EXAMS ROAD
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Handwritten Notes
On
Chemical Thermodynamics

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Chemical Thermodynamics.

* System | Rest is surrounding | system + surrounding = Universe

↳ Imaginary / Real boundary.

* **The Zeroth Law of Thermodynamics:** When two systems are in thermal equilibrium, then both have the same temperature.

* **The First Law of Thermodynamics:** $dU = \delta Q + \delta W$ (d → total differential, δ → partial differential).

In practical, $\Delta U = Q + W$ [U is internal energy, Q → heat, W → Work] [Statement of Conservation of Energy].

* **Some basics:**

- **Isolated system:** exchanging neither matter nor energy with surrounding.
- **Closed:** exchaning only energy. (U)
- **Open:** exchanging both (matter & energy).
- Homogeneous & Heterogeneous System (Same or different phase).
- **Heat:** When delivered to system - positive, otherwise negative.
- **Work:** When done on system - positive, otherwise negative.
- Intensive & Extensive Thermodynamic quantities -

Intensive are those whose value do not change when system is divided into sub-systems.

Extensive are those whose value is proportional to the amount of substance. (at cons. T & P).

- Reversible & Irreversible process:

Reversible, when at equilibrium at every point, direction of the process may be reversed by even a very slight change of initial condition. An ideal process, not real.

• Name of Process	Constant Quantity	Symbol
Isothermal	Temperature	[T]
Isobaric	Pressure	[P]
Isochoric	Volume	[V]
Adiabetic	Heat	[ad]
Isentropic	Entropy	[S]
Isenthalpic	Enthalpy	[H]
Polytropic	Heat capacity	

continued-

* $dU = dQ - pdV$ [exchanges reversible volume]

If isochoric, $\Delta U = Q$

* It follows from the 1st law, it's impossible to construct perpetual motion machine, of first type.

* Second Law of Thermodynamics: $dS = \frac{\delta Q}{T}$ (reversible)

[S → Entropy] for irreversible,

unit J/K $dS > \frac{\delta Q}{T}$

If in reversible process, then can be used.

It follows from the law, it's impossible to construct perpetual machine, 2nd type, gains heat & converts into work without loss.

Chemical Thermodynamics.

* Entropy is the degree of disorder in the movement of molecules.

* **The Third Law of Thermodynamics:** $\lim_{T \to 0} S = 0$.

It implies 0K cannot be attained by any process. Theoretically, at a temperature tending to 0K, the entropy is zero.

* **Enthalpy:** H is a state function, (unit J). $H = U + pV$

If system exchanges only heat & reversible volume work, $dH = \delta Q + V dP$

If isobaric, $dH = \delta Q$ | $\Delta H = Q$

$\Delta H = \Delta U + nR\Delta T$

* **Helmontz energy:** F, state function (unit J) $F = U - TS$.

during reversible isothermal process, $\Delta F = W$

For isothermal, $\Delta F = \Delta U - T\Delta S$

For non-isothermal, $\Delta F = \Delta U - T_2S_2 + T_1S_1$

* **Gibbs Energy:** G, state function, $G = H - TS$.

(unit J) $G = H - TS = U + pV - TS = F + pV$

$\Rightarrow \Delta G = \Delta F + \Delta(PV) = \Delta F + P_2V_2 - P_1V_1$

$\Delta G = W + p\Delta V$ [T, P, reversible].

* **Heat Capacities:** $C = \left(\frac{\delta Q}{\delta T}\right)_{process}$.

(Unit J/K). Isochoric $C_v = \left(\frac{\delta Q}{\delta T}\right)_{Isochoric} = \left(\frac{\delta U}{\delta T}\right)_v$

Isobaric $C_p = \left(\frac{\delta Q}{\delta T}\right)_{Isobaric} = \left(\frac{\delta U}{\delta T}\right)_P$.

