UNIT 3

FREE ENERGY IN CHEMICAL EQUILIBRIA AND THE SOULTIONS

THE SECOND LAW: THE ENTROPY OF THE UNIVERSE INCREASES

FREE ENERGY AND CHEMICAL EQUILIBRIA

FREE ENERGY AND CHEMICAL EQUILIBRIA

GIBBS FREE ENERGY

- **A new state function: Entropy**
- **Temperature Dependence of Gibbs Free Energy**
- **Pressure Dependence of Gibbs Free Energy**

1. **PARTIAL MOLAR GIBBS FREE ENERGY OR CHEMICAL POTENTIAL**
2. **CHEMICAL POTENTIAL IN REACTIONS OF GASES (IDEAL AND NON IDEAL SYSTEMS)**
3. **EQUILIBRIUM CONSTANT AND STANDARD GIBBS FREE ENERGIES OF REACTANTS AND PRODUCTS,**
4. **FREE ENERGY IN RELATION TO GALVANIC CELLS,**
5. **FREE ENERGY IN RELATION TO REDOX REACTIONS.**

GIBBS FREE ENERGY (*G*)

Chemical rxn in a closed system:

Amount of reactants decrease, amount of products increase (until equilibrium). At equilibrium, the reactants and products can interconvert but the composition of the system remains unchanged.

In most of the chemical reactions carried out in the laboratory:

- **Usually there are large changes in energy (*E*) and enthalpy (*H*)**
- **We are interested in whether a reaction WILL occur at constant *T* and *P***

The system is free to exchange heat with the surroundings to remain at room temperature and it can expand or contract in volume to remain at atmospheric pressure

The change in G of a system undergoing a spontaneous (تلقائي) rxn must be negative. If ΔG is positive, only the reverse rxn can spontaneously occur.
If ΔG is zero, the system is at equilibrium.

For open system:

G is dependent on the temperature, pressure, and the amounts of materials that make up the system. When a very small amount of a substance is added to the system at constant T and P without changing any of the other composition variables, the change in G per mole of the substance added is termed the Partial molar Gibbs Free energy of the added substance.

So that, ΔG of the rxn at constant T&P is determined by the partial molar Gibbs free energies of the reactants and products. Thus, the partial molar Gibbs free energy of a substance determines its chemical potential in a rxn at constant T&P.

A new variable is needed to describe the spontaneity of a chemical reaction – it is thus described in the form of a new thermodynamic variable, i.e., the Gibbs free energy, *G that is* defined as a combination of enthalpy (H), temperature (T) and entropy, S

$$G = H - TS$$

Gibbs free energy has the same unit as enthalpy (H) and energy (E)
Its definition was chosen because it can thus characterize whether a process will occur spontaneously at constant T and P

The chemical potential (μ) of a substance measured relative to the standard chemical potential (μ^0) of the same substance under a chosen set of conditions, its standard state. By choosing appropriate standard state, μ-μ^0 of any substance can be expressed as a function of more familiar variables:

Partial pressure for gases;
Concentration in Molarity for solutes;

- For a component of a mixture of ideal gases, μ-μ^0 can be readily calculated from its partial pressure.
- For a solute of an ideal solution, from its concentration.
- For pure liquid and solids, the difference of μ-μ^0 is closed to Zero at a moderate pressure.
- For real gases and solutions, the chemical potential of a substance is influenced by complex molecular interactions, but μ-μ^0 can be experimentally determined.

Thermodynamics tells us that in an equilibrium mixture at constant T&P a simple relation exists between the chemical potential of the reactants and products because ΔG is zero at equilibrium. so that, the composition of an equilibrium rxn is specified by the standard chemical potential (μ^0) of the participants of the rxn.

A new state function: Entropy

The second law of thermodynamics: Entropy is not conserved. Entropy is an extensive variable of state; ΔS depends on ONLY the initial and final states of the system. The dimensions of entropy are Energy/Temperature; we will use units of $J\ K^{-1}$. The unit for entropy in centimeter-gram-second (cgs) system is ($cal\ deg^{-1}$)

4.184 $J\ K^{-1}$ = 1 $cal\ deg^{-1}$, A calorie per degree is also called and entropy unit.

