Formula Sheet

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1 Thermodynamics

1.1 Fundamentals

The three laws of thermodynamics

$$\Delta U = q + w, \qquad U \text{ is internal energy, } q \text{ is heat to the system, } w \text{ is work on the system} \tag{1.1}$$

$$\Delta S_{\text{univ}} \geq 0 \qquad \text{the entropy of the universe does not decrease} \tag{1.2}$$

$$S(T \to 0) = 0 \qquad \text{the entropy of a perfect crystal tends to zero as } T \text{ goes to } 0\,\text{K} \tag{1.3}$$

Relations for heat and work

$$\mathrm{d}S = \frac{\delta q_{\text{rev}}}{T} \qquad q_{\text{rev}} \text{ is heat transferred reversibly} \tag{1.4}$$

$$\mathrm{d}S \geq \frac{\delta q}{T} \qquad \text{Clausius inequality} \tag{1.5}$$

$$\delta w = -p\,\mathrm{d}V \qquad \text{expansion work} \tag{1.6}$$

Auxiliary functions

$$H = U + pV \qquad \text{enthalpy} \tag{1.7}$$

$$A = U - TS \qquad \text{Helmholtz free energy} \tag{1.8}$$

$$G = H - TS \qquad \text{Gibbs free energy} \tag{1.9}$$

Fundamental thermodynamic relation

$$\mathrm{d}U = T\,\mathrm{d}S - p\,\mathrm{d}V + \sum_i \mu_i\,\mathrm{d}n_i \tag{1.10}$$

from which it follows

$$T = \left(\frac{\partial U}{\partial S}\right)_{V,n_i} \tag{1.11}$$

$$p = -\left(\frac{\partial U}{\partial V}\right)_{S,n_i} \tag{1.12}$$

$$\mu_i = \left(\frac{\partial U}{\partial n_i}\right)_{S,V,n_{j\neq i}} \qquad \text{chemical potential} \tag{1.13}$$

Combining the fundamental thermodynamic relation with definitions of auxiliary functions,

$$\mathrm{d}H = T\,\mathrm{d}S + V\,\mathrm{d}p + \sum_i \mu_i\,\mathrm{d}n_i$$

$$T = \left(\frac{\partial H}{\partial S}\right)_{p,n_i} \qquad V = \left(\frac{\partial H}{\partial p}\right)_{S,n_i} \qquad \mu_i = \left(\frac{\partial H}{\partial n_i}\right)_{S,p,n_{j\neq i}} \tag{1.14}$$

$$\mathrm{d}A = -S\,\mathrm{d}T - p\,\mathrm{d}V + \sum_i \mu_i\,\mathrm{d}n_i$$

$$S = -\left(\frac{\partial A}{\partial T}\right)_{V,n_i} \qquad p = -\left(\frac{\partial A}{\partial V}\right)_{T,n_i} \qquad \mu_i = \left(\frac{\partial A}{\partial n_i}\right)_{T,V,n_{j\neq i}} \tag{1.15}$$

$$dG = -S\,dT + V\,dp + \sum_i \mu_i\,dn_i$$

$$S = -\left(\frac{\partial G}{\partial T}\right)_{p,n_i} \qquad V = \left(\frac{\partial G}{\partial p}\right)_{T,n_i} \qquad \mu_i = \left(\frac{\partial G}{\partial n_i}\right)_{T,p,n_{j\neq i}}$$

(1.16)

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$-S$	U	V
H		A
$-p$	G	T

T, p, and μ_i are intensive quantities, which do not depend on system size (same as density).

U, S, V, and n_i are extensive quantities, which grow linearly with system size (same as mass).

From this and Eq. (1.10),

$$U = TS - pV + \sum_i \mu_i n_i \tag{1.17}$$

$$S\,dT - V\,dp + \sum_i n_i\,d\mu_i = 0 \qquad (T,\ p,\ \text{and } \mu_i \text{ are not mutually independent}) \tag{1.18}$$

1.2 Chemical equilibrium

Partial pressures:

$$p_i = \chi_i p \qquad \text{partial pressure of species } i;\ p \text{ is total pressure} \tag{1.19}$$

$$\chi_i = n_i/n_{\text{tot}} \qquad \text{molar fraction of species } i;\ n_i \text{ is corresponding molar amount} \tag{1.20}$$

