Thermodynamics

Chem 211: Lecture 10

Thermodynamics of

Phase Equilibria

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Standard molar Gibbs energies

$$\Delta_r G^0 = \Delta_r H^0 - T\Delta_r S^0$$

$$\Delta_r G^0 = \sum_{\text{Products}} \nu\Delta_f G^0 - \sum_{\text{Reactants}} \nu\Delta_f G^0$$

For the Rx $CO(g) + {}^1/_2\, O_2(g) \rightarrow CO_2(g)$

$$\Delta_r G^0 = \Delta_f G^0(CO_2) - \Delta_f G^0(CO) - {}^1/_2\, \Delta_f G^0(O_2)$$

$$\Delta_r G^0$$
$$= -394.4\ kJ\ mol^{-1} - \left(-137.2 - {}^1/_2\,(0)\right)\ kJ\ mol^{-1}$$
$$= -257.2\ kJ\ mol^{-1}$$

Criteria of Reversibility

For a change in a closed system of constant composition, and in the absence of any additional (non-expansion) work

Irreversible	Reversible
$(dS)_{V,U} > 0$	$(dS)_{V,U} = 0$
$(dU)_{V,S} < 0$	$(dU)_{V,S} = 0$
$(dH)_{P,S} < 0$	$(dH)_{P,S} = 0$
$(dS)_{P,H} > 0$	$(dS)_{P,H} = 0$
$(dA)_{T,V} < 0$	$(dA)_{T,V} = 0$
$(dG)_{T,P} < 0$	$(dG)_{T,P} = 0$

Combining 1st and 2nd Laws of Thermodynamics

Fundamental equations

- For a reversible change in a closed system of constant composition, and in the absence of any additional (non-expansion) work,

$$dU = dQ + dW$$

$$dW_{rev} = -PdV$$

$$dQ_{rev} = TdS$$

$$dU = TdS - PdV$$

Fundamental Equation

Note: ΔU is path independent

Partial molal free energy, $\bar{G}_1$

- As G is an extensive state property, thus for a system containing several components at constant *T*, *P*:

$$dG_{sys} = \sum dG_{components} = n_1\bar{G}_1 + n_2\bar{G}_2 + \ldots.$$

- $\bar{G}_1$: the increase in the total free energy of the system upon increasing n_1 by 1 mol while keeping other variables (n_2, n_3, …etc, P and T) constant.

$$\bar{G}_1 = \left(\frac{\partial G_{sys}}{\partial n_1}\right)_{n_2, n_3, \ldots\ldots, T, P}$$

Chemical Potential, μ

- For a pure substance (one component only), $\bar{G}_1$ is simply the free energy per mole, molar Gibb's free energy.
- In solutions, $\bar{G}_1$ is called the chemical potential, μ_1.

$$\mu_1 = \left(\frac{\partial G_{sys}}{\partial n_1}\right)_{n_2, n_3, \ldots\ldots, T, P}$$

For an ideal gas

$$\mu = \mu_0 + RT \ln P$$

- μ_0 is the standard (1 atm, 298 K) chemical potential.

For a real gas

$$\mu = \mu_0 + RT \ln f$$

f : fugacity or effective pressure

Effect of T and P on G

$$dG = VdP - SdT$$

+ve $\left(\frac{\partial G}{\partial P}\right)_T = V$ $\left(\frac{\partial G}{\partial T}\right)_P = -S$ –ve

- This equation was derived for systems containing one component of **fixed composition** and assuming only **PV work**. If components and composition are changed during the process, then,

$$dG = VdP - SdT + \mu_1 dn_1 + \mu_2 dn_2 + \ldots$$

If other work is assumed

$$dG = Vdp + EdQ - SdT + \mu_1 dn_1 + \mu_2 dn_2 + \ldots$$

Or $$dG = Vdp + \gamma d\sigma - SdT + \mu_1 dn_1 + \mu_2 dn_2 + \ldots$$

Consider this Rx

$$a_1A_1 + a_2A_2 + \ldots = b_1B_1 + b_2B_2 + \ldots$$

$$\Delta G = \sum G_{\text{products}} - \sum G_{\text{reactants}}$$

$$\Delta G = [b_1G_{B_1} + b_2G_{B_2} + \ldots] - [a_1G_{A_1} + a_2G_{A_2} + \ldots]$$

$$\left(\frac{d\Delta G}{dP}\right)_T = \Delta V$$

$$\left(\frac{d\Delta G}{dT}\right)_P = -\Delta S$$

- If a reaction proceeds with no change in volume between reactants and products at constant T, ΔG will be independent of P.
- If a reaction proceeds with no change in entropy between reactants and products at constant P, ΔG will be independent of T.

Effect of T on G

Consider the differentiation of *G/T* with respect to *T*

$$\left(\frac{d\left({}^{G}/_{T}\right)_{P}}{dT}\right) = \frac{1}{T}\left(\frac{\partial G}{\partial T}\right)_{P} - \frac{G}{T^2}$$

Utilizing these formulas $\left(\frac{\partial G}{\partial T}\right)_{P} = -S$ **and** $G = H - TS$

$$\left(\frac{d\left({}^{G}/_{T}\right)_{P}}{dT}\right) = \frac{-S}{T} - \left(\frac{H}{T^2} - \frac{S}{T}\right) = -\frac{H}{T^2}$$

$$\left(\frac{d\left({}^{\Delta G}/_{T}\right)_{P}}{dT}\right) = -\frac{\Delta H}{T^2}$$

Effect of T on A

$$dA = -PdV - SdT$$

Isochoric (const. V) processes

$$\left(\frac{dA}{dT}\right)_V = -S \qquad \boxed{\left(\frac{d\Delta A}{dT}\right)_V = -\Delta S}$$

Isothermal Processes

$$\left(\frac{dA}{dV}\right)_T = -P \qquad \boxed{\left(\frac{d\Delta A}{dV}\right)_T = -\Delta P}$$

$$\Delta A = \Delta U + T\left(\frac{d\Delta A}{dT}\right)_V$$

$$\left(\frac{d\left({}^{\Delta A}/_{T}\right)_V}{dT}\right) = -\frac{\Delta U}{T^2}$$

Gibbs-Helmholtz equation

For isothermal processes

$$\Delta G = \Delta H - T\Delta S$$

Utilizing this formula

$$\left(\frac{d\Delta G}{dT}\right)_P = -\Delta S$$

$$\Delta G = \Delta H + T\left(\frac{d\Delta G}{dT}\right)_P$$

Gibbs-Helmholtz equation

Kinetic limited/controlled Rx

- are reactions having a negative ΔG, yet they do not proceed spontaneously unless a barrier is overcome (energy is provided to initiate the Rx) by adding a catalyst.
- **Example,**

  $H_2(g) + O_2(g) \rightarrow H_2O(g)$ $\Delta G = -56{,}690$ cal/mol at 298 K.
- Just mixing of $H_2(g)$ and $O_2(g)$ do not produce unless a catalyst (electric spark, platinized asbestos) is added.
- A –Ve ΔG measures the driving force of reactions when these reactions occur.
- The catalyst does not affect ΔG (path independent).

