

Thermodynamic potentials

-1-

1st Law: $\sum_i E_i = \text{const} \equiv U \quad (1)$

(Sum of all energy forms in a closed system is constant)

Internal energy of an ideal gas:

only dependent on temperature (not on volume!)

Why? no interaction!

- in condensed phases, energy always function of volume!

intermolecular interactions increase with decreasing intermolecular distance!

→ change in volume is change of internal energy, so $U = f(T, V)$

total (exact) differential:

$$\downarrow \quad dU = \left(\frac{\partial U}{\partial T} \right)_V dT + \left(\frac{\partial U}{\partial V} \right)_T dV \quad (2)$$

Q.: Is a function as $U = f(T, V)$ a state function?

Can be answered by usage of the Schwarz Law

$$\frac{\partial}{\partial T} \left(\frac{\partial U}{\partial V} \right)_T = \frac{\partial}{\partial V} \left(\frac{\partial U}{\partial T} \right)_V \quad (\text{Schwarz}) \quad (3)$$

If this is the case, then $du =$ total differential, ⁻²⁻
can be integrated independent from the path;
or: the line integral over a closed path

$$\oint du = 0 \quad (4)$$

"With (2) and (3) one practically has complete control over the mathematical formalism of thermodynamics" (G.M. Barrow, Physical Chemistry)

Citation

Example ideal or perfect gas:

We already know that $\left(\frac{\partial u}{\partial V}\right)_T = 0 \quad (5)$

and the first partial differential is the "specific heat" or "heat capacity"

$$C_v = \left(\frac{\partial u}{\partial T}\right)_v \quad ; \quad (6)$$

Q: How does one get the internal energy of an arbitrary system at a specific temperature?

$$u_T = \int_{T=0}^T C_v dT + u_0 \quad (7)$$

C_v in most cases not explicitly known
(no perfect gas)

⇒ By the integration, one does not get the integration constant U_0 . (which could be \bar{E}_0 , the energy at point 0)
Consequence:

-3-

Standard conditions have to be defined, since TD can calculate only both energy differences or differences of state functions.

Example state function:

Volume, $V = V(p, T, n)$

if we only look at / consider volume changes at constant amount of moles:

$$dV = \left(\frac{\partial V}{\partial p}\right)_T dp + \left(\frac{\partial V}{\partial T}\right)_p dT \quad (8)$$

ideal/perfect gas: $V = \frac{nRT}{p}$

now we compare the 'mixed' second derivatives:

$$\frac{\partial}{\partial T} \left(\frac{\partial V}{\partial p}\right)_T = \frac{\partial}{\partial p} \left(\frac{\partial V}{\partial T}\right)_p = -\frac{nR}{p^2} \quad (9)$$

the volume of a perfect gas is a state function. One can relate the differentials to the volume at 1 atm, V^0 .

⇒ thermal expansion coefficient $\alpha = \frac{1}{V^0} \left(\frac{\partial V}{\partial T}\right)_p \quad (10)$

compressibility $\kappa = -\frac{1}{V^0} \left(\frac{\partial V}{\partial p}\right)_T \quad (11)$

1st Law with usage of 'work' and 'heat' (work = volume work) -4-

$$(12) \Delta U = q + w \quad (\text{exchange of heat and work with the environment changes the internal energy of a system!})$$

(and $\oint dU = 0$ prevents from construction of a 'perpetuum mobile')

For differential small changes of U , we write:

$$(13) dU = \delta q + \delta w$$

δq and δw are not state functions!

Now, one can calculate and measure q and w to obtain ΔU , which is in chemical transformations of molecules called "reaction energy".

Example: ideal gas expansion, isothermally 10 mol at 0°C from $p_i = 1 \text{ atm}$ to $p_f = 0.1 \text{ atm}$
internal energy: only dependent on T \leadsto

$$\begin{aligned} \Delta U = 0 &\leadsto q = -w && \text{with} \\ w = -\int_{V_i}^{V_f} p \, dV &= -nRT \ln V \Big|_{V_i}^{V_f} && \left(p = \frac{nRT}{V} \right) \\ &= -nRT \ln \frac{V_f}{V_i} = -nRT \ln \frac{p_i}{p_f} = -52,3 \text{ kJ} \\ \leadsto q = -w &= 52,3 \text{ kJ} \end{aligned}$$

At constant volume, the first Law becomes:

$$\Delta U = q + w \quad dV = 0 \Rightarrow p dV = 0 \quad -5-$$

$$\Delta U = q + 0$$

Much more frequently, processes under standard conditions are carried out under constant pressure. For a convenient description of these, we introduce a new thermodynamic potential, enthalpy.

$$H = U + PV \quad (\text{defined}) \quad (14)$$

which is a state function.

