Phase Equilibria & Kirchhoff Equation

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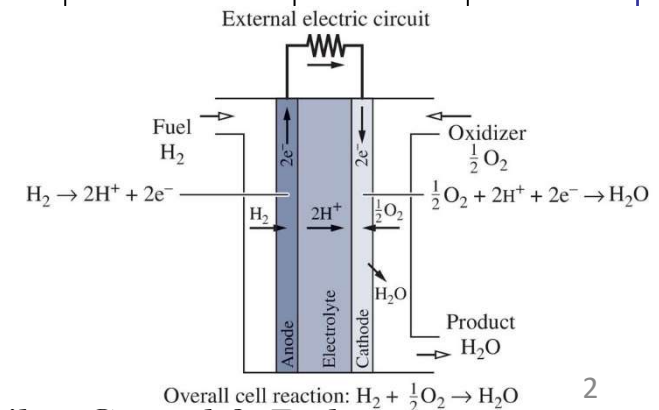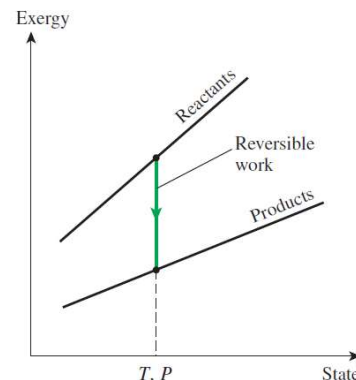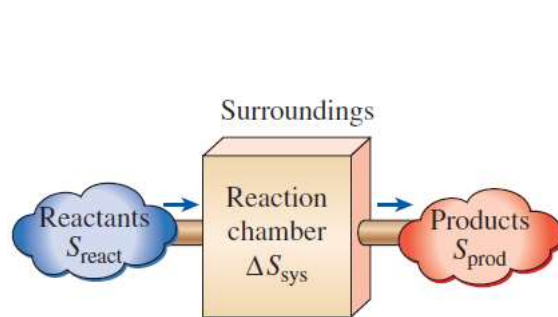
Indian Institute of Technology, Kanpur.

Previously: Thermal & Electrochemical combustion- Enthalpy & Gibbs Free Energy Changes

$$S_{\text{gen,adiabatic}} = S_{\text{prod}} - S_{\text{react}} \geq 0 \quad \bar{s}_i(T,P_i) = \bar{s}_i^\circ(T,P_0) - R_u \ln \frac{y_i P_m}{P_0} \quad (\text{kJ/kmol} \cdot \text{K})$$

$$X_{\text{destroyed}} = T_0 S_{\text{gen}} \quad (\text{kJ}) \qquad W^{\text{rev}} = \sum_R n_i \bar{g}_i - \sum_P n_e \bar{g}_e = -\Delta G \qquad \Delta G = -nFE$$
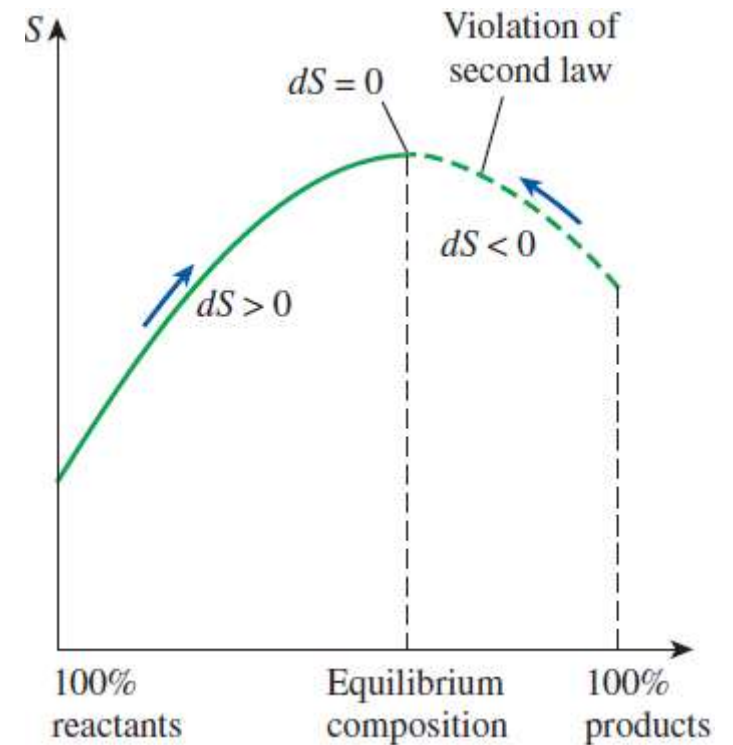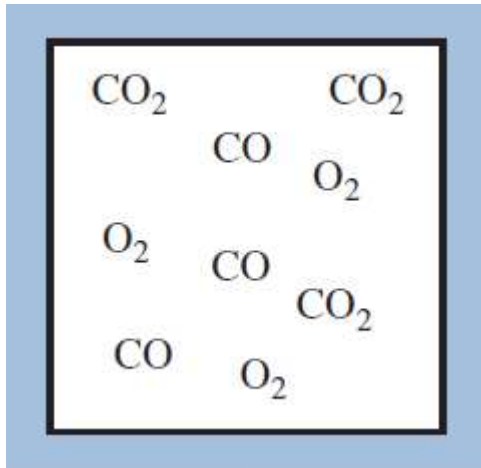
Thermochemical Properties of Selected Substances at 298K and 1 atm