Gibb's equation Interpretation

Criterion of spontaneity is the increase in the total entropy.

$$\Delta S_t = \Delta S_{sur} + \Delta S_{sys}$$

For chemical reactions (endothermic or exothermic),

$$\Delta S_{sur} = \frac{-Q_P}{T} = \frac{-\Delta H}{T} \Rightarrow \Delta S_t = \frac{-\Delta H}{T} + \Delta S_{sys}$$

$$-T\Delta S_t = \Delta H - T\Delta S_{sys}$$

$$\Delta G = \Delta H_{sys} - T\Delta S_{sys}$$

$$\Delta G = -T\Delta S_t$$

Thermodynamics of Phase Equilibria

Phase Eq. in pure substances

Consider the following equilibrium

$$H_2O_{(l)} \Leftrightarrow H_2O_{(s)} \qquad \Delta H_f = -334\ J\ g^{-1} at\ 0^oC$$

- Equilibrium means that $\Delta G_{P,T} = G_2 - G_1 = 0$.
- If equilibrium is interrupted infinitesimally (small reversible change,) by changing P or T, equilibrium will be restored quickly.

$$dG_1 = dG_2$$

$$V_1 dP - S_1 dT = V_2 dP - S_2 dT$$

$$\frac{dP}{dT} = \frac{S_2 - S_1}{V_2 - V_1} = \frac{\Delta S}{\Delta V}$$

- Since the phase change occurs reversibly and isothermally,

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

$$\frac{dP}{dT} = \frac{\Delta S}{\Delta V} = \frac{\Delta H}{T\Delta V}$$

$$\frac{dT}{dP} = \frac{T\Delta V}{\Delta H}$$

Clapeyron's equation

- It represents the effect of pressure on the equilibrium temperature of phase transformations.
- It helps in calculating the vapor pressure of liquids and sublimating solids.

Effect of P on equilibrium T

- Heterogeneous equilibria always occur at specified T (i.e., isothermally) and associated by ΔH and ΔV.
- The eq. T of a given reaction can be calculated at a given pressure as following:

$$\frac{dP}{dT} = \frac{\Delta H}{T\Delta V}$$

$$\int_{P_1}^{P_2} dP = \int_{T_1}^{T_2} \frac{\Delta H}{T\Delta V} dT$$

- If ΔH and ΔV as functions of T are known, we can substitute easily. Otherwise, assume them independent of T over a limited small range of T

$$\int_{P_1}^{P_2} dP = \frac{\Delta H}{\Delta V} \int_{T_1}^{T_2} \frac{dT}{T}$$

$$P_2 - P_1 = \frac{\Delta H}{\Delta V} \ln\left(\frac{T_2}{T_1}\right)$$

P vs. ln T is linear

Exercise

- The densities of liquid and solid Hg are listed below at the melting point and 1 atm. The latent heat of fusion is also given at melting point. Find the rate of changing the melting point with pressure ($^oC\ atm^{-1}$) and calculate the melting point at 50 atm?

Eq.	d_1, $g\ cm^{-3}$	V_1, $cm^3 g^{-1}$	d_2, $g\ cm^{-3}$	V_2, $cm^3 g^{-1}$	ΔH, $cal\ mol^{-1}$	T_{eq}, ^oC
$Hg_{(s)} \leftrightarrow Hg_{(l)}$	14.19		13.7		566	–38.87

Solution

$$V = \text{specific volume} \times \text{atomic mass}$$

As ΔH is given in cal/mol, V is the molar volume

Eq.	d_1, g cm^{-3}	V_1, cm^{3}g^{-1}	d_2, g cm^{-3}	V_2, cm^{3}g^{-1}	ΔH, cal mol^{-1}	T_{eq}, °C
$Hg_{(s)} \leftrightarrow Hg_{(l)}$	14.19	0.070	13.7	0.073	566	–38.87

$$V_1 = \left(\frac{0.070\ cm^3}{\text{g}}\right)\left(\frac{200.5\ g}{mol}\right) = \frac{14.1297\ cm^3}{\text{mol}}$$

$$V_2 = \left(\frac{0.073\ cm^3}{\text{g}}\right)\left(\frac{200.5\ g}{mol}\right) = \frac{14.6350\ cm^3}{\text{mol}}$$

$$\Delta V = V_2 - V_1 = \frac{0.5056\ cm^3}{\text{mol}}$$

$$\frac{dT}{dP} = \frac{T\Delta V}{\Delta H} = \frac{(234.28K)\left(\frac{0.5056\,cm^3}{\text{mol}}\right)}{\left(\frac{566\,cal}{mol}\right)\left(\frac{41.268\,cm^3 atm}{cal}\right)}$$

$$= 0.00507\,K\,atm^{-1} = 0.00507\,^{o}C\,atm^{-1}$$

- As we are concerning with change in T, therefore a change in ^{o}C is the same as in K.
- The mp increases by 0.00507 K per atm.

$$P_2 - P_1 = \frac{\Delta H}{\Delta V} \ln\left(\frac{T_2}{T_1}\right)$$

$$50\ atm - 1\ atm$$

$$= \frac{\left(\frac{566\ cal}{mol}\right)\left(\frac{41.268\ cm^3 atm}{cal}\right)}{\left(\frac{0.5056\ cm^3}{\text{mol}}\right)} \ln\left(\frac{T_2}{234.28K}\right)$$

$$T_2 = 234.53\ K$$

- Note this minute change in T (mp) with this large change in p

Homework

- Use the same data of Hg to calculate the pressure at which the mp of Hg is 1 °C higher than its mp at 1 atm?

Eq.	d_1, g cm^{-3}	V_1, cm^{3}g^{-1}	d_2, g cm^{-3}	V_2, cm^{3}g^{-1}	ΔH, cal mol^{-1}	T_{eq}, °C
$Hg_{(s)} \leftrightarrow Hg_{(l)}$	14.19		13.7		566	–38.87

Reference data at 1 atm

Substance	Standard (0 °C) Latent Heat of Fusion kJ/kg	Standard (100 °C) Latent Heat of Vaporization kJ/kg
Water	334.56	2264.76

Ice/water equilibrium

$H_2O_{(l)} \Leftrightarrow H_2O_{(S)}$ $\Delta H_f = -334.56\ J\ g^{-1} at\ 0^oC$

Eq.	d_1, g cm^{-3}	V_1, cm^{3}g^{-1}	d_2, g cm^{-3}	V_2, cm^{3}g^{-1}	ΔH, kJ g^{-1}	T_{eq}, K
$H_2O_{(s)} \leftrightarrow H_2O_{(l)}$	0. 916	1.0907	0.9999	1.0001	334.56	273

$$\frac{dT}{dP} = \frac{T\Delta V}{\Delta H} = \frac{(273K)\left(\frac{-0.0906\ cm^3}{\mathrm{g}}\right)}{\left(\frac{334.56\ \mathrm{J}}{g}\right)\left(\frac{1\ L\ \mathrm{atm}}{101.39\ J}\right)\left(\frac{1000\ \mathrm{cm}^3}{L}\right)} =$$

