Thermodynamics Quick Summary

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1 First Law: Conservation of Energy

The first law of thermodynamics states that the change in internal energy of a system is equal to the heat added to the system plus the work done on the system:

$$du = \delta q + \delta w \tag{1}$$

where du is a **state function** (exact differential, use d), while δq and δw are path functions (inexact differentials, use δ).

2 Second Law: Entropy

The second law has many forms, often related to entropy:

- In a spontaneous process, the entropy of the universe increases.

- The total entropy of an isolated system can never decrease.

2.1 Clausius Inequality

The Clausius inequality states:

$$dS_{sys} \geq \frac{\delta q}{T_{surr}} \tag{2}$$

where dS_{sys} is the change in entropy of system, δq is the heat supplied to the system, and T is the temperature of the surrounding.

The equality of Eq. (2) holds for reversible processes. A reversible process is infinitesimally slow (reversible heat flow due to infinitesimally small temperature difference) and does *not* produce entropy in the system, that is

$$dS = \text{ entropy supplied to system } = \frac{\delta q}{T} \tag{3}$$

This defines entropy change, i.e.,

$$dS = \frac{\delta q_{rev}}{T} \tag{4}$$

The inequality of Eq. (2) holds for irreversible processes. Irreversible processes cause finite changes in the system.

$\implies$ An increase in entropy due to internal irreversible changes.

$\Longrightarrow$ Entropy is created in the system.

$\Longrightarrow$ The entropy change in the system is greater than the entropy supplied (more entropy must be extracted to return the system to its original state).

The total entropy change of the system can be expressed as:

$$dS = \delta S^{(s)} + \delta S^{(p)} \tag{5}$$

where superscript s refers to entropy supplied (e.g., due to heat exchange with surrounding):

$$\delta S^{(s)} = \frac{\delta q}{T} \tag{6}$$

and superscript p refers to entropy produced (e.g., due to irreversible processes such as friction, mixing, or chemical reactions), where

$$\delta S^{(p)} = \begin{cases} 0 & \text{reversible process} \\ \neq 0 & \text{irreversible process} \end{cases} \tag{7}$$

The overall change of entropy of system is a state function (note d) but entropy supply and production are not (note δ).

For an *isolated* system, $\delta q = 0$, thus Eq. (2) becomes:

$$dS \geq 0 \tag{8}$$

i.e., entropy change of an isolated system remains the same or increases.

3 First and Second Laws Combined

The first and second laws of thermodynamics can be combined to obtain the thermodynamic inequality. Since $T > 0$, Eq. (2) gives:

$$\delta q \leq TdS \tag{9}$$

Write Eq. (1) as a sum of heat transfer, $p - V$ work done *on* the system and non-pV work (e.g., electrical work), we have:

$$dU = \delta q + \delta w_p + \delta w_e \tag{10}$$

$$= \delta q - pdV + \delta w_e \leq TdS - pdV + \delta w_e \tag{11}$$

Thus, we have:

$$dU \leq TdS - pdV + \delta w_e \tag{12}$$

where equality holds at equilibrium.

3.1   Other energy state functions

The enthalpy H, Helmholtz free energy A (or sometimes F), and Gibbs free energy G are defined as follows:

$$H = U + pV = A + TS \tag{13}$$

$$A = U - TS = G - pV \tag{14}$$

$$G = H - TS = U + pV - TS = A + pV \tag{15}$$

3.2   Fundamental relations

Other fundamental relations similar to Eq. (12) can be derived:

$$dH \leq TdS + Vdp + \delta w_e \tag{16}$$

$$dA \leq -SdT - pdV + \delta w_e \tag{17}$$

$$dG \leq -SdT + Vdp + \delta w_e \tag{18}$$

where equalities hold at equilibrium.

Considering equilibrium process without non-pV work, Eq. (12) becomes:

$$dU = TdS - pdV \tag{19}$$

Other fundamental relations can be similarly obtained:

$$dH = TdS + Vdp \tag{20}$$

$$dA = -SdT - pdV \tag{21}$$

$$dG = -SdT + Vdp \tag{22}$$

3.3   Maxwell relations

Maxwell relations follow from the fact that all the energy state functions are path independent and that their differentials are **exact**.

If $df = udx + vdy$ is an exact differential, then

$$\left(\frac{\partial u}{\partial y}\right)_x = \left(\frac{\partial v}{\partial x}\right)_y \tag{23}$$

So, given $dU = TdS - pdV$, we have

$$\left(\frac{\partial T}{\partial V}\right)_S = -\left(\frac{\partial p}{\partial S}\right)_V \tag{24}$$

Since dU is an exact differential, same things apply to dA, dG, dH.

3.4 Use of Maxwell relations

Any energy state function can be regarded as a function of any pair of variables from p, V, S, T.

For example, given

$$dU = TdS - pdV \quad \Rightarrow \quad U = U(S, V) \tag{25}$$

Suppose we want U as a function of T and V, i.e., $U = U(T, V)$, then

$$dU = \left(\frac{\partial U}{\partial T}\right)_V dT + \left(\frac{\partial U}{\partial V}\right)_T dV \tag{26}$$

Now, only need to find $\boxed{\left(\frac{\partial U}{\partial T}\right)_V}$ and $\boxed{\left(\frac{\partial U}{\partial V}\right)_T}$.

