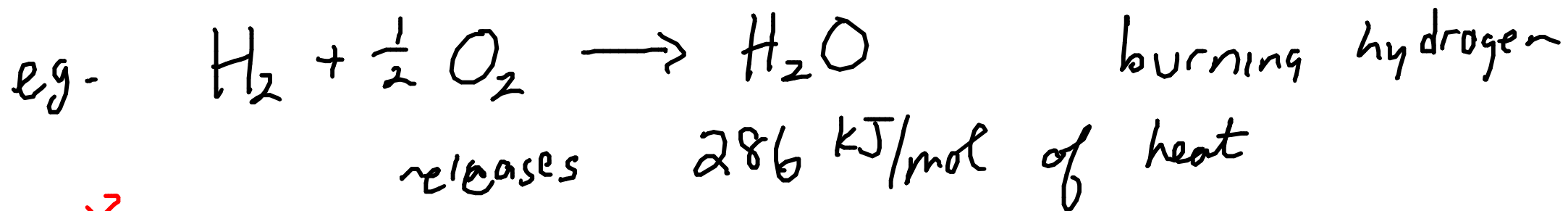


Thermodynamic Potentials & Chemical Reactions



U?
H?
F?
G?

$$\Delta H = -286 \text{ kJ/mol}$$

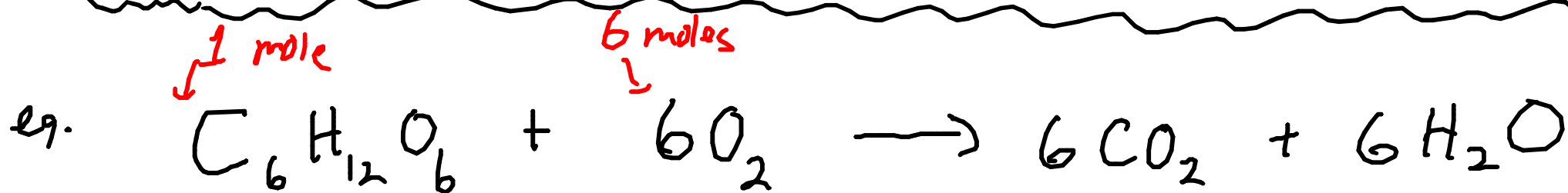
includes air rushing in
to fill newly available space

"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)



$$\Delta H_f (1\text{mol})(-1273 \text{ kJ/mol}) + (6\text{mol})(0 \text{ kJ/mol}) \quad 6(-393.5 \text{ kJ/mol}) + 6(-285.8 \text{ kJ/mol})$$

(pg 404) $-1273 \quad + 0 \quad -2371 \quad -1715$

$$H_i = -1273 \text{ kJ} \quad H_f = -4076 \text{ kJ}$$

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

Exothermic reaction

14.



$$\begin{aligned} @ T &= 300\text{K} \\ P &= 10^5 \text{ Pa} \end{aligned}$$

$$H = U + PV$$

$$F = U - TS$$

$$G = H - TS$$

$$\begin{aligned} G &= U + PV - TS \\ &= F + PV \end{aligned}$$

$$\Delta V = 0.04 \text{ m}^3/\text{mol}$$

$$\Delta S = 163 \text{ J/K/mol}$$

$$\Delta H = +286 \text{ kJ/mol}$$

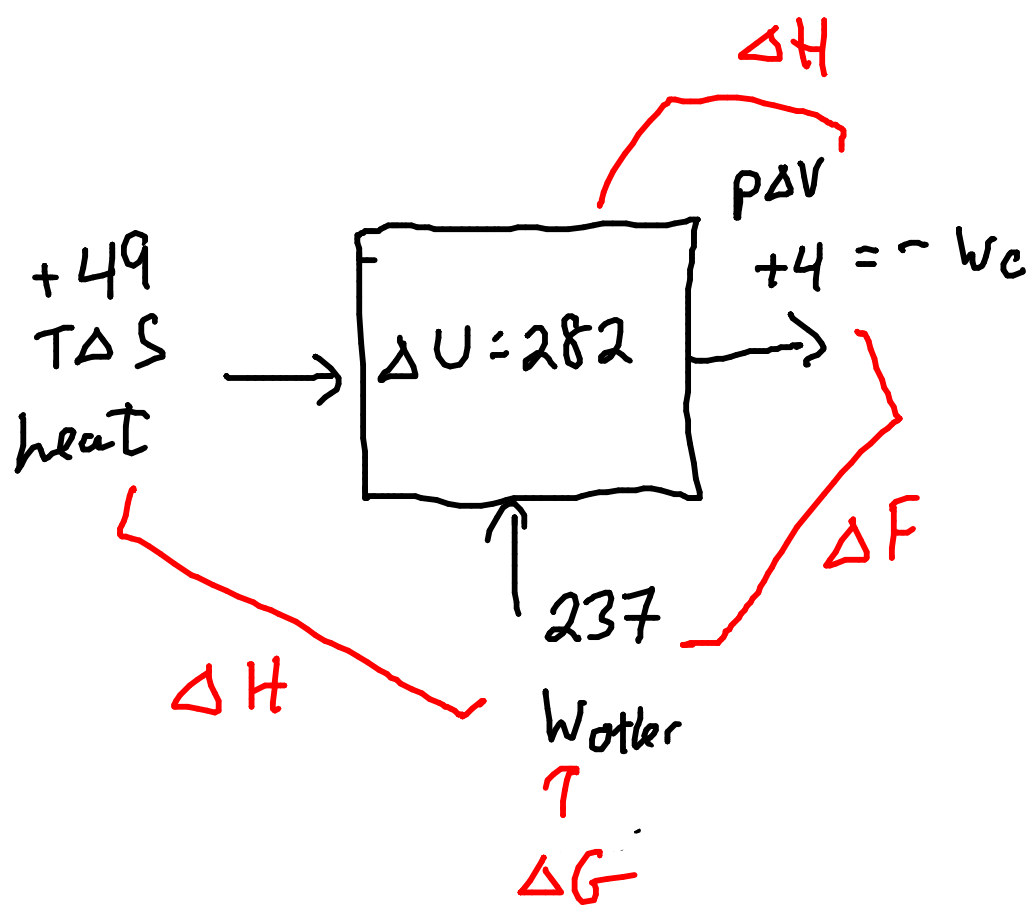
$$\begin{aligned} \Delta U &= \Delta H - P\Delta V = 286 \text{ kJ/mol} - \overbrace{(10^5)(0.04)}^{4 \text{ kJ/mol}} \\ &= 282 \text{ kJ/mol} \end{aligned}$$

$$\begin{aligned} \Delta F &= \Delta U - T\Delta S = 282 \text{ kJ/mol} - \overbrace{(300)(163)}^{49 \text{ kJ/mol}} \\ &= 233 \text{ kJ/mol} \quad \text{total work required} \end{aligned}$$

$$\Delta G = \Delta F + P\Delta V = 233 \text{ kJ/mol} + 4 \text{ kJ/mol}$$

$$= 237 \text{ kJ/mol} \quad \text{noncompression work required}$$

(e.g. via electricity)



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

1st
derivatives

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

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

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

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

conjugates

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

change in entropy
with increase pressure
at constant volume

at constant S

- insulated container
- relatively fast (but not too fast)
- "adiabatic"