Substance	Formula	Molar Mass, M (kg/ kmol)	Enthalpy of Formation, $\bar{h}_f^\circ$ (kJ/ kmol)	Gibbs Function of Formation, $\bar{g}_f^\circ$ (kJ/ kmol)	Absolute Entropy, $\bar{s}^\circ$ (kJ/ kmol·K)	Heating Values	
						Higher, HHV (kJ/ kg)	Lower, LHV (kJ/ kg)
Carbon	C(s)	12.01	0	0	5.74	32,770	32,770
Hydrogen	H₂(g)	2.016	0	0	130.57	141,780	119,950
Nitrogen	N₂(g)	28.01	0	0	191.50	–	–
Oxygen	O₂(g)	32.00	0	0	205.03	–	–
Carbon Monoxide	CO(g)	28.01	–110,530	–137,150	197.54	–	–
Carbon dioxide	CO₂(g)	44.01	–393,520	–394,380	213.69	–	–
Water	H₂O(g)	18.02	–241,820	–228,590	188.72	–	–
Water	H₂O(l)	18.02	–285,830	–237,180	69.95	–	–

Figs: TD-Borgnakke & Sonntag;Moran, Shapiro, Boettner & Bailey;Cengel & Boles

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From 2nd law to Chemical Equilibrium

$$dS_{sys} \geq \frac{\delta Q}{T}$$

Figs: TD-Cengel & Boles

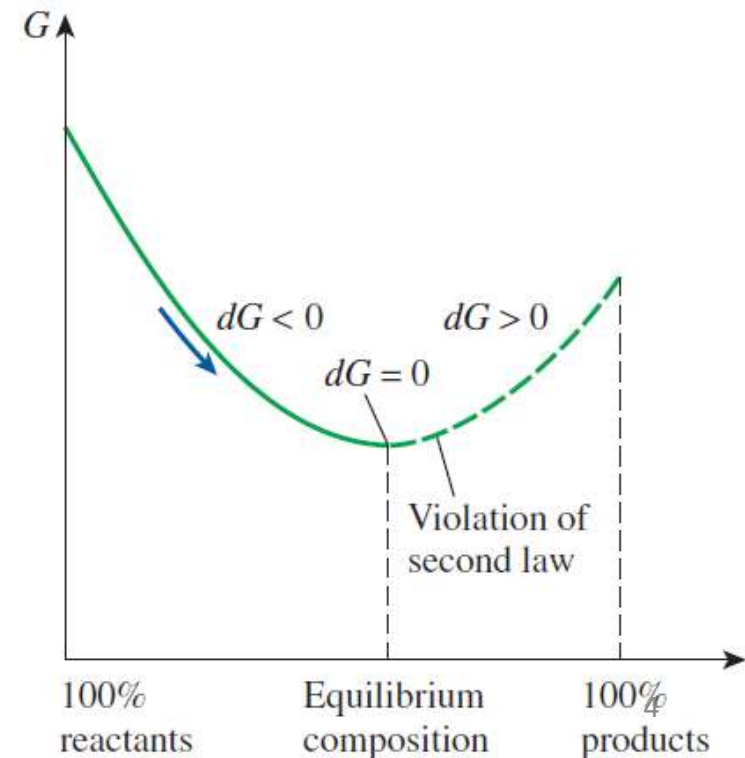# *Extremal condition for chemical equilibrium*