$$= -7.4957 \times 10^{-03}\ K\ atm^{-1}$$

$$= -7.4957 \times 10^{-03}\ ^oC\ atm^{-1}$$

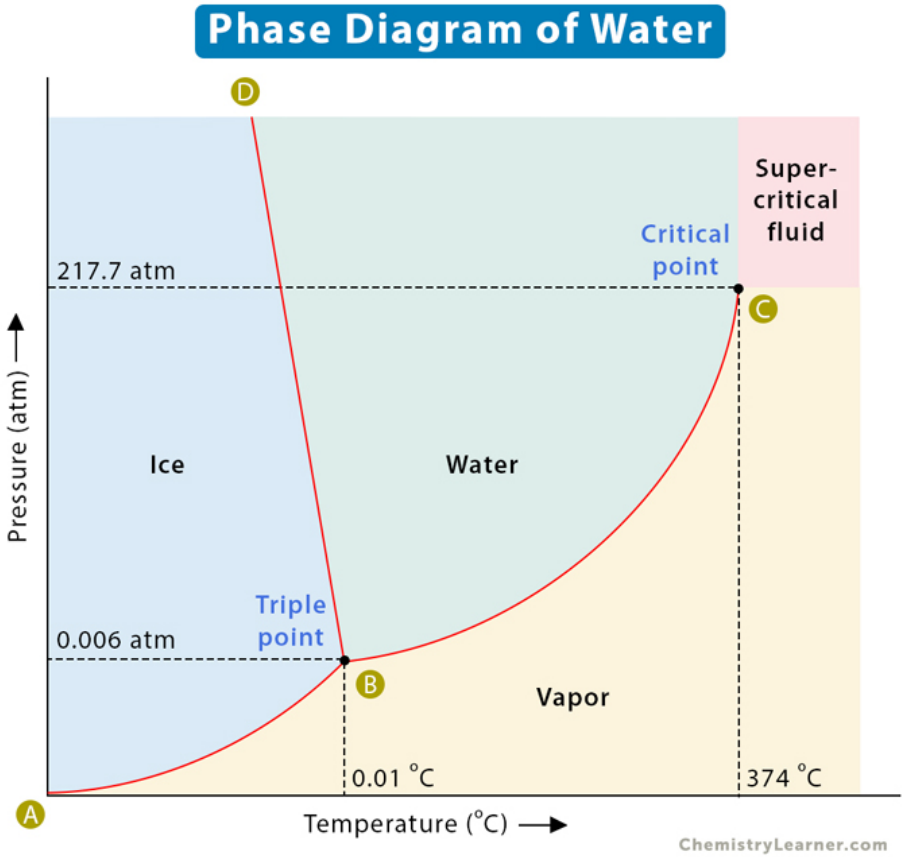
Important Note

- Unlike all liquid/solid transformations, the mp of ice decreases with increasing P. **Comment**?

- Water is actually an abnormal compound because of the strong H-bonding between water molecules that makes the volume increases abnormally upon freezing.

- Hence, the freezing/melting line in water phase diagram has a negative slope.

$$\frac{dT}{dP} = -7.4957 \times 10^{-03}\ ^{o}C\ atm^{-1}$$


Phase Diagram of Water
D
Super-
critical
fluid
Critical
point
217.7 atm
C
Pressure (atm)
Ice
Water
Triple
point
0.006 atm
B
Vapor
0.01 °C
374 °C
A
Temperature (°C)
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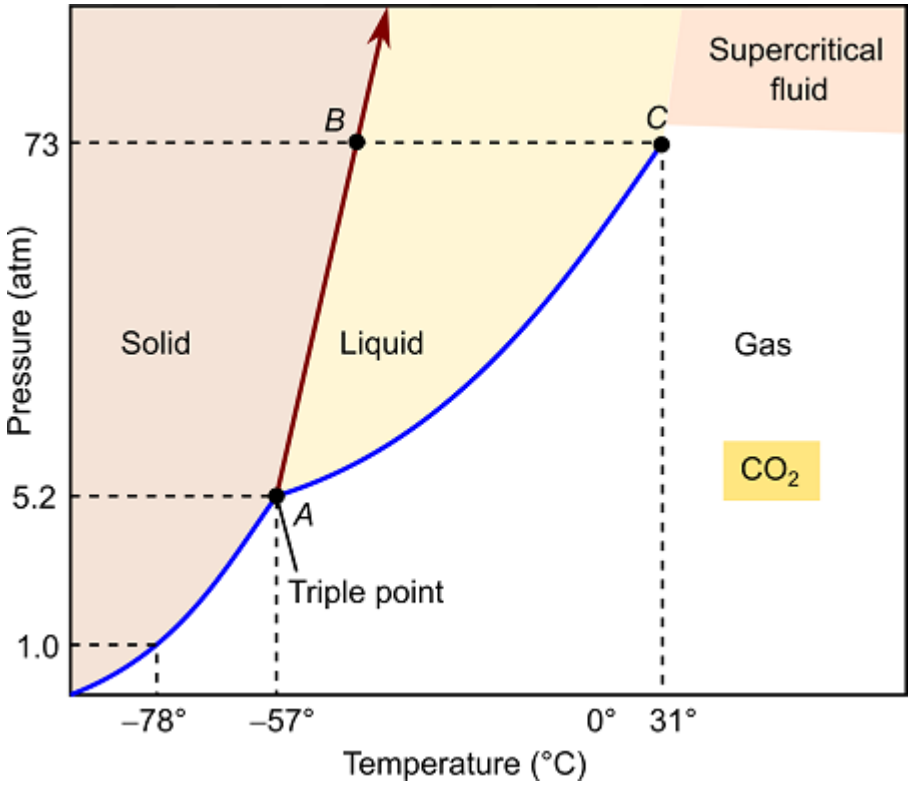

Supercritical
fluid
B
C
73
Pressure (atm)
Solid
Liquid
Gas
CO2
5.2
A
Triple point
1.0
–78°
–57°
0°
31°
Temperature (°C)

Water/vapor equilibrium

$H_2O_{(l)} \Leftrightarrow H_2O_{(g)}$ $\Delta H_v = 40.66\ kJ\ \mathrm{mol}^{-1} at\ 373\mathrm{K}$

Eq.	V_l, cm^3mol^{-1}	V_g, cm^3mol^{-1}	ΔH, kJ mol^{-1}	T_{eq}, K
$H_2O_{(l)} \leftrightarrow H_2O_{(g)}$	18.72	30078	40.66	373

$$\Delta V = V_g - V_l \approx V_g = \frac{RT}{P} \Rightarrow \frac{dP}{dT} = \frac{\Delta H}{T\Delta V} = \frac{P\Delta H}{RT^2}$$

$$\frac{dP}{P} = \frac{\Delta H}{R}\frac{dT}{T^2} \Rightarrow d\ln P = \frac{\Delta H_{vap}}{R}\frac{dT}{T^2}$$

$$\frac{d\ln P}{dT} = \frac{\Delta H_{vap}}{RT^2}$$

- If ΔH_{vap} is known as a functions of T, we can substitute easily. Otherwise, assume it independent of T over a limited small range of T.