Third law of thermodynamics states that the entropy of any pure, perfect crystal is zero at 0 K (absolute zero).

The sum of entropy changes of the system and surroundings is always positive. Even zero values can be approached only as a limit, and negative values are never found. If there is a decrease in entropy in a system, there must be an equal or larger increase in entropy in the surroundings.

ΔS (system) + ΔS (surroundings) ≥ 0

ΔS^0 (25°C, 1 atm)= ΔS^0 (products) - **ΔS^0** (reactants)

For the isolated system, since there is no energy or materials exchange between such a system and surroundings, there is no change in surroundings. Therefore,

ΔS (isolated system) ≥ 0

To show that the change in Gibbs free energy is related to the spontaneity of a process:

$G = H - TS$ --- definition of G

- **Small change dG in the Gibbs free energy is related to changes in other thermodynamic parameters**

$dG = dH - TdS - SdT$

- Since $H = E + PV$

$dG = dE + PdV + VdP - TdS - SdT$

Since $dE = dq_{rev} + dw_{rev}$ ----- **first law, reversible path**

$\therefore \quad dG = dq_{rev} + dw_{rev} + PdV + VdP - TdS - SdT$

$= TdS + dw_{rev} + PdV + VdP - TdS - SdT$ ---- $dq_{rev} = TdS$ (definition of S)

$= dw_{rev} + PdV + VdP - SdT$

- $dw_{rev} = -PdV + dw^*_{rev}$ ---- dw_{rev} as the sum of two types of work, the Pressure-Volume work ($-PdV$), owing to a change dV in the volume system and all other forms of work, (dw^*_{rev})

$dG = VdP - SdT + dw^*_{rev}$

- At constant T and P, $dP = dT = 0$

$dG = dw^*_{rev}$

- And upon integration: $\Delta G = w^*_{rev}$ or $-\Delta G = -w^*_{rev}$

This states that ΔG of a process at constant P and T is equal to w^*_{rev} or that $-\Delta G = -w^*_{rev}$

- In any process, such as in a chemical reaction, a system must do the necessary PV work associated with the change in system from its initial state to its final state.
- Therefore, the useful work that can be obtained from a reversible process at constant T and P is $-w^*_{rev}$, the non-expansion work (or the part of work that does not result in change of volume).
- Example: If a reversible process does electrical work other than PV work, then $-w^*_{rev}$ is the electrical work that the process is capable of doing.
- If a system undergoes a spontaneous process, it is capable of performing useful work, e,g, water flowing down a fall can be utilized to generate electricity or heat flowing from hot to a cold reservoir can be utilized to power a heat engine). On the other hand non-spontaneous process, such as water flowing uphill or heat flowing from cold to hot, the surroundings must do work on the system.

$-w^*rev$, the non-expansion work, a system can do on the surrounding, is positive for a spontaneous process or $-\Delta G = -w^*rev > 0$ for a spontaneous process at constant T and P $\Delta G < 0$ --spontaneous process at constant T and P.

If a process does not occur spontaneously, w^*_{rev} must be positive for it to occur:

$\Delta G > 0$ --non-spontaneous process at constant T and P.

If a system is already at equilibrium, it cannot perform useful work thus $w^*_{rev} = 0$ and $\Delta G = 0$ ---- system at equilibrium at constant T and P.