For the ideal gas, partial pressure is equal to the pressure it would exert if all other gaseous species were removed from the container, which means that its partial pressure depends **only** on its amount, temperature and volume, and not on the amount of any other gasses:

$$p_i V = n_i RT \tag{1.21}$$

For this reason, from Eq. (1.18) at constant temperature ($dT = 0$),

$$n_i\,d\mu_i = V\,dp_i \tag{1.22a}$$

$$\mu_i = \mu_i^{\ominus} + RT \ln\left(\frac{p}{p^{\ominus}}\right) \qquad (p^{\ominus} = 1\,\text{bar} = 10^5\,\text{Pa is the standard pressure}) \tag{1.22b}$$

From this, for an ideal-gas equilibrium $A_{(g)} \rightleftharpoons B_{(g)}$

$$\Delta_r G = \Delta_r G^{\ominus} + RT \ln\left(\frac{p_B/p^{\ominus}}{p_A/p^{\ominus}}\right) = \Delta_r G^{\ominus} + RT \ln(Q) \tag{1.23}$$

$$\Delta_r G^{\ominus} = \mu_B^{\ominus} - \mu_A^{\ominus} = -RT \ln\left(\frac{p_B/p^{\ominus}}{p_A/p^{\ominus}}\right)_{\text{eq}} = -RT \ln(K_{\text{eq}}) \tag{1.24}$$

where Q is the reaction quotient. At equilibrium, $\Delta_r G = 0$ and the quotient is equal to the equilibrium constant K_{eq}. For general stoichiometry $\sum_A \nu_A\,A_{(g)} \rightleftharpoons \sum_B \nu_B\,B_{(g)}$,

$$Q = \ln\left(\frac{\prod_B (p_B/p^{\ominus})^{\nu_B}}{\prod_A (p_A/p^{\ominus})^{\nu_A}}\right) \tag{1.25}$$

In solution, $p/p^{\ominus}$ is replaced with the activity a.

$$a = \begin{cases} 1 \text{ for a pure solid, liquid, or for the solvent} \\ [\ ] \text{ concentration in mol/dm}^{-3} \text{ for dilute solutes} \end{cases} \tag{1.26}$$

For a dissolving solid $AB_{(s)} \rightleftharpoons A^{+}_{(aq)} + B^{-}_{(aq)}$ the equilibrium constant is

$$K_{sp} = [A]_{eq}[B]_{eq} \qquad \text{[solubility product]}. \tag{1.27}$$

Van't Hoff isotherm:

$$\left(\frac{\partial G}{\partial T}\right)_{p,n_i} = -S \qquad\qquad \text{[from Eq. (1.16)]} \tag{1.28}$$

$$\left(\frac{\partial (G/T)}{\partial T}\right)_{p,n_i} = \frac{1}{T}\left(\frac{\partial G}{\partial T}\right)_{p,n_i} - \frac{G}{T^2} = -\frac{S}{T} - \frac{H-TS}{T^2} = -\frac{H}{T^2} \tag{1.29}$$

Also works if we replace the Gibbs energy with energy difference:

$$\left(\frac{\partial (\Delta_r G^{\ominus}/T)}{\partial T}\right)_{p,n_i} = -\frac{\Delta_r H^{\ominus}}{T^2} \qquad\qquad \text{[generally true]} \tag{1.30}$$

$$\left(\frac{\partial \ln K_{eq}}{\partial T}\right)_{p,n_i} = \frac{\Delta_r H^{\ominus}}{RT^2} \qquad\qquad \text{[from Eq. (1.24)]} \tag{1.31}$$

$$\ln\left(\frac{K_{eq}(T_2)}{K_{eq}(T_1)}\right) = -\frac{\Delta_r H}{R}\left(\frac{1}{T_2} - \frac{1}{T_1}\right) \qquad \text{[assuming that } \Delta_r H^{\ominus} \text{ does not depend on } T] \tag{1.32}$$

