Constant pressure

$$C_P = \left(\frac{\Delta U - (-P\Delta V)}{\Delta T}\right)_P = \left(\frac{\partial U}{\partial T}\right)_P + P\left(\partial_T V\right)_P$$

not quite the same as C_V ↑

$\underbrace{P\left(\partial_T V\right)_P}$ additional Q for W

Suppose quadratic DoF $U = \frac{f}{2}NkT$

$$C_V = \left(\partial_T U\right)_V = \partial_T \left(\underbrace{\frac{f}{2}NkT}\right) = \frac{f}{2}Nk$$

independent of P, V so either can be fixed
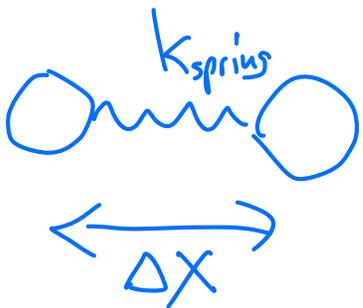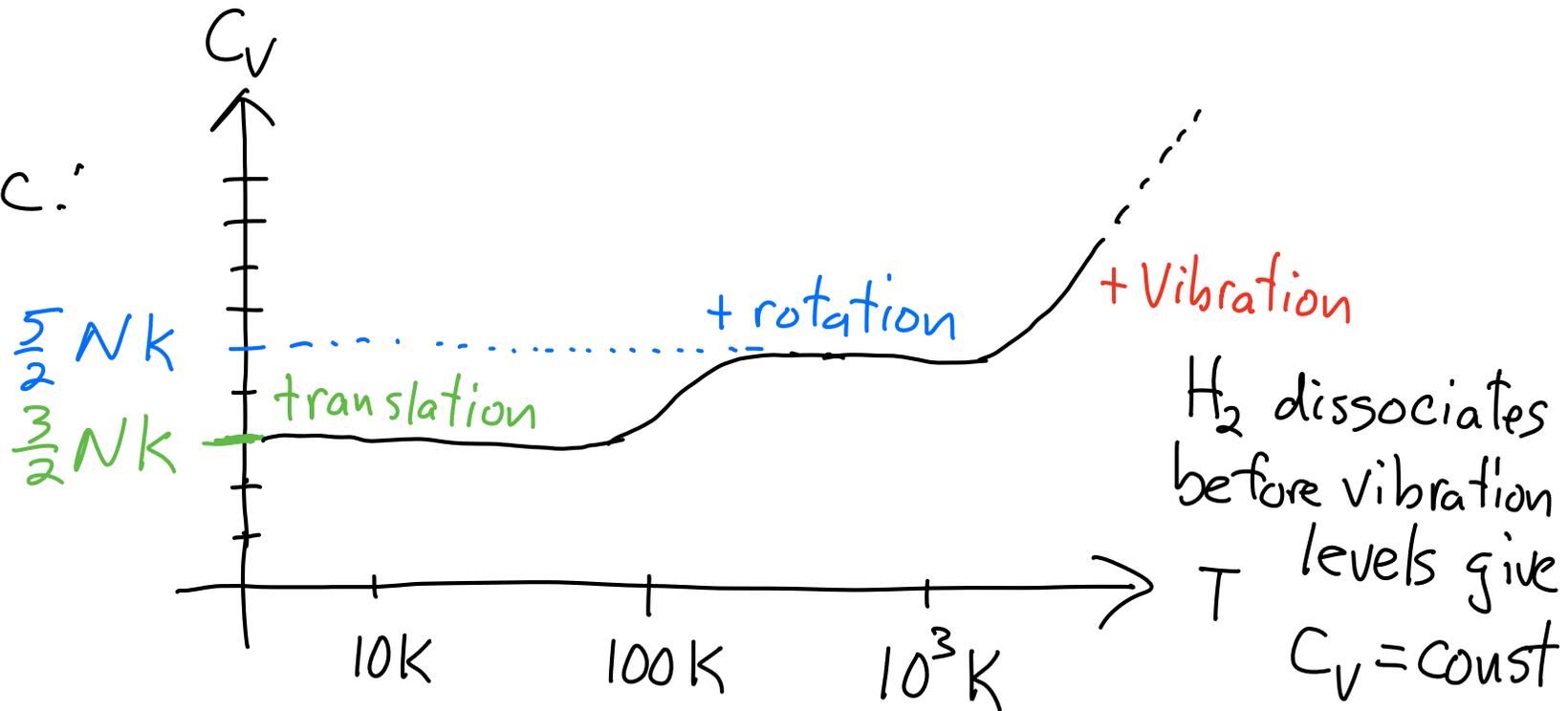
$$C_V = \frac{f}{2} N k T$$

monatomic gas: $\quad f = 3 \rightarrow C_V = \frac{3}{2} N k T$

solid $\qquad f = \underbrace{3}_{KE} + \underbrace{3}_{PE} \rightarrow C_V = 3 N k T \quad$ Dulong & Petit

diatomic:

$\frac{5}{2} N k$
$\frac{3}{2} N k$ — translation
+ rotation
+ Vibration

H_2 dissociates before vibration levels give $C_V = $ const

10K   100K 10^3 K   T

k_{spring}

ΔX

$$E = \frac{1}{2} m (\Delta \dot{x})^2 + \frac{1}{2} k_{spring} \Delta X^2$$

C_P for ideal gas

$$C_P = \textcolor{red}{(\partial_T U)_P} + \textcolor{green}{P(\partial_T V)_P}$$
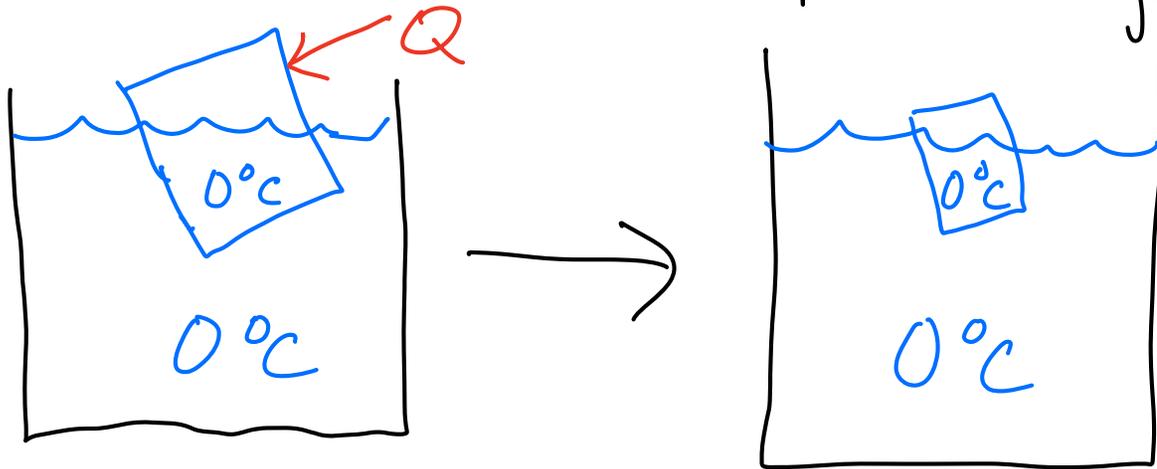
$$\textcolor{green}{P(\partial_T V)_P = P\partial_T\left(\frac{NkT}{P}\right) = P\frac{Nk}{P} = Nk}$$

$$\textcolor{red}{(\partial_T U)_P = \left(\partial_T \frac{f}{2}NkT\right)_P = \frac{f}{2}Nk}$$

$$C_P = \underbrace{\textcolor{red}{\frac{f}{2}Nk}}_{\textcolor{red}{C_V}} + \underbrace{\textcolor{green}{Nk}}_{\textcolor{green}{\text{extra for } C_P}}$$

Latent Heat

heat added to make phase change:

Solid $\rightarrow$ liquid

liquid $\rightarrow$ gas

$$C = \frac{Q}{\Delta T} = \frac{Q}{0} \,!$$

latent heat $\qquad L \equiv \dfrac{Q}{m}$

$H_2O: \quad L_{fusion} = 333 \;^{J}/_{g}$
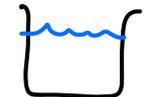
for phase transitions use latent heat