From

$$dU = TdS - pdV \tag{27}$$

we can take partial derivative of Eq. (27) with respect to T while keeping V constant, then

$$\left(\frac{\partial U}{\partial T}\right)_V = T\left(\frac{\partial S}{\partial T}\right)_V - p\left(\frac{\partial V}{\partial T}\right)_V \tag{28}$$

Since differentiating V with while keeping V constant, then second term above vanishes, and we get

$$\boxed{\left(\frac{\partial U}{\partial T}\right)_V = T\left(\frac{\partial S}{\partial T}\right)_V} \tag{29}$$

Similarly, take partial derivative of Eq. (27) with respect to V while keeping T constant, then

$$\boxed{\left(\frac{\partial U}{\partial V}\right)_T = T\left(\frac{\partial S}{\partial V}\right)_T - p\left(\frac{\partial V}{\partial V}\right)_T = T\left(\frac{\partial S}{\partial V}\right)_T - p} \tag{30}$$

Substituting Eq. (29) and (30) into Eq. (26), we have

$$dU = T\left(\frac{\partial S}{\partial T}\right)_V dT + \left[T\left(\frac{\partial S}{\partial V}\right)_T - p\right] dV \tag{31}$$

4 Heat Capacities

The heat capacities at constant pressure and constant volume are defined as:

$$\boxed{C_p = \left(\frac{\partial H}{\partial T}\right)_p} \tag{32}$$

$$\boxed{C_v = \left(\frac{\partial U}{\partial T}\right)_v} \tag{33}$$

4.1 Thermodynamic Differentials

From thermodynamic relations:

$$dH = V\,dp + T\,dS \quad \text{and} \quad dU = T\,dS - p\,dV \tag{34}$$

At constant pressure, $dp = 0$, and at constant volume, $dV = 0$:

$$dH = T\,dS \quad \text{and} \quad dU = T\,dS \tag{35}$$

This gives:

$$\boxed{C_p dT = T\,dS} \quad \text{and} \quad \boxed{C_v dT = T\,dS} \tag{36}$$

Thus, the entropy change dS is:

$$\boxed{dS = \frac{C_p dT}{T}} \quad \text{and} \quad \boxed{dS = \frac{C_v dT}{T}} \tag{37}$$

Integrating from T_1 to T_2:

$$\int_{T_1}^{T_2} dS = \int_{T_1}^{T_2} \frac{C_p dT}{T} \quad \text{and} \quad \int_{T_1}^{T_2} dS = \int_{T_1}^{T_2} \frac{C_v dT}{T} \tag{38}$$

The entropy change between states is:

$$\boxed{S(T_2) - S(T_1) = \int_{T_1}^{T_2} \frac{C_p}{T} dT} \quad \text{and} \quad \boxed{S(T_2) - S(T_1) = \int_{T_1}^{T_2} \frac{C_v}{T} dT} \tag{39}$$

4.2 Phase Transition and Total Entropy

If T_1 to T_2 includes T_{pc} at which phase transition occurs, then

$$\boxed{\Delta S_{\mathrm{pc}} = \frac{\Delta H_{\mathrm{pc}}}{T_{\mathrm{pc}}}} \tag{40}$$

Thus,

$$\boxed{S(T_2) = S(T_1) + \int_{T_1}^{T_2} \frac{C_p}{T} dT + \sum_{\mathrm{pc}} \frac{\Delta H_{\mathrm{pc}}}{T_{\mathrm{pc}}}} \tag{41}$$

5 Variation of Gibbs Free Energy G

The differential of Gibbs free energy is:

$$dG = -S\,dT + V\,dp \tag{42}$$

From this, we obtain the following using total differential of G:

$$-S = \left(\frac{\partial G}{\partial T}\right)_p \quad \text{and} \quad V = \left(\frac{\partial G}{\partial p}\right)_T \tag{43}$$

5.1   At constant T

At constant temperature $(dT = 0)$:

$$\int_{p_1}^{p_2} dG = \int_{p_1}^{p_2} V dp \tag{44}$$

$$G(p_2, T) - G(p_1, T) = \int_{p_1}^{p_2} V(p, T) dp \tag{45}$$

For an ideal gas $(V = \frac{RT}{p}$ per mole):

$$G(p_2, T) - G(p_1, T) = \int_{p_1}^{p_2} \frac{RT}{p} dp = RT \ln\left(\frac{p_2}{p_1}\right) \tag{46}$$

Setting $p_1 = p°$ (standard pressure):

$$G_m(p_2, T) = G_m°(p°, T) + RT \ln\left(\frac{p}{p°}\right) \tag{47}$$

Since, for ideal gas, $p \propto \frac{1}{V}$ at constant pressure:

$$\boxed{G(p_2, T) - G(p_1, T) = RT \ln \frac{p_2}{p_1} = RT \ln \frac{V_1}{V_2}} \tag{48}$$

