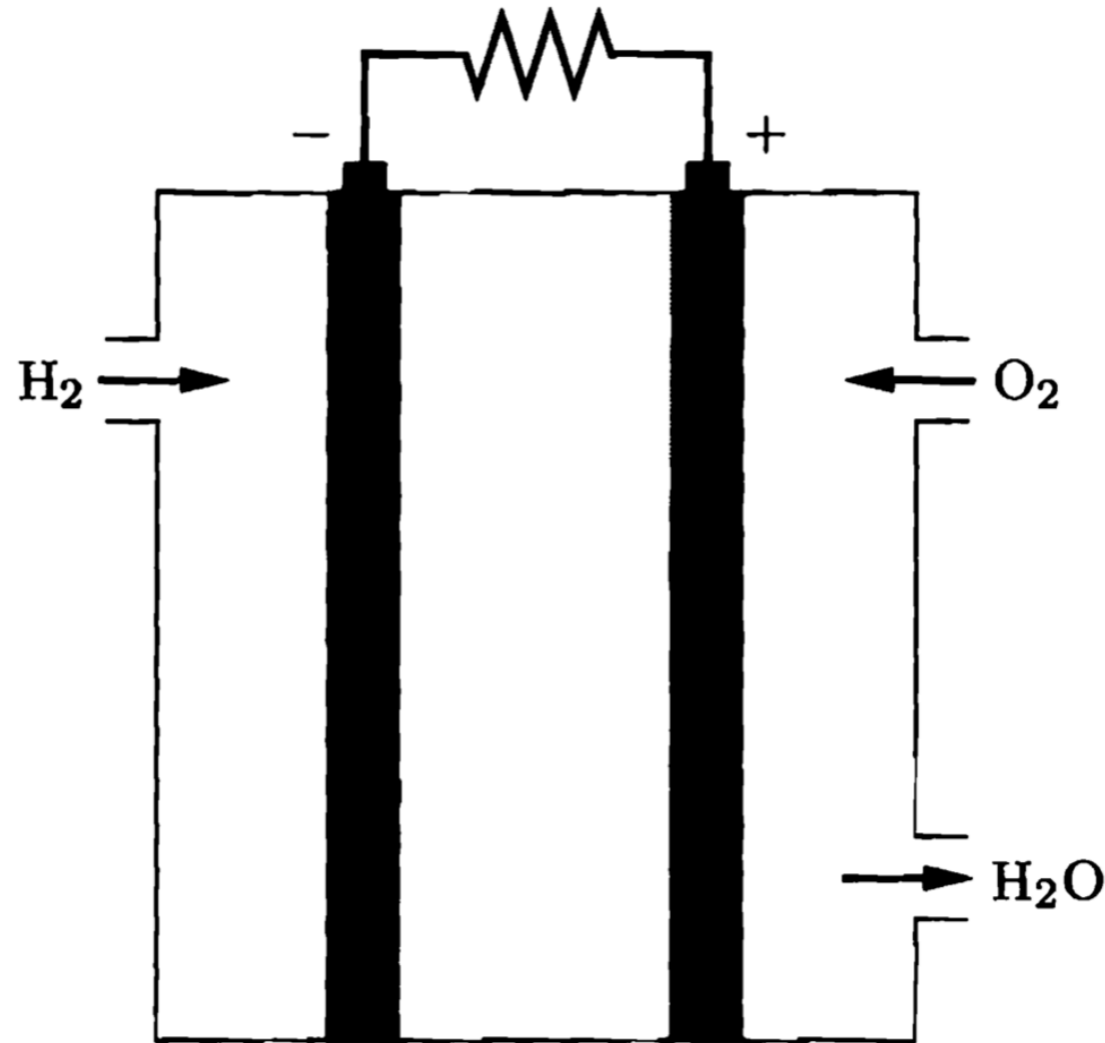$$\Delta S = (131 + \frac{1}{2}205) - 70 = 163J/K$$

at room temperature and so

$$Q = T\Delta S = (298 \text{ K})(163J/K) = 49 \text{ kJ}.$$

We can now combine this with measured ΔH to get at the electrical work (either put into the electrolysis or removed in the full cell)

$$\Delta G = \Delta H - T\Delta S = 286 \text{ kJ} - 49 \text{ kJ} = 237 \text{ kJ}$$

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III. So how does an actual fuel cell extract this energy?

While it amounts to book keeping, the formalism of the Gibbs free energy and the enthalpy are immensely useful in practice.

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The "microcanonical ensemble" assumes that the macroscopic energy is fixed and that all microstates consistent with this condition are equally likely (in fact we also imagined fixing the volume and the number of particles).

Consider a large environment, which we will treat as a reservoir— meaning that any energy exchanges with this environment, don't change the environment's temperature. This will amount to holding the system at a fixed temperature instead of a fixed energy.