To calculate Gibbs Free Energy:

- **The Gibbs Free Energy change for a reaction at constant T can be obtained from the enthalpy (H) and entropy (S) changes.**

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

- **Tables A.(5-7) in the appendix gives values $H^o = \Delta H^o_f$ and S^o for various substances at 25°C and 1 atm. These values can be used to calculate ΔH^o and ΔS^o and hence ΔG^o, at 25°C and 1 atm.**
- **ΔG^o_f, the standard free energy of formation of various substances are also given.**
- ***The molar* standard free energy of formation is defined as the free energy of formation of 1 mol of any compound at 1 atm pressure from its elements in their standard states at 1 atm.**

Example

Calculate the Gibbs free energy for the following reaction at 25°C and 1 atm. Will the reaction occur spontaneously?

$$H_2O(l) \longrightarrow H_2(g) + \frac{1}{2}O_2(g)$$

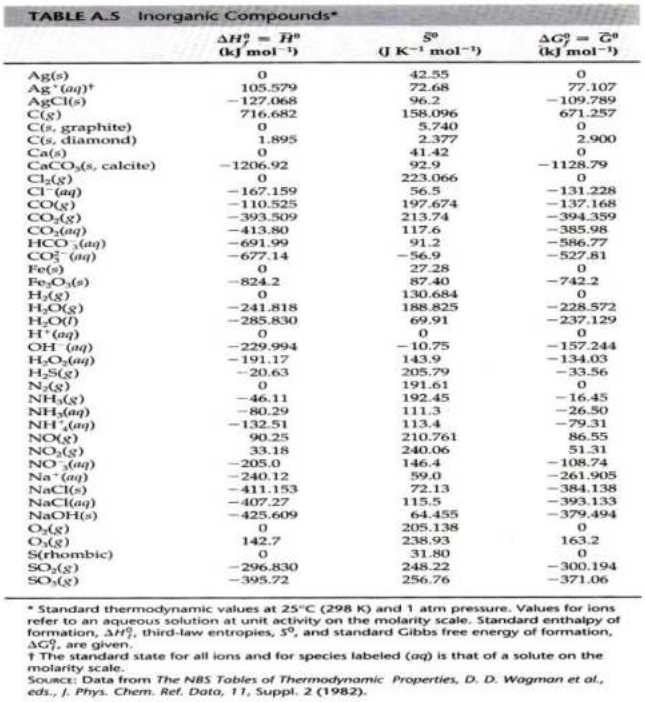


TABLE A.5 Inorganic Compounds*

	$\Delta H_f^0 = \bar{H}^0$ (kJ mol^{-1})	$\bar{S}^0$ (J K^{-1} mol^{-1})	$\Delta G_f^0 = \bar{G}^0$ (kJ mol^{-1})
Ag(*s*)	0	42.55	0
Ag^+(*aq*)†	105.579	72.68	77.107
AgCl(*s*)	−127.068	96.2	−109.789
C(*g*)	716.682	158.096	671.257
C(*s*, graphite)	0	5.740	0
C(*s*, diamond)	1.895	2.377	2.900
Ca(*s*)	0	41.42	0
$CaCO_3$(*s*, calcite)	−1206.92	92.9	−1128.79
Cl_2(*g*)	0	223.066	0
Cl^-(*aq*)	−167.159	56.5	−131.228
CO(*g*)	−110.525	197.674	−137.168
CO_2(*g*)	−393.509	213.74	−394.359
CO_2(*aq*)	−413.80	117.6	−385.98
HCO^-_3(*aq*)	−691.99	91.2	−586.77
CO_3^{2-}(*aq*)	−677.14	−56.9	−527.81
Fe(*s*)	0	27.28	0
Fe_2O_3(*s*)	−824.2	87.40	−742.2
H_2(*g*)	0	130.684	0
H_2O(*g*)	−241.818	188.825	−228.572
H_2O(*l*)	−285.830	69.91	−237.129
H^+(*aq*)	0	0	0
OH^-(*aq*)	−229.994	−10.75	−157.244
H_2O_2(*aq*)	−191.17	143.9	−134.03
H_2S(*g*)	−20.63	205.79	−33.56
N_2(*g*)	0	191.61	0
NH_3(*g*)	−46.11	192.45	−16.45
NH_3(*aq*)	−80.29	111.3	−26.50
NH^+_4(*aq*)	−132.51	113.4	−79.31
NO(*g*)	90.25	210.761	86.55
NO_2(*g*)	33.18	240.06	51.31
NO^-_3(*aq*)	−205.0	146.4	−108.74
Na^+(*aq*)	−240.12	59.0	−261.905
NaCl(*s*)	−411.153	72.13	−384.138
NaCl(*aq*)	−407.27	115.5	−393.133
NaOH(*s*)	−425.609	64.455	−379.494
O_2(*g*)	0	205.138	0
O_3(*g*)	142.7	238.93	163.2
S(rhombic)	0	31.80	0
SO_2(*g*)	−296.830	248.22	−300.194
SO_3(*g*)	−395.72	256.76	−371.06