mass of material converted from phase 1 $\rightarrow$ phase 2

$L_{vaporization} = 2260 \;^{J}/_{g}$

$L_{sublimation} = 2834 \;^{J}/_{g}$

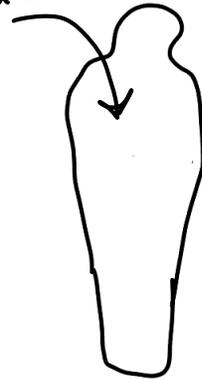$(T = 0°C)$

Enthalpy

Constant pressure is common. e.g. open beaker: (air)
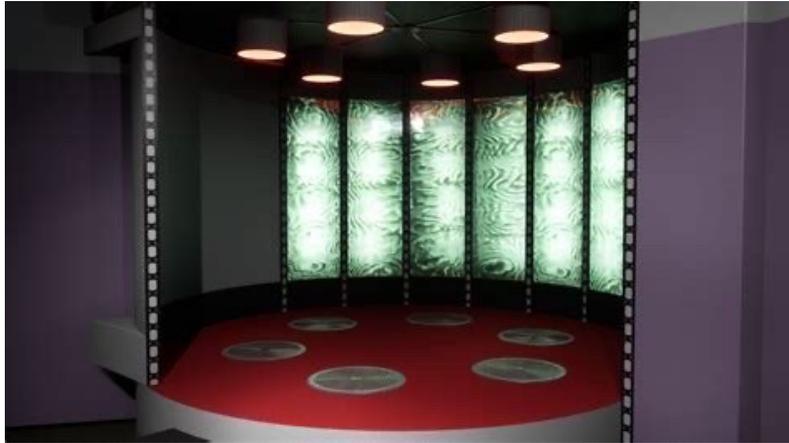
push air out of the way

$$W_{on} = -\int P\,dV = -P_{1atm} \cdot V_{person}$$

$$W_{by\ xporter} = PV$$

Vacuum → materialize matter inside "bubble"

work to make "bubble"

enthalpy $H = U + PV$

actual energy needed to create system in const. P env.

$H = U + PV$ is the freely available energy in a constant pressure environment.

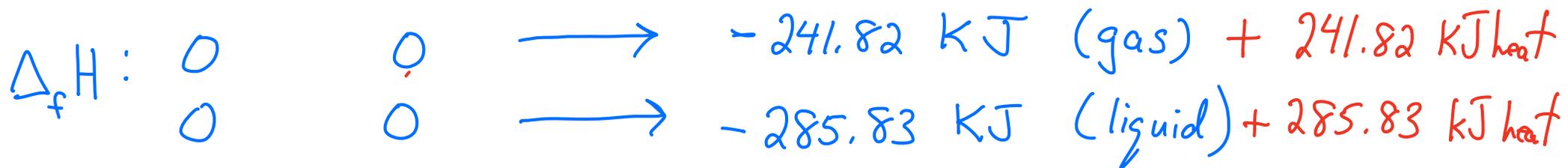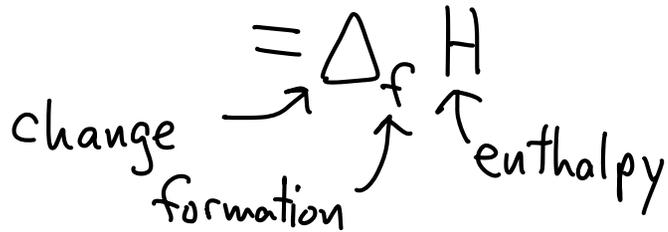= energy to create system AND work* to push environment medium out of the way.

* could be other forms of work (electrical, chemical, etc.)

Note that $C_p = \left(\partial_T U\right)_P + P\left(\partial_T V\right)_P = \left(\partial_T (U+PV)\right)_P = \left(\partial_T H\right)_P$

Thermodynamic Properties of Selected Substances

Substance (form)	$\Delta_f H$ (kJ)	$\Delta_f G$ (kJ)	S (J/K)	C_P (J/K)	V (cm^3)
H_2 (g)	0	0	130.68	28.82	
H (g)	217.97	203.25	114.71	20.78	
H^+ (aq)	0	0	0	0	
H_2O (l)	-285.83	-237.13	69.91	75.29	18.068
H_2O (g)	-241.82	-228.57	188.83	33.58	

Tables give "enthalpy of formation" = H to form 1 mole out of elements in most stable form. (at room temp, 1 atm)

$$= \Delta_f H$$

change → $\Delta_f H$ ← enthalpy
formation

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

$\Delta_f H:$ 0   0 $\longrightarrow$ -241.82 KJ (gas) $+ 241.82$ KJ heat

0   0 $\longrightarrow$ -285.83 KJ (liquid) $+ 285.83$ kJ heat

happens spontaneously   exothermic: final $\sum \Delta_f H <$ init $\sum \Delta H_f$

NOT spontaneous   endothermic: $($ $) > ($ $)$

U seems fundamental, the sum of energies of all particles in system.

Tables give H (or $\Delta_f H$ really). We can get U...

$$U = H - PV$$

$$U(1 \text{ mole of } H_2O \text{ gas @ STP})$$

$$= -241.82 \text{ kJ} - PV = -241.82 \text{ kJ} - (10^5 Pa) \times 2.476 \times 10^{-2} m^3$$

$$= -241.82 \text{ kJ} - 2476 J = -244.3 \text{ kJ}$$

$$V_{1 \text{mol}} = \frac{nRT}{P} = \frac{1 \text{mole} \times 8.31 \frac{J}{\text{mol-K}} \cdot 298 K}{10^5 Pa} = 2.476 \times 10^{-2} m^3$$