Phys 344.

Lecture 23.

- Electrolysis $P = 1$ bar (atm). $T = 300K$

$$H_2O \longrightarrow H_2 + \frac{1}{2} O_2$$

1 mol. 1 mol. 0.5 mol.

$$\Delta H = (\Delta_f H)_{products} + (\Delta_f H)_{reactants}.$$

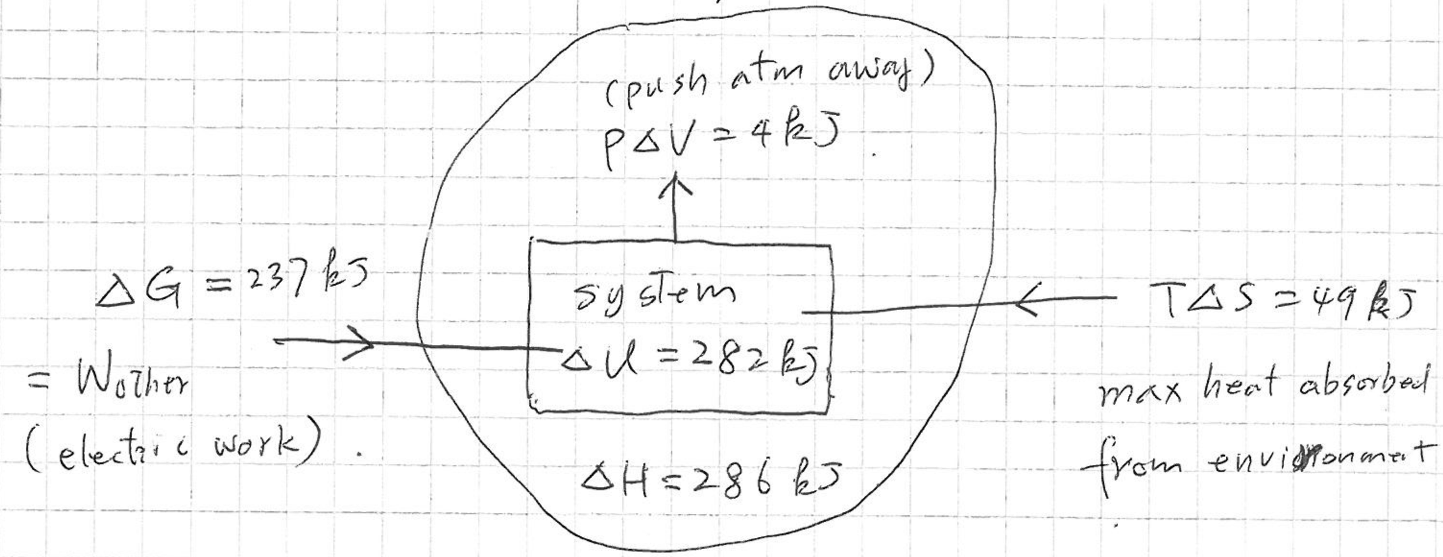
$$= 0 + 0 - (-285.83 \text{ kJ})$$

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

$$= \underbrace{\Delta U}_{282 \text{ kJ}} + \underbrace{P \Delta V}_{4 \text{ kJ}}$$

$$\left(\begin{aligned} PV &= nRT \\ &= 1.5 \times 8.31 \times 300 \\ &= 4 \text{ kJ}. \end{aligned} \right)$$

U = internal energy.



$\Delta S > 0$: System can absorb heat from environment.

Then, how much of the needed $\underbrace{286\ kJ}_{(\Delta H)}$ can come from the environment as heat (free!), and how much electric work we have to supply?

Max heat absorbed (ideally): $Q = T\Delta S$

$S_{H_2O} = 70\ J/K$, $S_{H_2} = 131\ J/K$, $S_{O_2} = 205\ J/K$

$\times 0.5$

$$\Delta S = 131 + 0.5 \times 205 - 70 = 163\ J/K.$$

$$T\Delta S = 49\ kJ.$$

Then, electric work required:

$$W_{other} = (\Delta G) = \Delta U + P\Delta V - T\Delta S \ (= \Delta H - T\Delta S)$$

$$\Delta G = 286 - 49 = 237\ kJ.$$

$\therefore$ ΔG = minimum "other" work to make it occur.

other than the "automatic" work $P \cdot \Delta V$ (pushing the atmosphere)

ΔG is just a short cut for $\Delta H - T\Delta S$.

It's been calculated for many cases and can be looked up in tables.

- look up ΔG directly.