$$\left.\begin{array}{c} \delta Q - P \, dV = dU \\[2mm] dS \geq \dfrac{\delta Q}{T} \end{array}\right\} \quad dU + P \, dV - T \, ds \leq 0$$
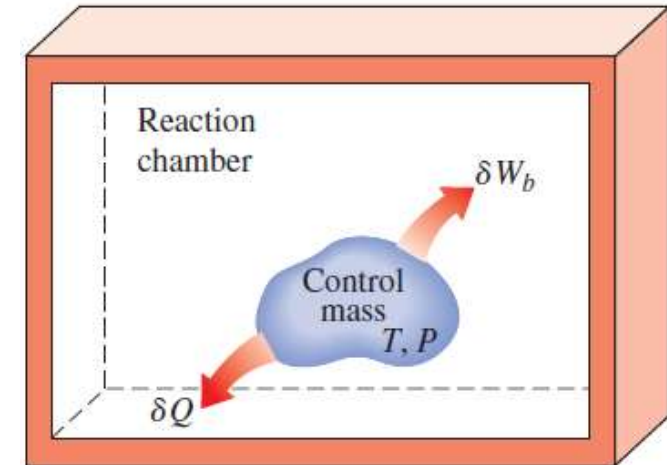
$$(dG)_{T,P} = dH - T \, dS - S \, dT$$

$$= (dU + P \, dV + V \, dP)^{\nearrow 0} - T \, dS - S \, dT^{\nearrow 0}$$

$$= dU + P \, dV - T \, dS$$

$$(dG)_{T,P} \leq 0 \qquad\qquad (dG)_{T,P} = 0$$

Figs: TD-Cengel & Boles

Centrality of chemical potential/molar Gibbs function

Reaction chamber
T, P

N_A moles of A
N_B moles of B
N_C moles of C
N_D moles of D

$$dN_A A + dN_B B \rightarrow dN_C C + dN_D D$$

$$\nu_A A + \nu_B B \rightleftharpoons \nu_C C + \nu_D D$$

$$(dG)_{T,P} = \sum (dG_i)_{T,P} = \sum (\bar{g}_i \, dN_i)_{T,P} = 0$$

$$\bar{g}_C \, dN_C + \bar{g}_D \, dN_D + \bar{g}_A \, dN_A + \bar{g}_B \, dN_B = 0$$

$$dN_A = -\varepsilon \nu_A \qquad dN_C = \varepsilon \nu_C$$
$$dN_B = -\varepsilon \nu_B \qquad dN_D = \varepsilon \nu_D$$

$$H_2 \rightarrow 2H$$
$$0.1 H_2 \rightarrow 0.2 H$$
$$0.01 H_2 \rightarrow 0.02 H$$
$$0.001 H_2 \rightarrow 0.002 H$$

$$\nu_{H_2} = 1$$

$$\nu_H = 2$$

$$\boxed{\nu_C \bar{g}_C + \nu_D \bar{g}_D - \nu_A \bar{g}_A - \nu_B \bar{g}_B = 0}$$

Criterion for chemical equilibrium

Figs: TD-Cengel & Boles

Chemical equilibrium of ideal-gas mixtures

$$\nu_C \bar{g}_C + \nu_D \bar{g}_D - \nu_A \bar{g}_A - \nu_B \bar{g}_B = 0$$

Criterion for chemical equilibrium

$$(\Delta \bar{g})_T = \Delta \bar{h}^{\nearrow 0} - T(\Delta \bar{s})_T = -T(\Delta \bar{s})_T = R_u T \ln \frac{P_2}{P_1} \qquad\qquad \bar{g}_i(T, P_i) = \bar{g}_i^*(T) + R_u T \ln P_i$$

$$\nu_C[\bar{g}_C^*(T) + R_u T \ln P_C] + \nu_D[\bar{g}_D^*(T) + R_u T \ln P_D]$$
$$- \nu_A[\bar{g}_A^*(T) + R_u T \ln P_A] - \nu_B[\bar{g}_B^*(T) + R_u T \ln P_B] = 0$$

$$\Delta G^*(T) = \nu_C \bar{g}_C^*(T) + \nu_D \bar{g}_D^*(T) - \nu_A \bar{g}_A^*(T) - \nu_B \bar{g}_B^*(T)$$

$$\Delta G^*(T) = -R_u T(\nu_C \ln P_C + \nu_D \ln P_D - \nu_A \ln P_A - \nu_B \ln P_B) = -R_u T \ln \frac{P_C^{\nu_C} P_D^{\nu_D}}{P_A^{\nu_A} P_B^{\nu_B}}$$