5.2   At constant p

At constant p:

$$\left(\frac{\partial G}{\partial T}\right)_p = -S \tag{49}$$

Consider:

$$\begin{aligned}
\left(\frac{\partial}{\partial T}\left[\frac{G}{T}\right]\right)_p &= \frac{T\left(\frac{\partial G}{\partial T}\right)_p - G\left(\frac{\partial T}{\partial T}\right)_p}{T^2} \\
&= \frac{T(-S) - G}{T_2} \quad \text{(substituting Eq. (49))} \\
&= -\frac{(G + TS)}{T_2} \\
&= -\frac{H}{T_2} \tag{50}
\end{aligned}$$

Eq. (50) gives the **Gibbs Helmholtz equation**.

From the Gibbs Helmholtz equation at equilibrium, we have

$$\left(\frac{\partial}{\partial T}\left[\frac{\Delta G°}{T}\right]\right)_p = -\frac{\Delta H°}{T_2} \tag{51}$$

At equilibrium, we also have $\Delta G^\circ = -RT \ln K$, which upon substituting into Eq. (51) becomes

$$\left(\frac{\partial}{\partial T} (-R \ln K) \right)_p = -\frac{\Delta H^\circ}{RT^2} \tag{52}$$

$$\boxed{\left(\frac{\partial \ln K}{\partial T} \right)_p = \frac{\Delta H^\circ}{RT^2}} \tag{53}$$

We can integrate Eq. (53) from T_1 to T_2 at constant p to obtain:

$$\int_{T_1}^{T_2} d \ln K = \int_{T_1}^{T_2} \frac{\Delta H^\circ}{RT^2} dT$$
$$\ln K(T_2) - \ln K(T_1) + \int_{T_1}^{T_2} \frac{\Delta H^\circ}{RT^2} dT \tag{54}$$

If assume ΔH° does not change over T_1 to T_2, then:

$$\ln K(T_2) = \ln K(T_1) + \frac{\Delta H^\circ}{R} \left[-\frac{1}{T} \right]_{T_1}^{T_2}$$
$$\boxed{\ln K(T_2) = \ln K(T_1) - \frac{\Delta H^\circ}{R} \left[\frac{1}{T_2} - \frac{1}{T_1} \right]} \tag{55}$$

We can also do indefinite integral of Eq. (53) at constant p to obtain:

$$\int d \ln K = \int \frac{\Delta H^\circ}{RT^2} dT$$
$$\boxed{\ln K(T) = -\frac{\Delta H^\circ}{RT} + c} \tag{56}$$

Thus, the plot of $\ln K(T)$ against $1/T$ allows ΔH° to be determined.

Alternatively, we can set

$$\Delta_r G^\circ = -RT \ln K = \Delta_r H^\circ - T \Delta_r S^\circ \tag{57}$$

to get

$$\boxed{\ln K = -\frac{\Delta_r H^\circ}{RT} + \frac{\Delta_r S^\circ}{R}} \tag{58}$$

6 Phase Equilibria

For two phases at equilibrium:
$$G_{m,1} = G_{m,2} \tag{59}$$

Since $dG = V dp - S dT$, we have:

$$dG_{m,1} = dG_{m,2} \tag{60}$$

$$V_{m,1} dp - S_{m,1} dT = V_{m,2} dp - S_{m,2} dT \tag{61}$$

$$(V_{m,1} - V_{m,2}) dp = (S_{m,1} - S_{m,2}) dT \tag{62}$$

This gives the Clapeyron equation:

$$\boxed{\frac{dp}{dT} = \frac{\Delta S}{\Delta V}} \tag{63}$$

The slope of the p-T phase boundary is thus $\dfrac{\Delta S}{\Delta V}$.

At phase equilibrium, $\Delta G = \Delta H - T\Delta S = 0$, so:

$$\Delta S = \frac{\Delta H}{T} \tag{64}$$

Substituting into the Clapeyron equation:

$$\boxed{\frac{dp}{dT} = \frac{\Delta H}{T\Delta V}} \tag{65}$$

For sublimation and vaporization, assume $\Delta V \approx V_g = \frac{RT}{p}$ (only gas phase volume change and negligible condensed phase volume):

$$\frac{dp}{dT} = \frac{\Delta H}{TV_g} = \frac{p\Delta H}{RT^2} \tag{66}$$

Integrating from (p_1, T_1) to (p_2, T_2) in the p-T phase diagram:

$$\int_{p_1}^{p_2} \frac{dp}{p} = \int_{T_1}^{T_2} \frac{\Delta H}{RT^2} dT \tag{67}$$

$$\ln\left(\frac{p_2}{p_1}\right) = \int_{T_1}^{T_2} \frac{\Delta H}{RT^2} dT \tag{68}$$

Assuming ΔH is constant over the temperature range, then:

$$\boxed{\ln\left(\frac{p_2}{p_1}\right) \approx \frac{\Delta H}{R}\left(\frac{1}{T_1} - \frac{1}{T_2}\right)} \tag{69}$$