* Standard thermodynamic values at 25°C (298 K) and 1 atm pressure. Values for ions refer to an aqueous solution at unit activity on the molarity scale. Standard enthalpy of formation, ΔH_f^0, third-law entropies, S^0, and standard Gibbs free energy of formation, ΔG_f^0, are given.

† The standard state for all ions and for species labeled (*aq*) is that of a solute on the molarity scale.

Source: Data from *The NBS Tables of Thermodynamic Properties*, D. D. Wagman *et al.*, eds., *J. Phys. Chem. Ref. Data*, *11*, Suppl. 2 (1982).

Temperature Dependence of Gibbs Free Energy

- ΔG of reactions of at 25°C and 1 atm can be calculated from the H and S data tabulated in **Tables A.(5-7)**

- **How do we find the ΔG at a different temperature T?**

$$\Delta G(T_2) - \Delta G(T_1) = -\Delta S(T_2 - T_1)$$

Assume ΔS is independent of T *(equation1)*

$$\frac{\Delta G(T_2)}{T_2} - \frac{\Delta G(T_1)}{T_1} = \Delta H\left[\frac{1}{T_2} - \frac{1}{T_1}\right]$$

Assume ΔH is independent of T *(equation2)*

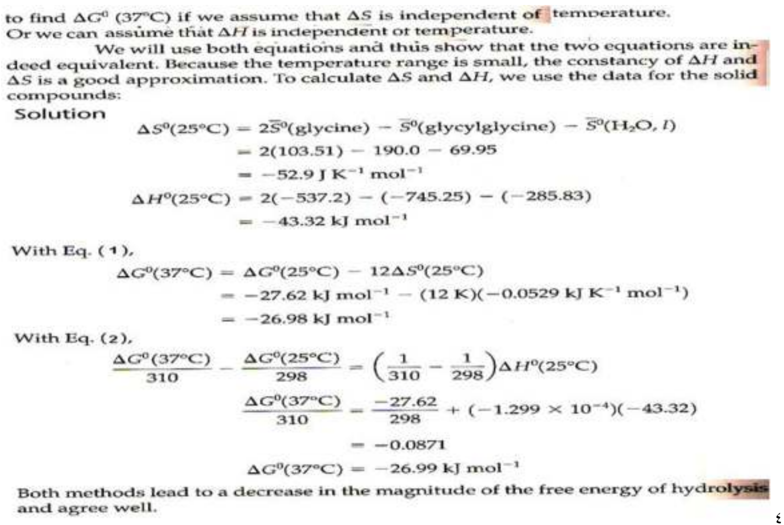
Example: **What is the free energy of hydrolysis of glycylglycine (reaction below) at 37°C and 1 atm. When:**

$$^{+}H_3NCH_2CONHCH_2COO^{-}(aq) + H_2O(l) \longrightarrow 2\,^{+}H_3NCH_2COO^{-}(aq)$$

glycylglycine glycine

ΔS is independent of T *(equation1)* **ΔH is independent of T *(equation2)***

Solution:



to find ΔG^0 (37°C) if we assume that ΔS is independent of temperature. Or we can assume that ΔH is independent of temperature.