$$K_P = \frac{P_C^{\nu_C} P_D^{\nu_D}}{P_A^{\nu_A} P_B^{\nu_B}} \qquad\qquad K_P = e^{-\Delta G^*(T)/R_u T}$$

$$P_i = y_i P = \frac{N_i}{N_{total}} P \qquad\qquad K_P = \frac{N_C^{\nu_C} N_D^{\nu_D}}{N_A^{\nu_A} N_B^{\nu_B}} \left(\frac{P}{N_{total}}\right)^{\Delta \nu}$$

$$\Delta \nu = \nu_C + \nu_D - \nu_A - \nu_B$$

Figs: TD-Cengel & Boles

$K_p(T)$, Van't Hoff & Kirchhoff equation

$$\ln K_P = -\frac{\Delta G^*(T)}{R_u T}$$

$$\frac{d(\ln K_p)}{dT} = \frac{\Delta H^*(T)}{R_u T^2} - \frac{d[\Delta H^*(T)]}{R_u T\, dT} + \frac{d[\Delta S^*(T)]}{R_u\, dT}$$

$$T\, ds = dh - v\, dP$$

$$T\, d(\Delta S^*) = d(\Delta H^*)$$

$$\frac{d(\ln K_p)}{dT} = \frac{\Delta H^*(T)}{R_u T^2} = \frac{\bar{h}_R(T)}{R_u T^2}$$

$$\ln \frac{K_{P_2}}{K_{P_1}} \cong \frac{\bar{h}_R}{R_u}\left(\frac{1}{T_1} - \frac{1}{T_2}\right)$$

$$\left(\frac{\partial h_i}{\partial T}\right)_p = c_{p_i}$$

$$\frac{d\Delta H}{dT} \equiv \frac{d}{dT}(\Sigma \nu_i h_i)$$
$$= \Sigma \nu_i c_{p_i}$$

TD-Cengel & Boles; The principles of Chemical Equilibrium by K. Denbigh

Fundamental equations of TD (Table TD)

Function	Extremum at Equilibrium	Fundamental Equation	Definition
$U(S,V,\mathbf{N})$	Minimum	$dU = T\,dS - p\,dV + \sum_j \mu_j\,dN_j$	
$S(U,V,\mathbf{N})$	Maximum	$dS = \left(\dfrac{1}{T}\right)dU + \left(\dfrac{p}{T}\right)dV - \sum_j \left(\dfrac{\mu_j}{T}\right)dN_j$	
$H(S,p,\mathbf{N})$	Minimum	$dH = T\,dS + V\,dp + \sum_j \mu_j\,dN_j$	$H = U + pV$
$F(T,V,\mathbf{N})$	Minimum	$dF = -S\,dT - p\,dV + \sum_j \mu_j\,dN_j$	$F = U - TS$
$G(T,p,\mathbf{N})$	Minimum	$dG = -S\,dT + V\,dp + \sum_j \mu_j\,dN_j$	$G = H - TS = F + pV$

Molecular Driving Forces by K. Dill & S. Bromberg

The Limits on Constructing Thermodynamic Functions

What are the limits on constructing functions of T, S, p, V, N, U, F, H, and G? You can divide thermodynamic functions into four categories:

FUNDAMENTAL AND USEFUL. Table TD lists the main fundamental thermodynamic functions and their natural variables. The states of equilibrium are identified by extrema in these functions.

USEFUL BUT NOT FUNDAMENTAL. $U(T, V, N)$, $S(T, V, N)$, $H(T, p, N)$, and $S(T, p, N)$ are not functions of natural variables. These functions do not have corresponding extremum principles, but they are useful because they are components of $F(T, V, N)$ and $G(T, p, N)$.

COMPLETE BUT NOT USEFUL. Rearrangements of the dependent and independent variables from a fundamental thermodynamic function are possible, but not often useful. For example, $T(F, V, N)$ is a rearrangement of the fundamental Helmholtz free energy function, $F(T, V, N)$. This function is not very useful because you usually cannot constrain F at the system boundary.

INCOMPLETE. Additional functions could be constructed, such as $U(p, V, N)$ or $S(U, \mu, N)$ but because these involve conjugate pairs p and V, or μ and N, and are missing other variables, they do not uniquely specify the state of a system. Such functions cannot be obtained by Legendre transforms of the fundamental equations.

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What's next?

- Phase rule