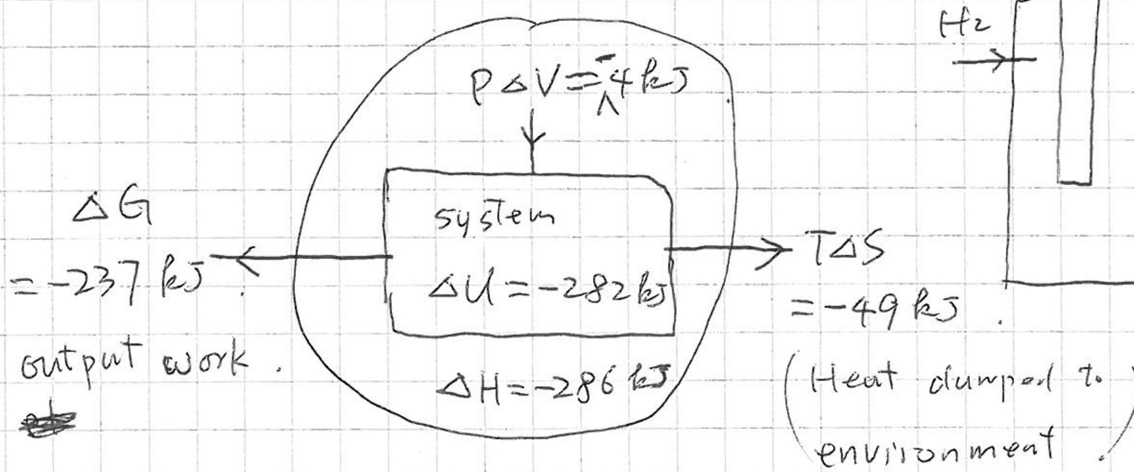
$$\Delta G = (\Delta_f G)_{products} - (\Delta_f G)_{reactants}$$

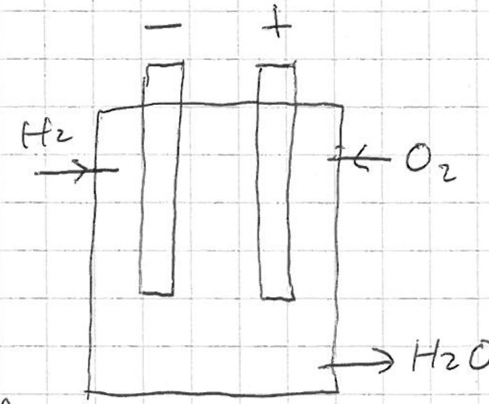
$$= 0 + 0 - (-237.13 \text{ kJ})$$

$$= 237 \text{ kJ}. \quad \text{(we can skip } \Delta H \text{ and } \Delta S\text{)}$$

- The reverse reaction. — Fuel cell.

$$H_2 + \frac{1}{2} O_2 \longrightarrow H_2O.$$





$T\Delta S = -49$ kJ = max heat absorbed by system.

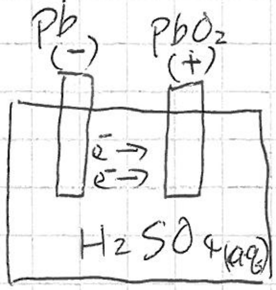
actual heat absorbed by system: $Q < T\Delta S < -49$ kJ.

(e.g. $Q = -60$ kJ)

$\therefore$ $|T\Delta S|$ — minimum heat dumped to environment

$|\Delta G|$ — max work output. (237 kJ)
(can be less).

- Battery in a car.



Discharge:

$$Pb + PbO_2 + 4H^+ + 2SO_4^{2-} \longrightarrow 2PbSO_4 + 2H_2O$$

	Pb	PbO_2	$4H^+$	$2SO_4^{2-}$	$2PbSO_4$	$2H_2O$
$\Delta_f G$	0	-217	0	-745×2	-813×2	-237×2
$\Delta_f H$	0	-277	0	-909×2	-920×2	-286×2

$$\Delta G = (\Delta_f G)_{products} - (\Delta_f G)_{reactants}$$

$$= (-813\times2 - 237\times2) - (-217 - 745\times2)$$

$$= -394 \text{ kJ/mol} \quad (= \Delta H - T\Delta S)$$

∴ Max work produced: 394 kJ/mol.

but: $\Delta H = -316$ kJ/mol.

∴ Energy comes out from the system including the automatic work done by the enviroment : 316 kJ

Then, output electric work > energy comes out of system.

Extra energy = 394 - 316 = 78 kJ. ($T\Delta S$)

comes as heat (max)
from environment.

- Voltage :

discharging

at − electrode . $Pb + HSO_4^- \longrightarrow PbSO_4 + H^+ + 2e^-$

\+ electrode $PbO_2 + HSO_4^- + 3H^+ + 2e^- \rightarrow PbSO_4 + 2H_2O$

2 electrons are moving arround the circuit

(for every reaction)

Electric work per electron :

$$\frac{394\ kJ}{2 \times 6.02 \times 10^{23}} = 3.27 \times 10^{-19} J = 2.04\ eV$$

$\therefore$ Voltage = 2.04 V .

with 6 cells in series :

Total voltage of a car battery : $6 \times 2.04 = 12\ V$