We will use both equations and thus show that the two equations are indeed equivalent. Because the temperature range is small, the constancy of ΔH and ΔS is a good approximation. To calculate ΔS and ΔH, we use the data for the solid compounds:

Solution

$$\begin{aligned}\Delta S^0(25°C) &= 2\overline{S}^0(\text{glycine}) - \overline{S}^0(\text{glycylglycine}) - \overline{S}^0(H_2O, l)\\ &= 2(103.51) - 190.0 - 69.95\\ &= -52.9\ \text{J K}^{-1}\ \text{mol}^{-1}\\ \Delta H^0(25°C) &= 2(-537.2) - (-745.25) - (-285.83)\\ &= -43.32\ \text{kJ mol}^{-1}\end{aligned}$$

With Eq. (1),

$$\begin{aligned}\Delta G^0(37°C) &= \Delta G^0(25°C) - 12\Delta S^0(25°C)\\ &= -27.62\ \text{kJ mol}^{-1} - (12\ \text{K})(-0.0529\ \text{kJ K}^{-1}\ \text{mol}^{-1})\\ &= -26.98\ \text{kJ mol}^{-1}\end{aligned}$$

With Eq. (2),

$$\frac{\Delta G^0(37°C)}{310} - \frac{\Delta G^0(25°C)}{298} = \left(\frac{1}{310} - \frac{1}{298}\right)\Delta H^0(25°C)$$

$$\begin{aligned}\frac{\Delta G^0(37°C)}{310} &= \frac{-27.62}{298} + (-1.299 \times 10^{-4})(-43.32)\\ &= -0.0871\end{aligned}$$

$$\Delta G^0(37°C) = -26.99\ \text{kJ mol}^{-1}$$

Both methods lead to a decrease in the magnitude of the free energy of hydrolysis and agree well.

Pressure Dependence of Gibbs Free Energy

- In the previous slides it was shown that ΔG of reactions at 25°C and at other temperature can be calculated from the H and S data tabulated by using appropriate equations. *All the tabulated values of ΔG^o are defined at 1 atm*
- **How do we find ΔG^o at a different pressure?**
- To calculate free energy at some other pressure we must know its dependence on pressure

$$\begin{aligned} dG &= V\,dP - S\,dT \\ &= V\,dP \qquad \text{(at constant temperature)} \end{aligned}$$

$$G(P_2) - G(P_1) = \int_{P_1}^{P_2} V\,dP$$

$$G(P_2) - G(P_1) \cong V(P_2 - P_1)$$ **--- For solid or liquid, *V* approx. constant**

$$G(P_2) - G(P_1) = \int_{P_1}^{P_2} \frac{nRT}{P}\,dP = nRT \ln \frac{P_2}{P_1}$$ **--- For gases**

$$\Delta G(P_2) - \Delta G(P_1) = \Delta V(P_2 - P_1)$$ **--- If all products and reactants are solids and liquids**

$$\Delta G(P_2) - \Delta G(P_1) = \Delta n\,RT \ln \frac{P_2}{P_1}$$ **--- If gas is involve, ignore solids and liquids**

CHEMICAL POTENTIAL IN REACTIONS OF GASES

Ideal gas system

- **Gases ,if the pressure is not too high, behaves as ideal gases.**
- **To find the relationship between chemical potential μ and P, at constant T *the* change in Gibbs free energy G when pressure of the gas changes from pressure P_1 to P_2 is:**

$$G(P_2) - G(P_1) = nRT \ln\left(\frac{P_2}{P_1}\right) \qquad (T = \text{constant})$$

- **P_1 is chosen as 1 atm (standard state denoted by $G(P_1 = 1\text{ atm})$ as G^o:**

$$G - G^0 = nRT \ln\left(\frac{P}{1\text{ atm}}\right)$$

- **Dividing both sides by *n*, we obtain:**

$$\mu = \mu^0 + RT \ln\left(\frac{P}{1\text{ atm}}\right)$$

where μ is the chemical potential of the ideal gas and μ^o is its chemical potential at the standard state of 1 atm

- **For ideal gas A in a mixture of ideal gases, the pressure of A is the partial pressure P_A**

$$\mu_A = \mu_A^0 + RT \ln\left(\frac{P_A}{1\text{ atm}}\right)$$

EQUILIBRIUM CONSTANT AND STANDARD GIBBS FREE ENERGIES OF REACTANTS AND PRODUCTS

- **Equilibrium constant of a chemical reaction is related to the thermodynamic properties of the reactants and products in the reaction**
- **Consider this reaction (involve gases only):**