$$\int d \ln P = \int \frac{\Delta H_{vap}}{R} \frac{dT}{T^2}$$

$$\ln P = \frac{-\Delta H_{vap}}{R} \frac{1}{T} + const$$

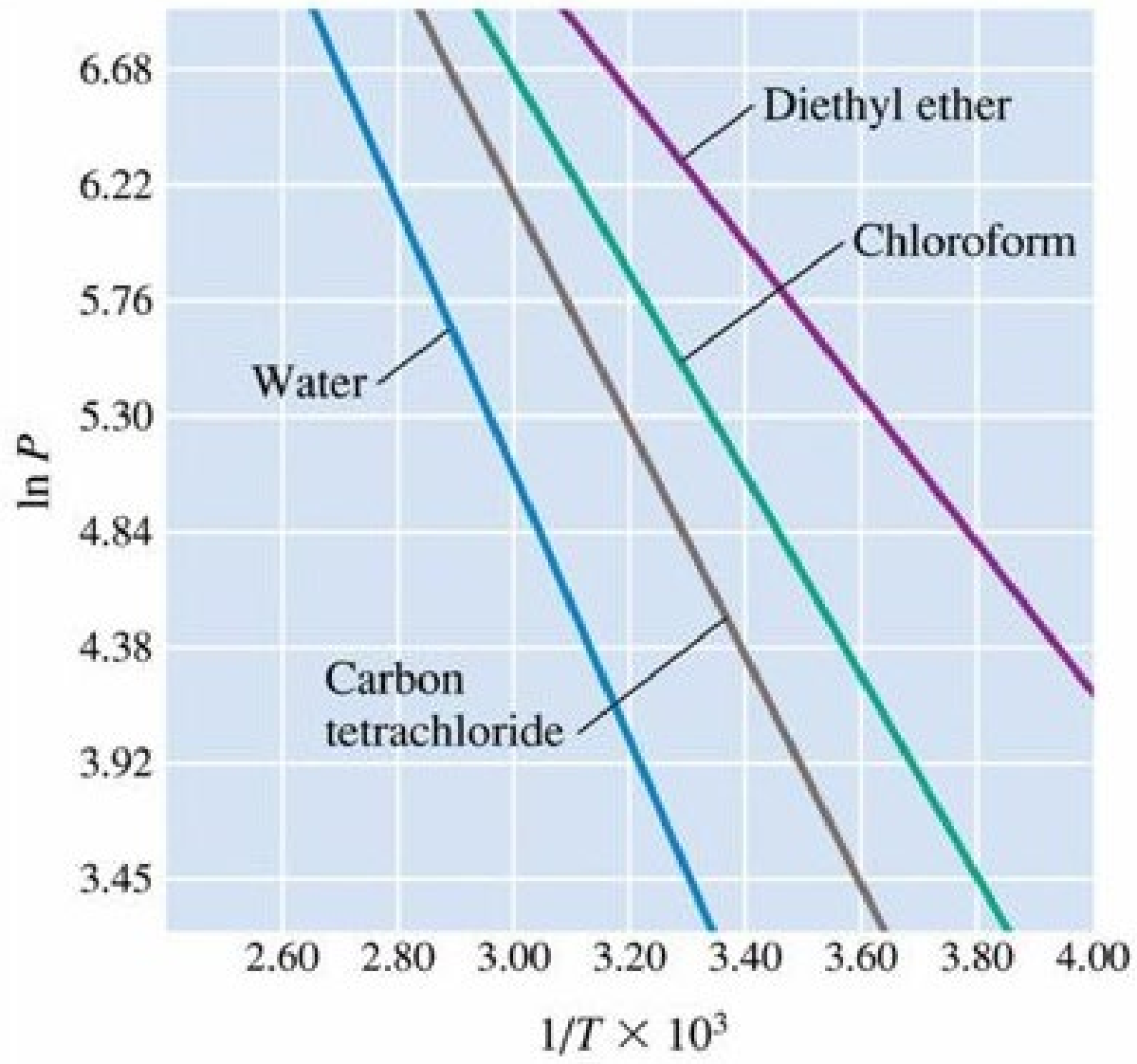
ln P vs. 1/T is linear

P increases exponentially with T

- As T ↑ , (1/T) ↓, P↑ exponentially.
- It corresponds to variation of vapor pressure of liquids with T

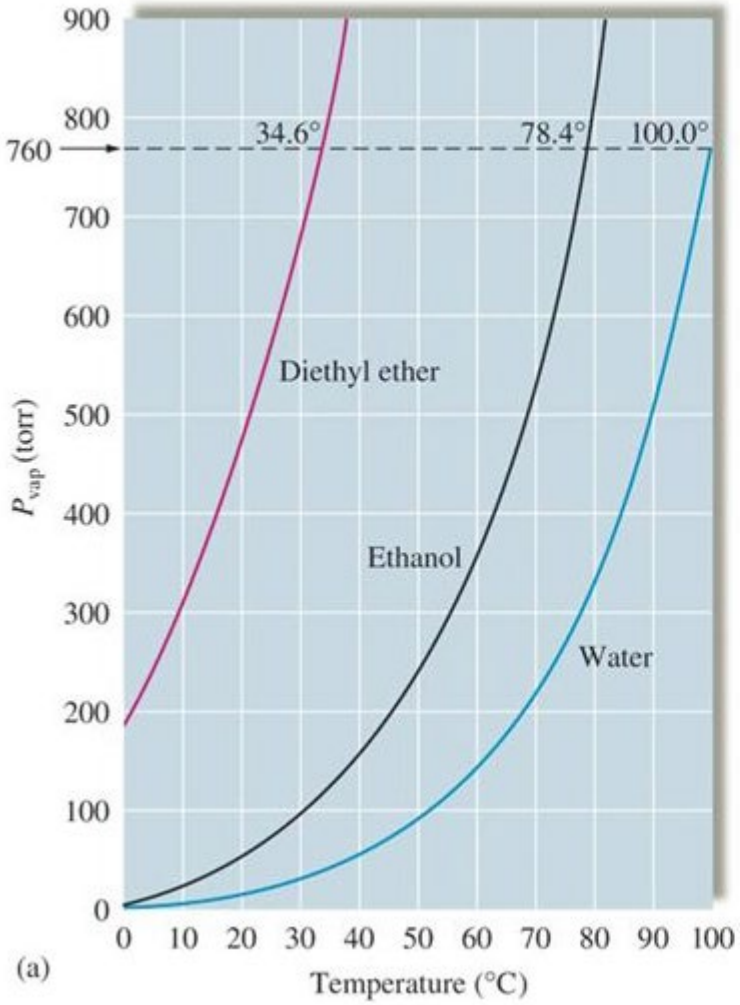
$$\ln P = \frac{-\Delta H_{vap}}{R}\frac{1}{T} + const$$

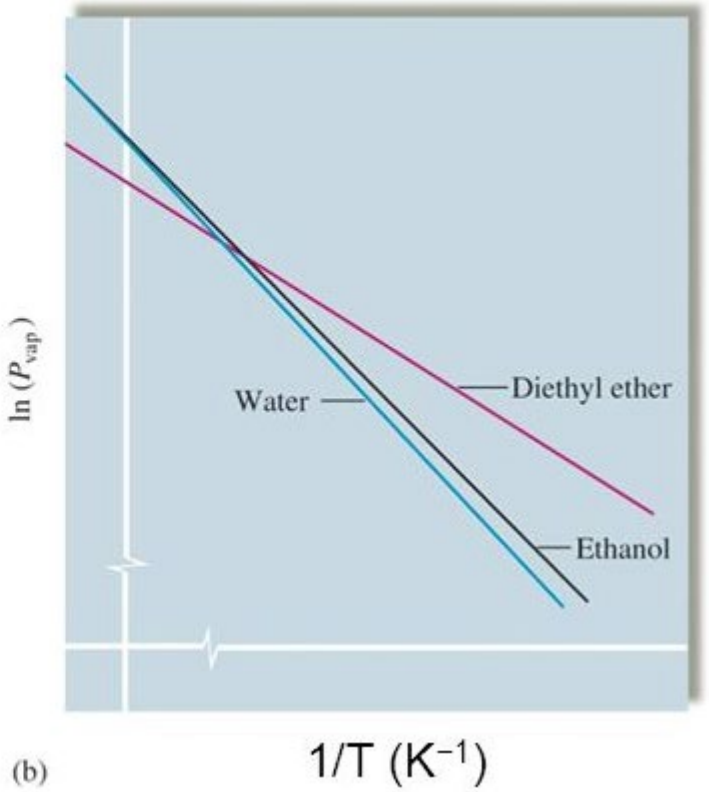
$$\ln \frac{P_2}{P_1} = \frac{\Delta H_{vap}}{R}\left(\frac{1}{T_1} - \frac{1}{T_2}\right)$$



$$\log \frac{P_2}{P_1} = \frac{\Delta H_{vap}}{2.303R}\left(\frac{1}{T_1} - \frac{1}{T_2}\right)$$

T is in K!