Q.: Is this a useful definition?

Change dH of a system:

$$(15) \quad dH = dU + p dV + V dp \quad \text{with } d(pV) = p dV + V dp$$

only volume work (no other work applied on the system)

$$\text{then } w = -p dV$$

and with the first law $dU = \delta w + \delta q$ (follows

$$dH = \delta q + V dp \quad \text{and at constant pressure } dp = 0$$

$$V dH = \delta q \quad (16)$$

- at constant pressure: exchanged heat δq leads only to a change in enthalpy dH

- Solids/liquids: small expansion coefficients \Rightarrow dH almost as large as dU (small pV -contributions)

The second Law:

-6-

$$\delta Q \stackrel{\text{irr}}{\leq} T dS \quad (17)$$

inequal for irreversible processes

reversible process: $dS = \frac{\delta q_{rev}}{T}$

- at constant pressure:

$$\delta q_{rev} = C_p dT$$

From the first and second Law follows:

$$dU = T dS - p dV \quad (18)$$

$$= \left(\frac{\partial U}{\partial S} \right)_V dS + \left(\frac{\partial U}{\partial V} \right)_S dV \Rightarrow \left(\frac{\partial U}{\partial S} \right)_V = T \text{ etc.}$$

when the composition of the system is constant.

Irreversible processes: expansion of gas into volume

ΔS: measurement for a system for the transfer

from non-equilibrium to equilibrium. State

however, energy / enthalpy - changes have

to be taken into account! (Need for another state function, including S!!)

The Free Enthalpy / energy

- reversible state changes non-closed systems:
Enthalpy + entropy - changes must be considered!

defined:

free energy, Helmholtz energy

$$(19) \quad A = U - TS \quad (\text{sometimes also denoted as "F"})$$

$$dA = dU - d(TS)$$

$$\Delta A = \Delta U - \Delta(TS)$$

(20) free enthalpy / Gibbs enthalpy, Gibbs free energy - $G = H - TS$

$\Delta G = \Delta H - \Delta(TS)$
 $\Delta G = \Delta H + \Delta(TS)$

ΔG : state changes at constant pressure
 ΔA : at constant volume
 or described

Δ = variation of variable with respect to constant p and T, differential

(21) $dG = \left(\frac{\partial G}{\partial T}\right)_p dT + \left(\frac{\partial G}{\partial p}\right)_T dp$

physical meaning of $\left(\frac{\partial G}{\partial T}\right)_p$ and $\left(\frac{\partial G}{\partial p}\right)_T$ in partial differentials?

$dG = dH - TdS - SdT = dU + pdv + vdp - TdS - SdT$
 with $dU = dq + dw = TdS - pdv$

(22) $dG = vdp - SdT$

$\left(\frac{\partial G}{\partial T}\right)_p = -S$ and $\left(\frac{\partial G}{\partial p}\right)_T = v$

Chemical Potentials

- Consider two particles can vary with composition (which was got $\sum_{i=1}^n \mu_i dn_i$ (which was get))

$\mu_i \equiv \left(\frac{\partial U}{\partial n_i}\right)_{S, V, n_{j \neq i}}$

change of the amount of component k
 chemical potential of component k in the system

(23)

Under conditions of constant temperature and pressure - 8 -

$$(24) \mu_k = \left(\frac{\partial G}{\partial n_k} \right)_{p, T, n_j \neq k}$$

$$G = \sum_{k=1}^c \mu_k n_k \quad \left. \begin{array}{l} \text{Under composition change,} \\ p, T = \text{const.} \end{array} \right\}$$

$$dG = \sum_{k=1}^c \mu_k dn_k + \sum_{k=1}^c n_k d\mu_k \quad \left. \begin{array}{l} \\ \end{array} \right\} \text{ must be equal}$$

and $dG = Vdp - SdT + \sum_{k=1}^c \mu_k dn_k$

$$\Rightarrow \sum_{k=1}^c n_k d\mu_k = Vdp - SdT \quad \text{Gibbs-Duhem equation}$$

$$(25) \text{ at const } p, T : \sum_{k=1}^c n_k d\mu_k = 0$$

Significance:

potential of one component of a mixture can not change independently of the chemical potential of the other components.