$C_{Pm} = \frac{C_p}{n}$, $C_{Vm} = \frac{C_V}{n}$. [intensive now, molar heat capacity]

- State functions give exact differential, that can be integrated over limits.

$$\int_a^b dU = U_b - U_a \quad \text{but} \quad \int_a^b dW = W,$$ because W depends on the path followed.

- For reversible expansion, $P_{ext} = P_{int}$

$$W_{rev} = -\int_{V_1}^{V_2} P_{ext}\, dV = -\int_{V_1}^{V_2} P_{int}\, dV = -2.303\, nRT \log \frac{V_2}{V_1}.$$

- For irreversible expansion, $W_{irr} = -\int_{V_1} P_{ext}\, dV.$

$$= -P_{ext}(V_2 - V_1)$$

- $W_{rev} > W_{irr}$.

- Work in different processes.

i) Isobaric – $W = -P_{ext}\Delta V = -nR(T_2 - T_1)$.

ii) mass lifting or falling – $W = -mgh = -p\Delta V$

$W = mgh = -p\Delta V$.

iii) Isothermal reversible – $W = -2.303\, nRT \log \frac{P_1}{P_2}$

$= -2.303\, nRT \log \frac{V_2}{V_1}$.

$\Delta U = 0$, $\Delta H = 0$, $q = -W = 2.303\, nRT \log \frac{P_1}{P_2}$

iv) Isothermal irreversible – $W_{irr} = -nRT\left[1 - \frac{P_2}{P_1}\right]$.

$q = nRT\left[1 - \frac{P_2}{P_1}\right]$.

v) Isochoric – $W = 0$, $q = \Delta U$.

vi) Adiabatic – $q = 0$. $W = \Delta U = nC_v \Delta T$.

$W = \frac{nR}{\gamma - 1}(T_2 - T_1)$ [reversible adiabatic]

- $\Delta H = \Delta U + P\Delta V$.

- Energy changes:

$\Delta U = q_v$ $\quad q_v \rightarrow$ heat exchange at cons. vol.

$\Delta H = q_p$ $\quad q_v \rightarrow$ 〃 〃 at 〃 press.

C. Chemical Thermodynamics.

- $\Delta H = \Delta U + \Delta n_g RT$
- Heat capacity, $C = \frac{\Delta q}{\Delta T}$, $C_v = \left(\frac{\delta U}{\delta T}\right)_V$, $C_p = \left(\frac{\delta H}{\delta T}\right)_P$.
- Extensive Properties: Volume, Number of moles, mass, free energy (G), Entropy (S), Enthalpy (H), Internal energy (U), Heat capacity.
- Intensive Properties: Molar volume, density, refractive index, surface tension, viscosity, free energy/mole, specific heat, pressure, temperature, BP, FP.
- Exothermic reaction - ΣH (product) $<$ ΣH (reactant)

  Endothermic reaction - ΣH (product) $>$ ΣH (reactant)
- Hess's Law - Total enthalpy change is equal to the sum of sequence reaction's' enthalpy change.

  $\Delta H^0 = \Sigma \Delta H_f^0$ (products) $- \Sigma \Delta H_f^0$ (reactants).

  (standard state - 1 atm; 101.325 kPa & 298 K is assigned a zero value).
- Kirchoff's equ^{n}s: $\Delta C_p = \frac{\Delta H_2 - \Delta H_1}{T_2 - T_1}$

  $\Delta C_v = \frac{\Delta U_2 - \Delta U_1}{T_2 - T_1}$.
- Trouton's Rule: Entropy of vaporisation of non-associated or non-dissociated liquid is constant & may be taken as 87.3 J/mol K

* Average bond energy : $\dfrac{\Delta H_f \text{ of molecules}}{\text{no. of bonds}}$

BE is an additive property.

* $\Delta S = \dfrac{q_{rev}}{T}$ [q_{rev} heat supplied isothermally & reversibly].

* for reversible cycle, $\dfrac{q_1}{T_1} + \dfrac{q_2}{T_2} = 0$

for irreversible engine, $\dfrac{q_1}{T_1} + \dfrac{q_2}{T_2} < 0$.