Exercise

- The standard vapor pressure of benzene is 90.76 and 450.79 torr at 20 and 60 ^{o}C, respectively. Calculate:
  a) ΔH_{vap} for benzene?
  b) the boiling point (bp) of benzene on a top of hill where the prevailing pressure is 622 torr?
  c) the boiling point (bp) of benzene at the bottom of a valley where the prevailing pressure is 843 torr?

Solution

$$\log \frac{P_2}{P_1} = \frac{\Delta H_{vap}}{2.303R}\left(\frac{1}{T_1} - \frac{1}{T_2}\right)$$

$$\log\frac{450.79}{90.76} = \frac{\Delta H_{vap}}{2.303(8.314\,JK^{-1}mol^{-1})}\left(\frac{1}{293} - \frac{1}{333}\right)$$

$$\Delta H_{vap} = 32509.841\,J\,mol^{-1} = 32.5\,\mathrm{k}J\,mol^{-1} = 7.8\,kcal\,mol^{-1}$$

$$\log\frac{622}{90.76} = \frac{32509.841\,J\,mol^{-1}}{2.303(8.314\,JK^{-1}mol^{-1})}\left(\frac{1}{293} - \frac{1}{T_2}\right)$$

$$T_2 = 438.7K = 165^oC$$

$$\log\frac{843}{90.76} = \frac{32509.841\,J\,mol^{-1}}{2.303(8.314\,JK^{-1}mol^{-1})}\left(\frac{1}{293} - \frac{1}{T_2}\right)$$

$$T_2 = 476.1K = 203^oC$$

Solid/Vapor (sublimation) equilibrium

- Many solids (e.g., iodine and dry ice (solid CO_2)) have measurable vapor pressure.
- The saturated vapor pressure of a certain solid is called the sublimation pressure, that can be obtained similarly as vapor pressure of liquids from Clapeyron's equation.

$$\ln P = \frac{-\Delta H_{sub}}{R}\frac{1}{T} + const$$

$$\ln \frac{P_2}{P_1} = \frac{\Delta H_{sub}}{R}\left(\frac{1}{T_1} - \frac{1}{T_2}\right)$$

$$\Delta H_{sub} = \Delta H_{fus} + \Delta H_{vap}$$

Trouton's rule

- Over narrow ranges of T, ΔH_{vap} can be considered as a linear function of T.
- Over a wide range of T, ΔH_{vap} approaches zero at the **critical T**, the temperature above which a gas cannot be **liquefied**, regardless of the pressure applied.
- If ΔH_{vap} is not known, **Trouton's rule** estimates its value.
- **Trouton's rule** states that the **entropy of vaporization** is almost the same value, ~ 85–88 J K^{-1} mol^{-1}, for various kinds of liquids at their standard (1 atm) boiling points.
- The **entropy of vaporization** is defined as the ratio between the *enthalpy of vaporization* and the boiling temperature.

$$\Delta S_{vap} = \frac{\Delta H_{vap}}{T_b} \cong 88\ J\ K^{-1}\ mol^{-1}$$

Richard's rule

- The entropy of fusion at the standard (1 atm) freezing point of a solid is constant, about 8.36 J K^{-1} mol^{-1}.

$$\Delta S_{fus} = \frac{\Delta H_{fus}}{T_f} \cong 8.36\ J\ K^{-1}\ mol^{-1}$$

ΔG / activity relations

Consider this reaction

$$aA + bB + \ldots \Leftrightarrow cC + dD + \ldots$$

- G is related to the activity (a , **effective concentration**) of each specious by:

$$G_i = G_i^0 + RT \ln a_i$$

G_i^0 is the standard free energy at unit activity.

$$\Delta G = (cG_C + dG_D + \ldots\ldots) - (aG_A + bG_B + \ldots\ldots)$$

$$\Delta G = \Delta G^0 + RT \ln \frac{a_C^c a_D^d}{a_A^a a_B^b}$$

Interpretation

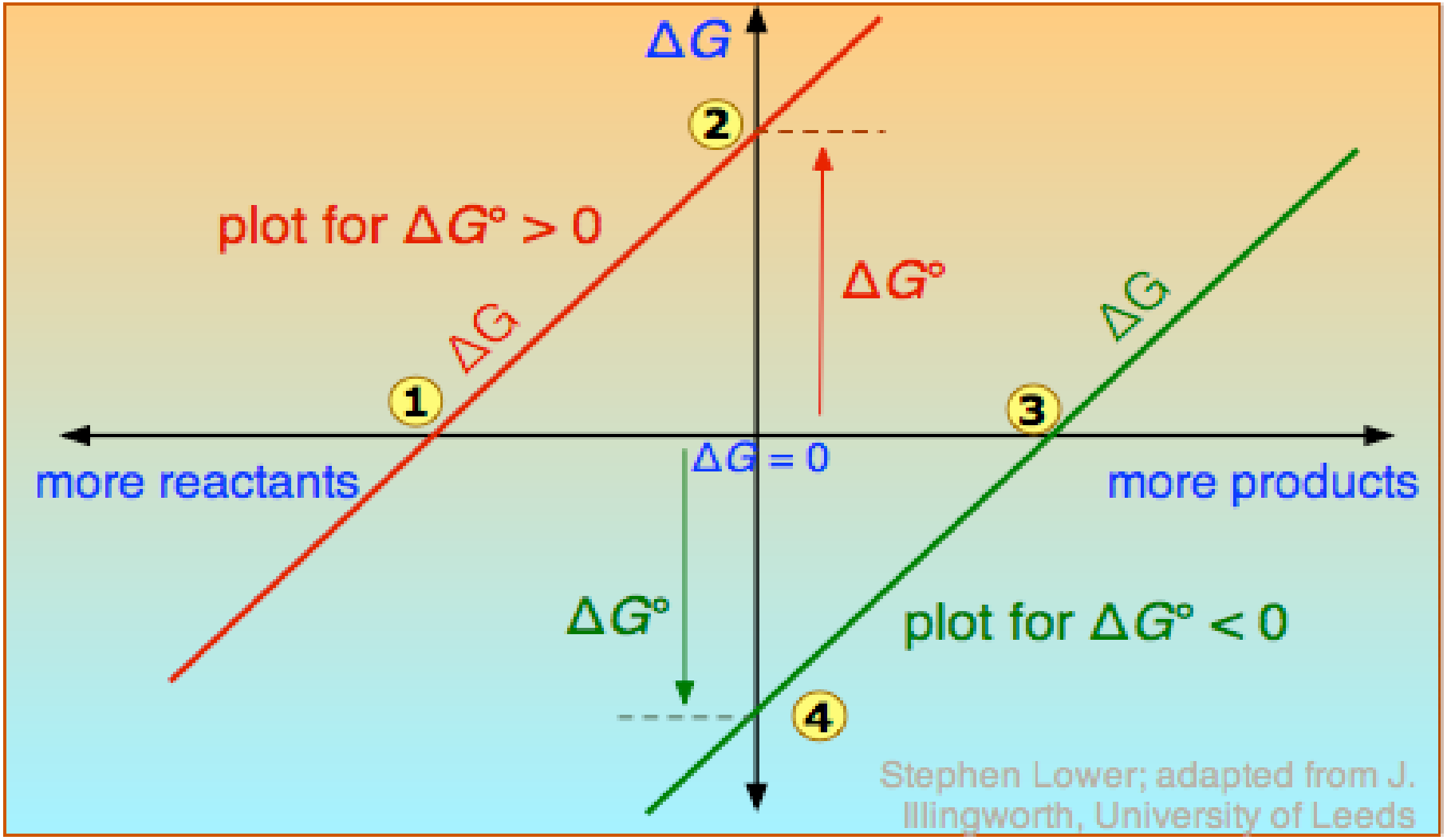
$$\Delta G = \Delta G^0 + RT \ln \frac{a_C^c a_D^d}{a_A^a a_B^b}$$

