

APSC - ~~132~~ 132 January 10th 2022

Gibbs energy & chemical equilibrium

Define  $\rightarrow$  appropriate system boundary

$\rightarrow$  thermodynamic processes

$\rightarrow$  Gibbs energy

- how we define the system matters  
- by looking at only 1 part, we can miss changes in others

Equilibrium Thermodynamics

- At a given pressure and temp, what state(s) is the ~~best~~ system

Systems & Surroundings

$\rightarrow$  quantity of matter

$\rightarrow$  Region in space

$\rightarrow$  everything outside of the system

if it's not part of the system, it's part of the surroundings

Lack of concern for surroundings has caused issues

e.g. climate change, ozone depletion, environmental microplastics

Physically Bounded Systems  $\rightarrow$  obvious boundaries

Control Volumes  $\rightarrow$  often defined when dealing with flows that enter and exit a ~~system~~ region of interest

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# Types of systems A most common

Open system  $\rightarrow$  Can exchange energy and matter with the surroundings

Closed systems  $\rightarrow$  Can exchange energy but not matter

Isolated systems  $\rightarrow$  No transfer of any kind

Intensive properties  $\rightarrow$  independent of the amount of matter

e.g. pressure, surface tension, viscosity, refractive index

Extensive properties  $\rightarrow$  are additive, the system property is the sum of the values of the parts  
Internal energy ( $U$ ), entropy ( $S$ ), enthalpy ( $H$ )

Specific/Molar property: Normalizing an extensive property quantity by the amount of matter  
( $E_i/m$ ) yields an intensive property

Specific enthalpy, molar volume  
 $\hookrightarrow J/kg$   $\hookrightarrow m^3/mol$

$$\boxed{\Delta U = q + w}$$

heat work

Thermodynamics is only concerned with internal energy

Example:

Consider hydrogen in a fuel cell vehicle storage tank. closed system. 5kg @ 500 atm & 20°C.

(a)  $\Delta E_k = \frac{1}{2}mv^2 = \frac{1}{2}(5kg)(v^2) = 1929 J$

(b)  $\Delta E_p = mgh = (5kg)(9.8 m/s^2)(100m) = 4905 J$

(c)  $\Delta U = q + w = mC_v \Delta T$ ;  $C_v = 10183 J/kg \cdot K$   
 $= 763725 J$

Find the change in energy for:

- (a) acceleration from 0-100 km/h
- (b) travelling up a hill, (100m)
- (c) inc in temp to 35°C at constant volume



## Entropy

↳ state function

$$\Delta S_{\text{system}} + \Delta S_{\text{surroundings}} \geq 0$$

example continued

(d) what is the change in entropy for (c)

given:  $\Delta S = m(C_v + R) \ln\left(\frac{T_2}{T_1}\right) - mR \ln\left(\frac{P_2}{P_1}\right)$

- find  $P_2$  by ideal gas law:  $\frac{nR}{V} = \frac{P_1}{T_1} = \frac{P_2}{T_2}$

- change units on R for  $H_2$

$$R = 8.314 \frac{\text{J}}{\text{mol}\cdot\text{K}} = 4124 \frac{\text{J}}{\text{kg}\cdot\text{K}}$$

$$\Delta S = (5\text{kg}) \left( 10183 + 4124 \frac{\text{J}}{\text{kg}\cdot\text{K}} \right) \ln\left(\frac{308}{293}\right) - 5\text{kg} \left( 4124 \frac{\text{J}}{\text{kg}\cdot\text{K}} \right) \ln\left(\frac{P_2}{500}\right) = 526 \text{ atm}$$

$$- 5\text{kg} \left( 4124 \frac{\text{J}}{\text{kg}\cdot\text{K}} \right) \ln\left(\frac{526}{500}\right)$$

## Equilibrium

Gibbs energy combines properties

$G \equiv U + PV - TS \equiv H - TS$ , where H is enthalpy  
spontaneous  $\rightarrow \Delta G < 0$

Molar Gibbs energy and phase behaviour

A system at equilibrium will follow Gibbs energy

Solid-Liquid = m Vapour-Liquid = m

minimization

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