

# Some recollections of thermodynamics

Internal energy of a system  $U$ : all interactions between microscopic constituents of the system

$$U = U(S, V, N)$$

$S$  = entropy (not a directly measured quantity - no "entropy thermometer")

$V$  = volume

$N$  = molar number (in other notations:  $n$ )

→ extensive quantities (grow proportionally to mass or volume increase)

vs

intensive quantities ( $T$  temperature,  $\rho$  density,  $p$  pressure)

① First law of thermodynamics (it's about  $U$ )

$$\text{Since } dU = TdS - pdV + \mu dN \quad (*)$$

internal energy variation

→ linked to variations of these

chemical potential

(energy exchanged due to variation of system's number of particles)

in closed system (only heat & exchanged with outer world)

$$dV=0, \quad dN=0$$

$$\Rightarrow \boxed{\delta Q \equiv dU = TdS}$$

exchanged heat:  $U$  variation =  $S$  variation at constant  $T$

$$\Rightarrow dS = \delta Q/T$$

(\*) tells us  $T = \partial U / \partial S$ ;  $p = -\partial U / \partial V$ ;  $\mu = \partial U / \partial N$  eqs. of state

also, 
$$U = TS - pV + \mu N$$

[ $\epsilon \equiv U/M$  internal en. per unit mass]

① Thermodynamic potentials (or free energies)

used to describe thermodynamic state;  $U$  is the first of them;  
any can be used according to convenience; they are

F Helmholtz potential ( $f \equiv F/M$  per unit mass)

H enthalpy ( $w = H/M$ )

G Gibbs potential ( $\phi = G/M$ )

$F$ : measure of work that can be obtained from a closed system at constant  $T$ .

(Transform  $V(S, V, N) \rightarrow F(T, V, N)$ )

$$F = U - TS = -pV + \mu N \quad (\text{per unit mol: } f = \varepsilon - Ts)$$

$$dF = -SdT - pdV + \mu dN$$

Equilibrium of a system at constant  $T$  (thermal bath) = minimum  $\bar{F}$

$H$ : measure of work that can be obtained from a closed system at constant  $p$ .

(Transform  $U(S, V, N) \sim H(S, p, N)$ )

$$H = U + pV = TS + \mu N \quad (\rightarrow \text{per unit mass: } w = \epsilon + p/\rho = \epsilon + p/\rho)$$

$$dH = TdS + Vdp + \mu dN$$

Note: closed system at  $p = \text{const.} \Rightarrow dH = TdS = \delta Q_{\text{rev}}$

(enthalpy is equal to exchanged heat for reversible process)

$G$ : measure of work obtained from closed system at  $p, T = G_{\text{constant}}$ .

(Transform  $O(S, V, N) \rightarrow G(T, P, N)$ )

$$G = \mu N$$

( $\mu = G/N$  so chem. pot. = specific Gibbs pot.)

$$dG = -SdT + Vdp + \mu dN$$

## ① Maxwell relations

$$\left. \frac{\partial T}{\partial V} \right|_S = - \left. \frac{\partial p}{\partial S} \right|_V \quad \text{I Maxwell relation}$$

$$\left. \frac{\partial T}{\partial p} \right|_S = \left. \frac{\partial V}{\partial S} \right|_p \quad \text{II " "}$$

$$\left. \frac{\partial S}{\partial V} \right|_T = \left. \frac{\partial p}{\partial T} \right|_V \quad \text{III " "}$$

$$\left. \frac{\partial S}{\partial p} \right|_T = - \left. \frac{\partial V}{\partial T} \right|_p \quad \text{IV " "}$$

## ② Specific heats

$$C \doteq \frac{\delta Q}{dT} \quad \text{heat capacity of a portion of system = ratio absorbed heat / T variation}$$

$$c \doteq \frac{1}{M} C = \frac{1}{M} \frac{\delta Q}{dT} \quad \text{specific heat per unit mass}$$

$$C \doteq \frac{1}{N} C = \frac{1}{N} \frac{\delta Q}{dT} \quad \text{specific molar heat (per mole)}$$

Specific heats depend on the process:

$$c_p \doteq \frac{1}{M} \frac{\delta Q}{dT} \text{ at constant } p / c_v \doteq \frac{1}{M} \frac{\delta Q}{dT} \text{ at constant } V$$

$$\text{Constant } V: dU = \delta Q - p dV \Rightarrow c_v = \frac{1}{M} \left. \frac{\partial U}{\partial T} \right|_V = \left. \frac{\partial E}{\partial T} \right|_V$$

$$\text{Constant } p: dH = T dS + V dp \Rightarrow c_p = \frac{1}{M} \left. \frac{\partial H}{\partial T} \right|_p = \left. \frac{\partial W}{\partial T} \right|_p = T \left. \frac{\partial S}{\partial T} \right|_p$$

## ③ Ideal gas law $pV = NRT$

$$\Rightarrow H = U + pV = U + NRT$$

$$\Rightarrow \underline{C_p = C_v + R} \quad \text{molar specific heats are related}$$

## ① Adiabatic processes

↳ no heat exchange,  $\delta Q = 0$

with  $\gamma \doteq C_p/C_v$

$$TV^{\gamma-1} = \text{constant}$$

$$pV^{\gamma} = \text{constant}$$

$$Tp^{\frac{\gamma}{\gamma-1}} = \text{constant}$$

## ② Coefficient of thermal expansion $\beta$

Heat exchange is associated to a volume variation  $\Rightarrow$

$$\beta \doteq \frac{1}{V} \left( \frac{\partial V}{\partial T} \right)_p$$

For ideal gas  $pV = NRT \Rightarrow \beta = \frac{1}{T}$

## ③ Second law of thermodynamics (it's about $S$ )

Many ways to express it; in a nutshell, for isolated system,

$$dS \geq 0$$

entropy cannot decrease (= sign of irreversibility)