- As the reaction proceeds, the activities of products increases and those of reactants decreases; making ΔG getting closer to zero (equilibrium position).
- Notice that before reaction, ΔG was negative to drive the spontaneity.

ΔG, ΔG_f^0, ΔG^0

- $\Delta G°$: free energy change of a reaction when all components (reactants and products) are in their standard states.
- $\Delta G_f°$: free energy change of a reaction in which a substance is formed from the elements as they exist in their most stable forms at **1 atm** pressure and (usually) **298 K**.
- $\Delta G_f°$ and $\Delta H_f°$ are by definition **zero** for elements in their **standard** states with some minor exceptions for $\Delta G_f°$.
- ΔG is plotted on a vertical axis for two hypothetical reactions having opposite signs of $\Delta G°$. The horizontal axis schematically expresses the relative **concentrations** of reactants and products at any point of the process.

ΔG, ΔG^0



The origin corresponds to the composition at which half of the reactants have been converted into products

Important Remarks

- For the red line ($\Delta G^\circ > 0$) at (point 2) $\Delta G = \Delta G^\circ$.
- At point 1, $\Delta G = 0$; some products have been formed, but the composition is still dominated by reactants.
- If we begin at a composition to the left of point 1, ΔG will be negative and the composition will move to the right.
- Similarly, if we begin with a composition to the right of point 1, ΔG will be positive and the composition will move to the left.

Important Remarks

- For the green line ($\Delta G^\circ < 0$), ΔG° is shown at point 4.
- At its equilibrium point (point 3, $\Delta G = 0$), there are more products than reactants.
- If we start at a composition to the right of point 3, the composition will tend to move to the left. If the initial composition is to the left of point 3, the reaction will tend to proceed to the right.
- What would happen if ΔG° were 0? The equilibrium point of such a reaction would be at the origin, corresponding to half the reactants being converted to product.

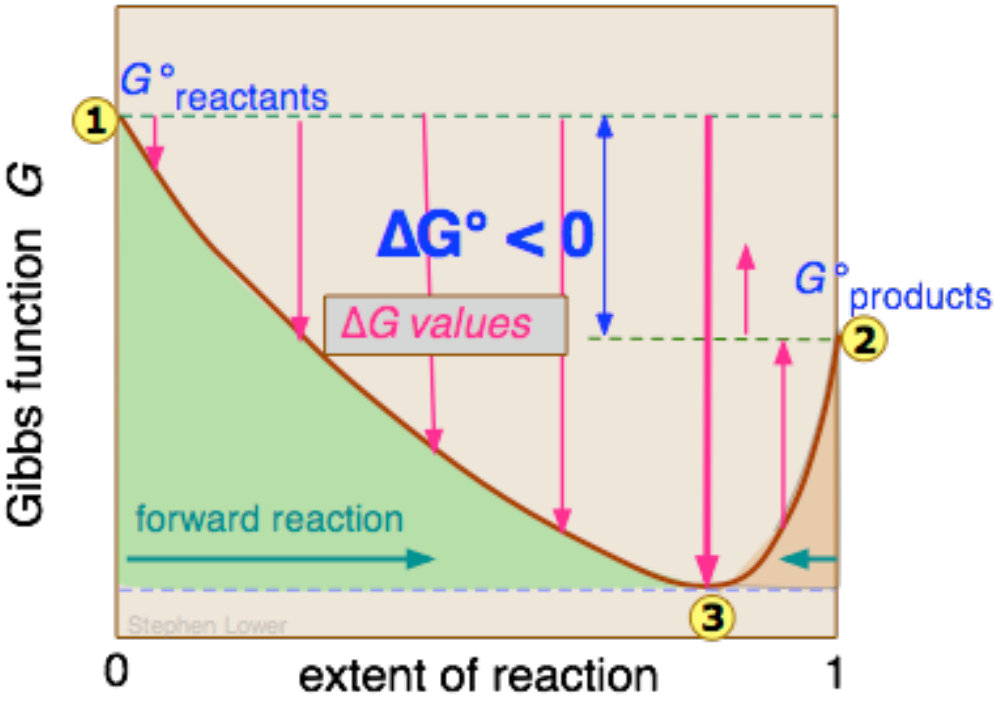
Important Principles

- A negative ΔG° does not mean that the reactants will be completely transformed into products.
- By the same token, a positive ΔG° does not mean that no products are formed at all.
- The reason for the Gibbs energy minimum at equilibrium relates to the increase in entropy when products and reactants coexist in the same phase.

$$\Delta G^0 = \Delta H^0 - T\Delta S^0$$

Spontaneous reactions

- Rx will take place spontaneously.
- This does not mean that each mole of pure A will be converted into one mole of pure B.

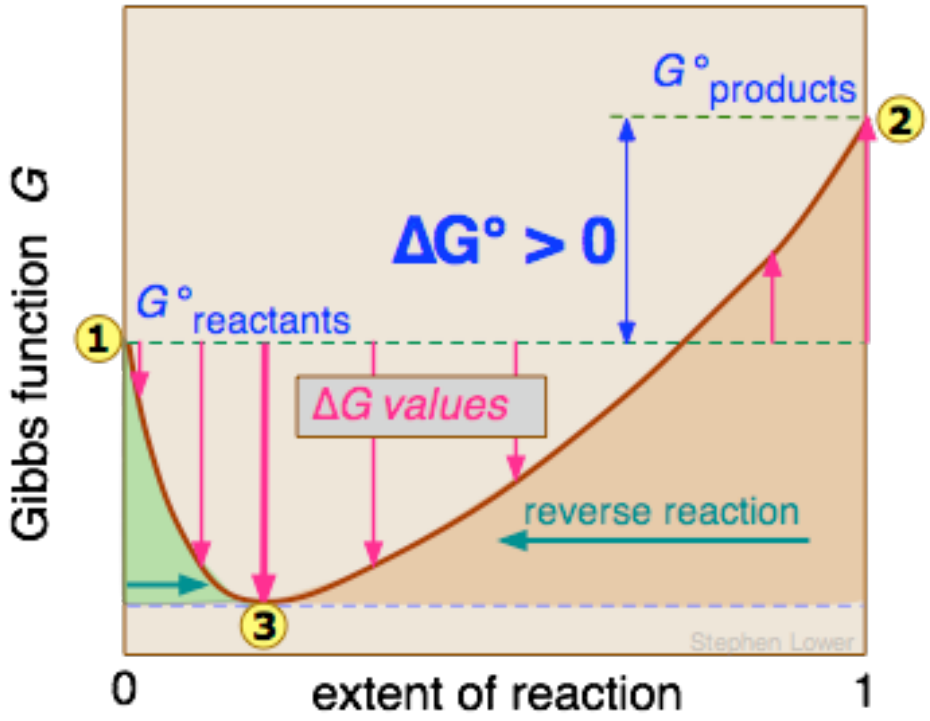


G° (reactants) > G° (reactants)

- For reactions in which products and reactants occupy a single phase (gas or solution), the meaning of "spontaneous" is that the equilibrium composition will correspond to an extent of reaction greater than **0.5** but smaller than unity.

