P. Chem I 2/10/23

Constant V: $\Delta U = q$

$$\Rightarrow \Delta U = \int_{U_1}^{U_2} dU = \int_{T_1}^{T_2} \left(\frac{\partial U}{\partial T}\right)_V dT = \int_{T_1}^{T_2} C_V dT$$

$\Delta V = 0$

$dU = \delta q + \delta w = \delta q$ choose rev path

$$\Rightarrow dU = \delta q_{rev} = T dS \Rightarrow dS = \frac{1}{T} dU$$

$$\Delta S = \int_1^2 dS = \int_{T_1}^{T_2} \frac{1}{T}\left(\frac{\partial U}{\partial T}\right)_V dT = \int_{T_1}^{T_2} \frac{C_V}{T} dT$$

Constant P: $\Delta H = q$

$$\Delta H = \int_1^2 \Delta H = \int_{T_1}^{T_2} \left(\frac{\partial H}{\partial T}\right)_P dT = \int_{T_1}^{T_2} C_P dT$$

$$dH = \delta q_{rev} = T dS \quad \therefore \Delta S = \int \frac{1}{T}\left(\frac{\partial H}{\partial T}\right)_P dT = \int_{T_1}^{T_2} \frac{C_P}{T} dT$$

3rd Law: $S(T=0) = 0$

$\Delta S = S(T_2) - S(T_1)$ Put $T_1 = 0$

$$\Rightarrow S(T_2) = \int_0^{T_2} \frac{C_P}{T} dT$$

+ phase transitions

ex water at 1atm, 100°C, liquid $\rightleftharpoons$ vapor

* at const P $\Delta H = q$

$$\Delta S = \frac{q_{rev}}{T} = \frac{\Delta H_{vap}}{T_{vap}} = \frac{\Delta H_{vap}}{T_{boiling}}$$

$\Delta S_{rxn} = S(\text{products}) - S(\text{reactants})$

beginning ? end of Chapter 21

Ch 22 Free energy.

Motivation → S = entropy gives a criterion for spontaneity but not convenient because we need to know too much about surroundings

$$dS \geq \frac{\delta q}{T}$$

Constant V, T * Claussius inequality

$dU = \delta q + \delta w = \delta q \leq dT$ (constant V) * using Kelvin bc always pos.

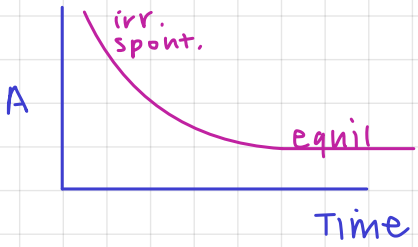
$dU - TdS \leq 0$

$= d(U - TS) \leq 0$ (constant T)

$A \equiv U - TS$

(Helmholtz free energy)

isn't $\Delta U = 0$ at $\Delta T = 0$? No this is general. Not ideal gas.



A drops for spontaneous process
A constant at equilibrium or reversible

Suppose that $w = \cancel{w_{pv}}$ (0 at const V) $+ w_{useful}$

Maximum work obtainable is under reversible conditions $dq_{rev} = TdS$

$dU = \delta q + \delta w_{useful}$

$\delta w_{useful,max} = dU - TdS = d(U - TS) = dA$

TS is the "bound" energy

$w_{useful} = \Delta A$

$U - TS = A$ is the "available" or "free"

Spont: ΔA is the maximum amount of work that you can get out of the system.

irrev: ΔA is the minimum amount of energy required to drive the process forward

* like charging a battery

Table 9.2 Different kinds of work that can be done by a system.

Type of work	Intensive variable	Extensive differential	Expression for work
General	force, F	change in distance, dr	$w = \int F\ dr$
Expansion	pressure, P	change in volume, dV	$w = \int P\ dV$
Electrical	voltage difference, ΔE	change in charge, dq	$w = \int \Delta E\ dq$
Surface	surface tension, γ	change in surface area, dA	$w = \int \gamma\ dA$
Stretching	tension, τ	change in length, dl	$w = \int \tau\ dl$
Chemical	chemical potential difference, $\Delta\mu$	change in number of moles of the molecule, dn	$w = \int \Delta\mu\ dn$

(Adapted from D.S. Eisenberg and D.M. Crothers, Physical Chemistry: With Applications to the Life Sciences. Menlo Park, CA: Benjamin/Cummings, 1979. With permission from Benjamin/Cummings.)

*on website "different types of useful work"