Thermodynamic Potentials & Chemical Reactions

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

releases 286 kJ/mol of heat

U?
H?
F?
G?

$\Delta H = -286$ kJ/mol includes air rushing in to fill newly available space

"enthalpy of formation" of water

(change in enthalpy required to create water from basic components)

$\Delta H < 0$: exothermic reaction (releases energy)

$\Delta H > 0$: endothermic reaction (absorbs energy)

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eg. $\underbrace{C_6H_{12}O_6}_{\text{1 mole}} + \underbrace{6O_2}_{\text{6 moles}} \longrightarrow 6CO_2 + 6H_2O$

ΔH_f (pg 404) $(1\,\text{mol})(-1273\,\text{kJ/mol}) + (6\,\text{mol})(0\,\text{kJ/mol})$ $\quad 6(-393.5\,\text{kJ/mol}) + 6(-285.8\,\text{kJ/mol})$

$-1273 + 0 \qquad -2371 - 1715$

$H_i = -1273$ kJ $\qquad H_f = -4076$ kJ

$\Delta H = -4076 - (-1273) = -2803$ kJ/mol

exothermic reaction

4. $H_2O \rightarrow H_2 + \frac{1}{2} O_2$ @ $T = 300K$, $P = 10^5$ Pa

$H = U + PV$
$F = U - TS$
$G = H - TS$
$G = U + PV - TS$
$= F + PV$

$\Delta V = 0.04 \, m^3/mol$

$\Delta S = 163 \, J/K/mol$

$\Delta H = +286 \, kJ/mol$

$\Delta U = \Delta H - P\Delta V = 286 \, kJ/mol - \overbrace{(10^5)(0.04)}^{4 \, kJ/mol}$

$= 282 \, kJ/mol$

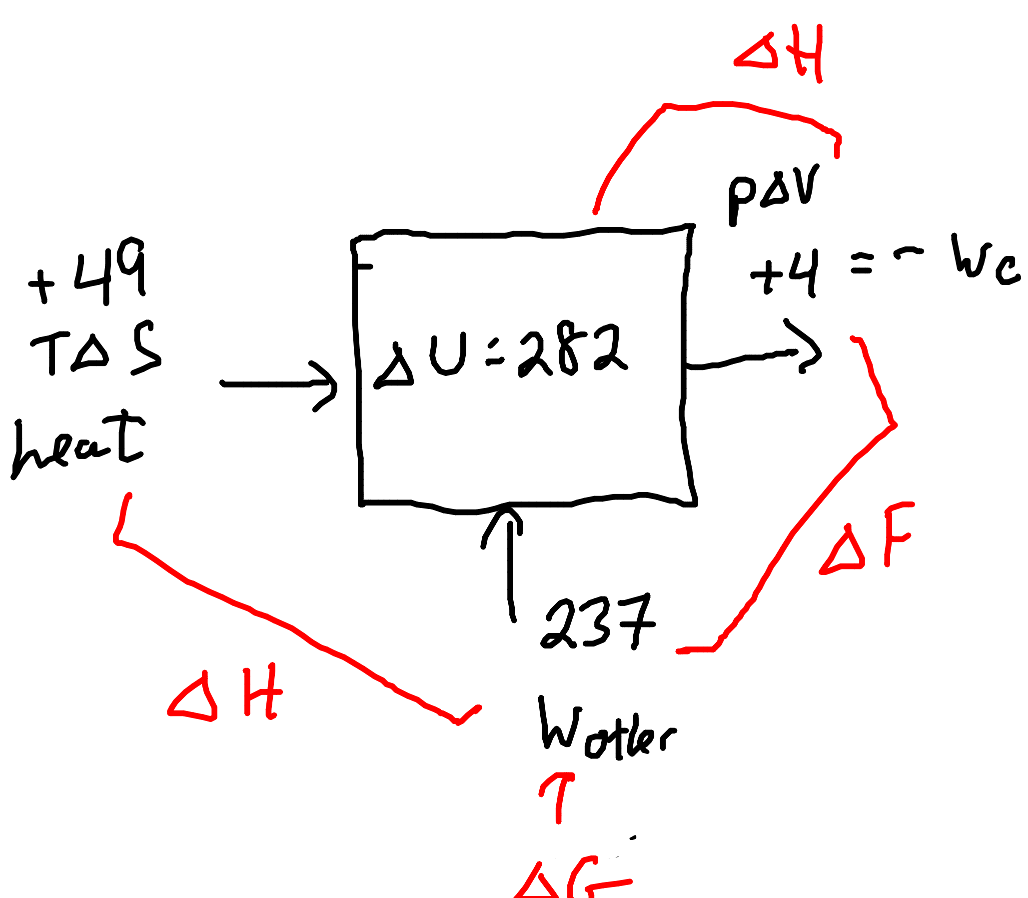
$\Delta F = \Delta U - T\Delta S = 282 \, kJ/mol - \overbrace{(300)(163)}^{49 \, kJ/mol}$

$= 233 \, kJ/mol$ total work required

$\Delta G = \Delta F + P\Delta V = 233 \, kJ/mol + 4 \, kJ/mol$

$= 237 \, kJ/mol$ noncompression work required

(e.g. via electricity)



$$dU = T\,dS - P\,dV + \mu\,dN$$

1st derivatives

$$\left(\frac{\partial U}{\partial S}\right)_{V,N} = T \qquad \left(\frac{\partial U}{\partial V}\right)_{S,N} = -P$$

2nd derivatives

$$\frac{\partial^2 U}{\partial S\,\partial V} = \frac{\partial}{\partial V}\frac{\partial U}{\partial S} = \frac{\partial}{\partial V}(T) = \left(\frac{\partial T}{\partial V}\right)_{S,N}$$

$$= \frac{\partial}{\partial S}\frac{\partial U}{\partial V} = \frac{\partial}{\partial S}(-P) = -\left(\frac{\partial P}{\partial S}\right)_{V,N}$$

Maxwell Relation

conjugates

$$\underbrace{\left(\frac{\partial T}{\partial V}\right)_{S,N}}_{\text{natural variables}} = - \underbrace{\left(\frac{\partial P}{\partial S}\right)_{V,N}}_{\text{natural variables}}$$

$-P\,dV + T\,dS$

different signs

reciprocal

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

volume expansion as T rises

at constant S
- insulated container
- relatively fast (but not too fast)

"adiabatic"

change in entropy with increase pressure at constant volume