Non-spontaneous reactions

- Rx will take place non-spontaneously.
- The equilibrium composition will correspond to an extent of reaction greater than zero but less than 0.5.



G° (reactants) < G° (reactants)

- In this case, the minimum at point 3 reflects the increase in entropy when the reactants are "contaminated" by a small quantity of products.

Important Remarks

- For $\Delta G^\circ > \pm 50$ kJ mol^{-1}, the equilibrium composition will be negligibly different from **zero** or **unity** extent-of-reaction.
- The physical meaning of ΔG is that it tells us how far the free energy of the system has changed from G° of the pure reactants (point 1).
- As the reaction proceeds to the right, the composition changes, and ΔG begins to fall. When the composition reaches point 3, ΔG reaches its **minimum** value and further reaction would cause it to **rise**.
- But because *free energy can only decrease* but never increase, this does not happen. The composition of the system remains permanently at its **equilibrium** value.

ΔG / equilibrium constants

For this reaction $aA + bB + \ldots \Leftrightarrow cC + dD + \ldots$

$$\Delta G = \Delta G^0 + RT \ln \frac{a_C^c a_D^d}{a_A^a a_B^b}$$

At equilibrium, ΔG=0

$$\Delta G^0 = -RT \ln \left(\frac{a_C^c a_D^d}{a_A^a a_B^b} \right)_{eq} = -RT \ln K_{th}$$

K_{th} is called the thermodynamic equilibrium constant

$$K_{th} = \exp\left(\frac{-\Delta G^0}{RT} \right)$$

Exercise

- Calculate the thermodynamic equilibrium constant for the following reaction:

$^1/_2\, N_2(g) + {}^3/_2\, H_2(g) \Leftrightarrow NH_3(g),\ \Delta G^0_{298.15K} = -3.98\ kcal\ mol^{-1}$

Solution

$$K_{th} = \exp\left(\frac{-(-3980\ cal\ mol^{-1})}{(1.987\ cal\ K^{-1}\ mol^{-1})(298.15\ K)}\right)$$

$$= 827.1$$

Exercise

- Find the standard Gibbs energy change for the following reaction knowing these ΔG° for CaCO (s): –1128 kJ mol^{-1} , CaO(s): –603.5 kJ mol^{-1} , CO (g): –137.2 kJ mol^{-1}?

$CaCO_3(s) \Leftrightarrow CaO(s) + CO_2(g)$, $\Delta G^0_{298.15K} = ?$

Solution

$$\Delta G^0 = [(-603.5 - 137.2) - (-1128)]$$
$$= +130.9\ kJ\ mol^{-1}$$

Process is not spontaneous under standard conditions. If conditions are changed, this process can be spontaneous.

Equilibrium /Conventional constants

$$aA + bB + \ldots \Leftrightarrow cC + dD + \ldots$$

$$K_{th} = \left(\frac{a_C^c a_D^d}{a_A^a a_B^b} \right)_{eq}$$

$$K = \frac{[C]^c [D]^d}{[A]^a [B]^b}$$

[ ] = molar concentration

$a_A = \gamma_A [A]$

γ_A: activity coefficent of A

If $\gamma_A = 1, K = K_{th}$ for ideal dilute solutions

$$K_{th} = \left(\frac{a_C^c a_D^d}{a_A^a a_B^b}\right)_{eq} = K\left(\frac{\gamma_C^c \gamma_D^d}{\gamma_A^a \gamma_B^b}\right) = KK_\gamma$$

Fugacity, *f* (Effective pressure)

- Similar to activity and activity coefficient in solids and liquids, fugacity (*f*) and fugacity coefficient γ, account for real gas corrected P.
- γ =1 for ideal gases.

$$f = \gamma P$$

$$^1/_2\, N_2(g) + {}^3/_2\, H_2(g) \Leftrightarrow NH_3(g), \qquad \Delta G^0_{298.15K} = -3.98\ kcal\ mol^{-1}$$

$$K_{th} = \frac{f_{NH_3}}{f_{N_2}^{1/2} f_{H_2}^{3/2}} = \left(\frac{P_{NH_3}}{P_{N_2}^{1/2} P_{H_2}^{3/2}}\right)\left(\frac{\gamma_{NH_3}}{\gamma_{N_2}^{1/2} \gamma_{H_2}^{3/2}}\right) = K_P K_\gamma$$

Properties of *K*

- *K* has a single **constant** value at a given temperature.
- If T changes, ΔH or better say ΔG will change, hence *K*.
- *K* is independent on the activity of reactants and products but for single *K* value at a given T, there are many **equilibrium positions** with different activities.
- If a reaction is reversed, the new *K* will equal the reciprocal of the first one.

Effect of T on K

$$\Delta G^0 = -RT \ln K$$

$$R \ln K = \frac{-\Delta G^0}{T} = \frac{-\left(\sum G^0_{products} - \sum G^0_{reac\,tants}\right)}{T}$$

Differentiate with respect to T

$$\frac{d(R \ln K)}{dT} = \frac{-d\left({}^{\Delta G^0}/_{T}\right)}{dT}$$

Previously we estimated

$$\frac{d\left({}^{\Delta G}/_{T}\right)_P}{dT} = \frac{-\Delta H}{T^2}$$

Interpretation

$$\frac{d(\ln K)}{dT} = \frac{\Delta H^0}{RT^2}$$

- This equation gives a quantification for **Le Chatelier's** principle in one of its aspects.
- For **exothermic** reactions, $\Delta H^0 < 0$, as *T* increases, K decreases. This means that increasing *T* favors the direction **to** the **reactants** and Vice versa.

$$\int d \ln K = \int \frac{\Delta H^0}{RT^2} dT$$

If ΔH^0 is independent of *T*, (otherwise integrate it)

$$\ln K = \frac{-\Delta H^0}{RT} + const$$

$$\ln\frac{K_2}{K_1} = \frac{-\Delta H^0}{R}\left(\frac{1}{T_2} - \frac{1}{T_1}\right)$$

Exercise

- Calculate the equilibrium constant at 250 K for the following reaction,

$$2NaHCO_3(s) \Leftrightarrow Na_2CO_3(s) + CO_2(g) + H_2O(g),$$
$$\Delta G^0_{298K} = 7080\ cal$$

$$\Delta H^0 = 29320 + 9.15T - 12.75 \times 10^{-3}T^2$$

Solution

$$\Delta G^0 = -RT \ln K$$

$$K = \exp\left(\frac{-\Delta G^0}{RT}\right) =$$

$$\exp\left(\frac{-7080\ cal/_{2mol}}{(1.987\ cal\ K^{-1}\ mol^{-1})(298\ K)}\right) = 394.83$$

$$\frac{d(\ln K)}{dT} = \frac{\Delta H^0}{RT^2}$$

$$\int d \ln K$$

$$= \int \frac{(29320 + 9.15T - 12.75 \times 10^{-3}T^2)}{RT^2} dT$$

$$\ln\frac{K_2}{K_1} = \frac{\left(\left(\frac{-29320}{T_2 - T_1}\right) + 9.15\ln\frac{T_2}{T_1} - 12.75\times10^{-3}(T_2 - T_1)\right)}{R}$$

$$\ln\frac{K_2}{394.83}$$

$$= \frac{\left(\left(\frac{-29320}{250 - 298}\right) + 9.15\ln\frac{250}{298} - 12.75\times10^{-3}(250 - 298)\right)}{1.987\ cal\ K^{-1}\ mol^{-1}}$$

Effect of P on K

- The extent of a reaction means the degree or percentage to which the reactants have changed to products.
- The extent of reaction depends on ***P*** (for gases) or concentration (***C***) and temperature.
- The effect of ***P*** or ***C*** on the extent of reaction depends on the nature of reactions, i.e., no of **moles** of **gaseous** reactants and products and **activity coefficients**.