$N_2 + 3H_2 \longrightarrow 2NH_3$ **(Haber process of nitrogen fixation to form ammonia)**

- **The Gibbs free energy change for the reaction is:**

$$\begin{aligned}\Delta G &= 2\mu_{NH_3} - \mu_{N_2} - 3\mu_{H_2}\\ &= 2\left[\mu^0_{NH_3} + RT\ln\left(\frac{P_{NH_3}}{1\text{ atm}}\right)\right] - \left[\mu^0_{N_2} + RT\ln\left(\frac{P_{N_2}}{1\text{ atm}}\right)\right]\\ &\quad - 3\left[\mu^0_{H_2} + RT\ln\left(\frac{P_{H_2}}{1\text{ atm}}\right)\right]\end{aligned}$$

- **“1 atm” is omitted, and partial pressure term become unitless**

$$\begin{aligned}\Delta G &= (2\mu^0_{NH_3} - \mu^0_{N_2} - 3\mu^0_{H_2}) + RT[2\ln P_{NH_3} - \ln P_{N_2} - 3\ln P_{H_2}]\\ &= \Delta G^0 + RT\left[\ln\left(\frac{P^2_{NH_3}}{P_{N_2}P^3_{H_2}}\right)\right]\end{aligned}$$

- **Where ΔG^o is equal to $(2\mu^o_{NH3} - \mu^o_{N2} - 3\mu^o_{H2})$ ---- the standard Gibbs free energy per mole of the reaction at T when all participants of the reaction are in their standard states (Pressure is 1 atm).**

- **When the system reaches EQUILIBRIUM (at constant T and P), $\Delta G = 0$:**
- **Therefore** $$0 = \Delta G^0 + RT\ln\frac{(P^{eq}_{NH_3})^2}{(P^{eq}_{N_2})(P^{eq}_{H_2})^3}$$ **---- Superscript ‘eq’ specifies the quantity at equilibrium**
- **Or** $$\Delta G^0 = -RT\ln\frac{(P^{eq}_{NH_3})^2}{(P^{eq}_{N_2})(P^{eq}_{H_2})^3}$$

- **ΔG^o for a particular reaction is a constant at any chosen T because the states of the reactants and products are all specified to be their standard states and the Gibbs free energy is a state function.**
- **Therefore at constant temperature and total pressure, the ratio $(P^{eq}_{NH3})^2$ / $(P^{eq}_{N2})(P^{eq}_{H2})$ must be a constant, which is denoted by K:**

$$\frac{(P^{eq}_{NH_3})^2}{(P^{eq}_{N_2})(P^{eq}_{H_2})^3} = K$$

- **Where K is the equilibrium constant of the reaction and directly related to ΔG^o by:**

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

- **At constant T and P, the K is related to ΔG^o and not ΔG (which is 0 at equilibrium)**

- **Thus, any reaction involving only gases that do not deviate too much from ideal gas behavior in terms of their free energy dependence on partial pressure can use the relationship stated in the previous slide**
- **Therefore to generalize, for a reaction of ideal gases at temperature *T*:**

$$aA + bB \longrightarrow cC + dD$$

$$\Delta G_T = \Delta G_T^0 + RT \ln Q$$

$$Q = \frac{(P_C)^c (P_D)^d}{(P_A)^a (P_B)^b}$$

- **Where P_A, P_B, P_C and P_D are the partial pressure of A, B, C and D, respectively, each divided by 1 atm**
- ***Q* is the ratio of the numerical values of partial pressures (in atm) of reactants and products, each raised to the power of its coefficients in the chemical reaction**
- ***Q* is large if product pressures are large or reactant pressures are small, a large *Q* means <u>positive or bad (unfavorable)</u> contribution to the free energy**
- ***Q* is small if product pressures are small or reactant pressures are large, a small *Q* means a <u>negative or good (favorable)</u> contribution to the free energy**