Heat capacities:

$$C_V = \left(\frac{\partial U}{\partial T}\right)_V \qquad\qquad \text{constant-volume} \tag{1.33}$$

$$C_p = \left(\frac{\partial H}{\partial T}\right)_p \qquad\qquad \text{constant-pressure} \tag{1.34}$$

$$C_p = C_V + nR \qquad\qquad \text{for the ideal gas} \tag{1.35}$$

For a gas of non-interacting rigid (non-vibrating) molecules

	monoatomic	**linear**	**non-linear**
C_V	$\frac{3}{2}nR$	$\frac{5}{2}nR$	$3nR$

If the molecules are vibrating, add an extra nR for every "active" normal mode.
Kirchhoff's law (second equality assumes constant C_p)

$$H(T_2) = H(T_1) + \int_{T_1}^{T_2} C_p\, dT = H(T_1) + C_p(T_2 - T_1) \tag{1.36}$$

$$S(T_2) = S(T_1) + \int_{T_1}^{T_2} C_p\frac{dT}{T} = S(T_1) + C_p\ln\left(\frac{T_2}{T_1}\right) \tag{1.37}$$

The above is valid for heating of a single phase. If a phase transition occurs at temperature T_{tr} and with enthalpy $\Delta_{tr}H$ then

$$H(T_2) = H(T_1) + \int_{T_1}^{T_{tr}} C_p\, dT + \Delta_{tr}H + \int_{T_{tr}}^{T_2} C_p\, dT \tag{1.38}$$

$$S(T_2) = S(T_1) + \int_{T_1}^{T_{tr}} C_p \frac{dT}{T} + \frac{\Delta_{tr} H}{T_{tr}} + \int_{T_{tr}}^{T_2} C_p \frac{dT}{T} \tag{1.39}$$

Consider Eq. (1.18) for a single species in phase α (e.g., liquid) and phase β (e.g., gas).

$$d\mu_\alpha = V_{\alpha,m} \, dp - S_{\alpha,m} \, dT \qquad d\mu_\beta = V_{\beta,m} \, dp - S_{\beta,m} \, dT \tag{1.40}$$

where $V_{\alpha,m}$ is the *molar* volume of phase α, $S_{\alpha,m}$ is the *molar* entropy of phase α, etc. At equilibrium, $\mu_\alpha = \mu_\beta$, so that $d\mu_\alpha = d\mu_\beta$ and along the phase boundary

$$V_{\alpha,m} \, dp - S_{\alpha,m} \, dT = V_{\beta,m} \, dp - S_{\beta,m} \, dT \tag{1.41}$$

or

$$\frac{dp}{dT} = \frac{\Delta_{tr} S_m}{\Delta_{tr} V_m} = \frac{\Delta_{tr} H_m}{T \Delta_{tr} V_m} \qquad \text{Clapeyron equation} \tag{1.42}$$

For a liquid-to-gas transition (vaporisation) or solid-to-gas (sublimation), the change in volume is essentially equal to the volume of gas formed. Asuming ideality,

$$\Delta_{tr} V_m = \frac{RT}{p} \quad \Rightarrow \quad \frac{dp}{dT} = \frac{\Delta_{tr} H_m}{RT^2/p} \quad \Rightarrow \quad \frac{d\ln p}{dT} = \frac{\Delta_{tr} H_m}{RT^2} \qquad \text{(Clausius–Clapeyron)} \tag{1.43}$$

1.3 pH calculation

For $H_2O_{(l)} \rightleftharpoons H^+_{(aq)} + OH^-_{(aq)}$, the equilibrium constant

$$K_w = [H^+][OH^-] = 10^{-14} \tag{1.44}$$

For a monoprotic acid $HA_{(aq)} \rightleftharpoons H^+_{(aq)} + A^-_{(aq)}$,

$$K_a = \frac{[H^+][A^-]}{[HA]} \tag{1.45}$$

We define

$$\text{pH} = -\log_{10}[H^+], \qquad pK_a = -\log_{10} K_a \tag{1.46}$$

For a monoprotic acid with total concentration c_a:

pK_a	c_a/M	$[H^+]$
< 0	$> 10^{-6}$	c_a
< 0	$< 10^{-6}$	$\frac{c_a}{2} + \sqrt{\left(\frac{c_a}{2}\right)^2 + K_w}$
$0 \ldots 8$	$> 10^{-6}$	$-\frac{K_a}{2} + \sqrt{\left(\frac{K_a}{2}\right)^2 + K_a c_a}$
> 8	any	$\sqrt{K_a c_a + K_w}$

Henderson–Hasselbalch equation:

$$\text{pH} = pK_a + \log_{10}\left(\frac{[A^-]}{[HA]}\right) \tag{1.47}$$