Exercise

- Find the effect of pressure on the Boundouard's reaction?

Solution

$$C\,(s,gr) \quad + \quad CO_2(g) \quad \Leftrightarrow \quad 2CO(g)$$

Start with 1 mol

1-α 2α

Total moles at eq. =1+ α

Start with n mol

n(1-α) 2nα

Total moles at eq. =n(1+ α)

$$K_{th} = \left(\frac{P^2_{CO(g)}}{P_{CO_2(g)}}\right)\left(\frac{\gamma^2_{CO(g)}}{\gamma_{CO_2(g)}}\right)$$

Ideal behavior

$$K_{th} = \left(\frac{P^2_{CO(g)}}{P_{CO_2(g)}}\right)$$

Partial pressures can be calculated from **Dalton's** law

$$P_i = X_i P_t$$

Start with 1 mol CO_2

$$P_{CO_2} = X_{CO_2} P_t = \left(\frac{1-\alpha}{1+\alpha}\right) P_t$$

$$P_{CO} = X_{CO} P_t = \left(\frac{2\alpha}{1+\alpha}\right) P_t$$

Ideal behavior

$$K_{th} = \left(\frac{P^2_{CO(g)}}{P_{CO_2(g)}}\right) = \left(\frac{\left(\left(\frac{2\alpha}{1+\alpha}\right) P_t\right)^2}{\left(\frac{1-\alpha}{1+\alpha}\right) P_t}\right)$$

$$= \frac{4\alpha^2 P_t}{(1+\alpha)(1-\alpha)} = \frac{4\alpha^2 P_t}{1-\alpha^2}$$

as P_t increases, α increases in order to sustain a **constant K_{th}**

Effect of inert gases on α

- For ideal gas mixtures, where γ=1, adding inert (**non reacting**) gases to a chemical reaction does not affect *K*.
- For non-ideal gas mixtures, adding inert (**non reacting**) gases to a chemical reaction affect γ and hence α to keep K constant

For Boundouard's reaction

$$K_{th} = \left(\frac{P_{CO(g)}^2}{P_{CO_2(g)}}\right)\left(\frac{\gamma_{CO(g)}^2}{\gamma_{CO_2(g)}}\right) = \frac{4\alpha^2 P_t}{1-\alpha^2}\left(\frac{\gamma_{CO(g)}^2}{\gamma_{CO_2(g)}}\right)$$

Thermodynamics prediction

- The practical importance of the Gibbs energy is that it allows us to make predictions based on the properties (**ΔG° values**) of the reactants and products themselves, eliminating the need to experiment.

- While thermodynamics always correctly predicts whether a given process can take place (spontaneous), it is unable to tell us if it will take place at an **observable rate**.

When thermodynamics says "**no**", it means exactly ***that***.
When it says "**yes**", it means "***maybe***".

Exercise

H_2/O_2 Fuel Cells

- The reaction ½ O_2 (g) + H_2 (g) → H_2O(l) is used in fuel cells to produce an electrical current. The reaction can also be carried out by direct combustion. Thermodynamic data: molar entropies in J mol^{-1} K^{-1}: O_2(g) 205.0; H_2(g) 130.6; H_2O(l) 70.0; $\Delta H_f°$ of H_2O(l) = –285.9 kJ mol^{-1}. Use this information to find

  a) the amount of heat released when the reaction takes place by **direct combustion**;

  b) the amount of electrical work the same reaction can perform when carried out in a fuel cell at 298 K under reversible conditions;

  c) the amount of **heat released** under the same conditions.

Solution

- First, we need to find ΔH° and ΔS° for the process.
- Recalling that the standard enthalpy of formation of the elements is zero,

$$\Delta H^0 = \Delta H_f^0(\text{products}) - \Delta H_f^0(\text{reactants})$$
$$= -285.9\ kJ\ mol^{-1} - 0 = -285.9\ kJ\ mol^{-1}$$

$$\Delta S^0 = S_f^0(\text{products}) - S_f^0(\text{reactants})$$
$$= (70.0) - (\tfrac{1}{2} \times 205.0 + 130.6)$$
$$= -163\ J\ K^{-1}\ mol^{-1}$$

a) When H_2 and O_2 are combined directly, the heat released will be **ΔH° = –285.9 kJ mol^{-1}**.

b) The maximum electrical work the fuel cell can perform is given by

$$\Delta G^0 = \Delta H^0 - T\Delta S^0 =$$
$$(-285.9\ kJ\ mol^{-1}) - [(298\ K)(-163\ JK^{-1}\ mol^{-1})]$$
$$= -237.2\ kJ\ mol^{-1}$$

c) The heat released in the fuel cell reaction is the difference between the enthalpy change (the total energy available) and the reversible work that was expended

$$\Delta H^0 - \Delta G^0 = T\Delta S^0 =$$
$$[(298\ K)(-163\ JK^{-1}\ mol^{-1})] = -48800\ J\ mol^{-1}$$
$$= -48.8\ kJ\ mol^{-1} = -237.2\ kJ\ mol^{-1}$$

Note

- ✓ In this Rx 1.5 moles of gas disappear, to be replaced by 18 mL (1 mole) of water.
- ✓ The system undergoes a marked contraction in which the atmosphere performs pressure-volume work on the system.
- ✓ But this PV work is the "non-useful" work that is not included in the ΔG value.

Absolute Entropy
Third Law of Thermodynamics

The entropy of any pure perfectly crystalline solid is ZERO at the absolute zero (0 K).

Criteria

- Pure: because impure substances would have a finite entropy at 0K (ΔS of mixing the substance with impurities)
- Perfectly: because imperfections would add crystal defects that increase the disordering and S
- Solid: because liquids have a finite entropy even at 0K which equals ΔS of fusion

Absolute S of pure perfectly crystalline solids at a given T

$$\int_{S_0}^{S_T} dS = S_T - S_0 = \int_0^T \frac{C_P}{T} dT = \int_0^T C_P d \ln T$$

$$S_T = S_0 + \int_0^T C_P d \ln T$$

$$S_0 = 0 \; at \; 0 \; K$$

$$S_T = \int_0^T \frac{C_P}{T} dT$$

As C_P is always +Ve, S_T should also be +Ve

At very low temperatures,

$$C_P = aT^3$$

Debye's Law of third power

$$S_T = \int_0^T \frac{aT^3}{T} dT = \int_0^T aT^2 dT = \frac{aT^3}{3} = \frac{C_P}{3}$$

The absolute entropy of a certain pure crystalline solid at low temperature is one third of its heat capacity

End of Class

Your Duaa