- **For any reaction:**

$$aA + bB \longrightarrow cC + dD$$

- **At equilibrium**

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

- **With**

$$K = \frac{(P_C^{eq})^c (P_D^{eq})^d}{(P_A^{eq})^a (P_B^{eq})^b}$$

---- Where P^{eq}_A, P^{eq}_B, P^{eq}_C and P^{eq}_D are partial pressures, each divided by 1 atm at equilibrium

- **Since $\Delta G_T = \Delta G_T^o + RT \ln Q$**
- **Therefore:**

$$\Delta G_T = -RT \ln K + RT \ln Q$$
$$= RT \ln \frac{Q}{K}$$

- **The equation above relate free energy change for a reaction to experimentally measurable quantities.**
- **ΔG^o values of reaction can be calculated from experimental measurable quantities and as a result, equilibrium constant, *K*, can be determined and this is vice versa.**

Example: What is the Gibbs free-energy change, relative to that under standard conditions, of forming 1 mol of NH_3 at 298 K if (a) 10.0 atm of N_2 and 10.0 atm of H_2 are reacted to give 0.0100 atm of NH_3 and (b) 0.0100 atm of N_2 and 0.0100 atm of H_2 are reacted to give 10.0 atm of NH_3? For part (b), NH_3 could be introduced with the reactants to give a high enough product partial pressure. The reaction is

$$N_2(g) + 3H_2(g) \longrightarrow 2NH_3(g) \qquad \Delta G^0_{298} = -32.90\ \text{kJ}$$

Conclusion :

To calculate the equilibrium constant *K* of a reaction:

(Note: Find ΔG^o and then relate it to K)

Calculate the equilibrium constant at 25°C for the decarboxylation of liquid pyruvic acid to form gaseous acetaldehyde and CO_2.

- **The solvent standard state for a component of a solution defines the pure component as the standard state**
- **For a liquid solution, the standard state for the solvent is defined as the pure liquid, e.g., for dilute aqueous solution $X_{H2O} = 1$**
- **Mole fraction (X): is the no. of moles of A divided by total no. of moles of all components present in the solution. $X_A = n_A / n_T$**

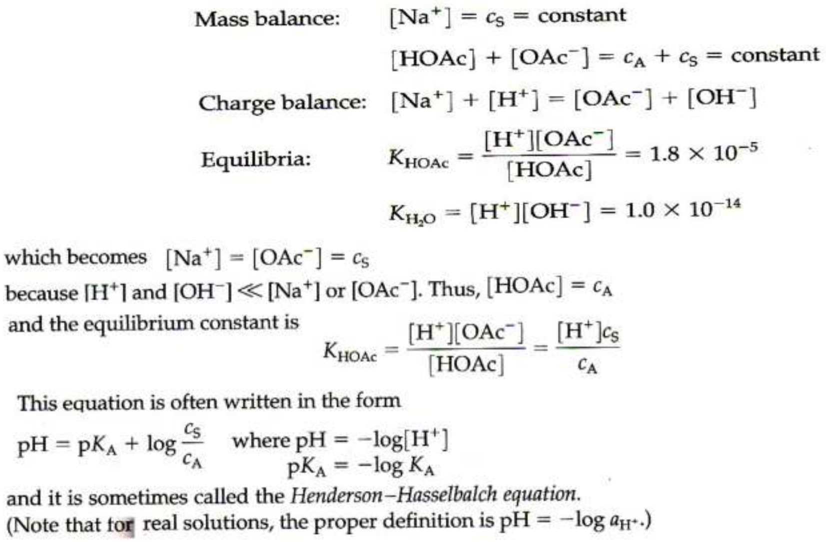
where: X_{solv} is the mole fraction of Solvent = n_{solv}/n_T, T = total no. of moles of all component, Thus X_{solv} is the mole fraction of solvent,

From Equilibrium Constant, *K*, Equilibrium concentrations can be calculated

In any reaction: Mass is conserved – the total mass of each elements is not altered by any chemical reaction. Charge is conserved – the number of positive charges must always equal the number of negative charges in the mixture.