* $\Delta S = nC_v \ln \dfrac{T_2}{T_1} + nR \ln \dfrac{V_2}{V_1}$.

* Isobaric heating/cooling : $\Delta U = nC_v \Delta T$

$\Delta H = nC_p \Delta T = q_p$.

$\Delta S = nC_p \ln \dfrac{T_2}{T_1}$.

* Isochoric heating/cooling : $\Delta U = C_v \Delta T = q_v$

$\Delta H = C_p \Delta T$.

$\Delta S = nC_v \ln \left(\dfrac{T_2}{T_1}\right)$.

* Adiabetic : $\Delta U = C_v \Delta T$, $\Delta H = C_p \Delta T$

$\Delta S = nC_v \ln \dfrac{T_2}{T_1} + nR \ln \dfrac{V_2}{V_1}$ (irreversible)

$\Delta S = 0$ (reversible).

* $\Delta G^\circ_r = \Sigma \Delta G^\circ_f$ (products) $- \Sigma \Delta G^\circ_f$ (reactants)

$\Delta G^\circ = -2.303\, RT \log K_{eq}$

$\Delta G^\circ = W_{max}$ (for reversible change [P][T]).

$\Delta G = -nFE_{cell}$

* $\log \dfrac{P_2}{P_1} = \dfrac{\Delta H}{2.303R} \left[\dfrac{1}{T_1} - \dfrac{1}{T_2}\right]$ [liquid↔gas equlibrium, Clausius Clapeyron's eqⁿ]

P_1, P_2 vapour pressure at T_1, T_2.

* $\Delta S^\circ = \Sigma S^\circ$(products) $- \Sigma S^\circ$(reactants).

Thermodynamics.
Formula Sheet

* Work done for reversible process: $W_r = -p\,dV$

* $W_{isothermal} = -nRT\ln\frac{V_2}{V_1} = -nRT\ln\frac{P_1}{P_2}$

$W_{isobaric} = -P_g\,\Delta V$; $W_{isochoric} = 0$.

$W_{adiabatic} = \frac{1}{\gamma-1}(P_2V_2 - P_1V_1) = \frac{nR}{\gamma-1}(T_2 - T_1)$.

* $dU = \delta Q + \delta W$

* $Q = c\,m\,\Delta T$; $Q = n\,C_m\,\Delta T$

$C_v = \cancel{nc}\,\frac{1}{n}\frac{\Delta U}{\Delta T}$; $C_p = \frac{1}{n}\frac{\Delta H}{\Delta T}$, $\Delta H = nC_p\Delta T$.

$\Delta U = nC_v\Delta T$; $\Delta U = nC_p\Delta T - nR\Delta T$.

* for Bomb Calorimeter, $\Delta U_{sys} + Q_{water} = 0$

$nC_v\,\Delta T_{sys} = -m\,C_{water}\cdot\Delta T_{water}$

* for Adiabatic Process, $PV^{\gamma} = const.$ $TV^{\gamma-1} = const.$

$T^{\gamma}P^{1-\gamma} = const.$

* $\Delta H = \Delta U + P\Delta V$ | $Q_p = \Delta U + P\Delta V$

$\Delta H = \Delta U + (\Delta n_g)RT$

* $S = \int \frac{dQ_{rev}}{T}$; $\Delta S = nc_v\ln\frac{T_2}{T_1} + nR\ln\frac{V_2}{V_1}$

$\Delta S = nc_p\ln\frac{T_2}{T_1} + nR\ln\frac{P_1}{P_2}$.

* $\Delta G_{sys} = \Delta H_{sys} - T\Delta S_{sys}$.

* $dG = Vdp - SdT$ (reversible change in pressure & temperature).

$dG = nRT\ln\frac{V_1}{V_2} = nRT\ln\frac{P_2}{P_1}$ (for isothermal process).