Example: A solution is prepared by adding C_A mol of acetic acid and C_S mol of sodium acetate to water to form 1L of aqueous solution at 298K

This solution will contain HOAc, OAc^-, Na^+, H^+ and OH^-, and this is in addition to the solvent water. There are five species and these are described by five equations:



Mass balance: $[Na^+] = c_S = \text{constant}$

$$[HOAc] + [OAc^-] = c_A + c_S = \text{constant}$$

Charge balance: $[Na^+] + [H^+] = [OAc^-] + [OH^-]$

Equilibria: $$K_{HOAc} = \frac{[H^+][OAc^-]}{[HOAc]} = 1.8 \times 10^{-5}$$

$$K_{H_2O} = [H^+][OH^-] = 1.0 \times 10^{-14}$$

which becomes $[Na^+] = [OAc^-] = c_S$

because $[H^+]$ and $[OH^-] \ll [Na^+]$ or $[OAc^-]$. Thus, $[HOAc] = c_A$

and the equilibrium constant is

$$K_{HOAc} = \frac{[H^+][OAc^-]}{[HOAc]} = \frac{[H^+]c_S}{c_A}$$

This equation is often written in the form

$$pH = pK_A + \log\frac{c_S}{c_A} \quad \text{where } pH = -\log[H^+], \quad pK_A = -\log K_A$$

and it is sometimes called the *Henderson–Hasselbalch equation.* (Note that for real solutions, the proper definition is $pH = -\log a_{H^+}$.)

Example: What are the concentrations of all species in pure water?

Solution:

Charge balance: $[H^+] = [OH^-]$

Equilibrium: $[H^+][OH^-] = 1.0 \times 10^{-14}$

Therefore, $[H^+]^2 = 1.0 \times 10^{-14}$

$$[H^+] = 1.0 \times 10^{-7}$$

$$[OH^-] = 1.0 \times 10^{-7}$$

In a buffer involving acetic acid (A) and sodium acetate (S):

Definition:

A solution containing either a weak acid and its salt or a weak base and its salt, which is resistant to changes in pH.

c_S = concentration of salt, c_A = concentration of acid

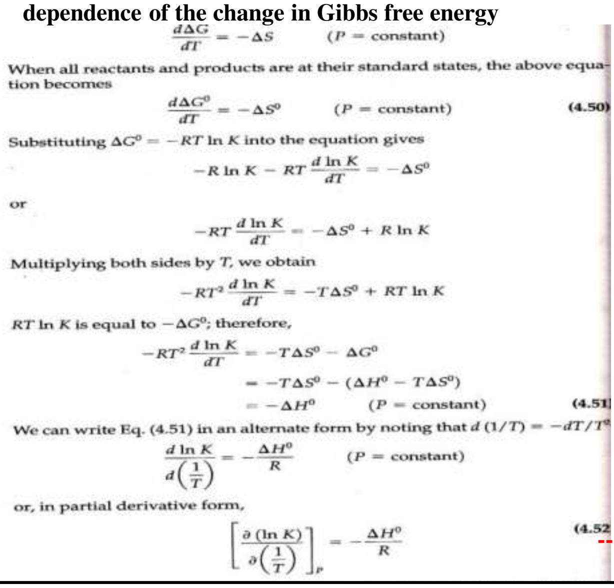
For buffer solutions; the computations are usually simpler because both the acid and the salt (both the base and its corresponding salt) are present at an appreciable concentration. Furthermore, these concentrations are large compared with either [H+] or [OH-]. In the case of buffer involving acetic acid and sodium acetate.

Example: What amount of solid sodium acetate is needed to prepare a buffer at pH 5.00 from 1 L of 0.10 *M* acetic acid?

Solution:

Temperature Dependence of the Equilibrium constant

- **If we know the equilibrium constant of a chemical reaction at one temperature, we can find the equilibrium constant at another temperature**
- **The T dependence of an equilibrium constant can be readily derived from the T dependence of the change in Gibbs free energy**



$$\frac{d\Delta G}{dT} = -\Delta S \qquad (P = \text{constant})$$

When all reactants and products are at their standard states, the above equation becomes

$$\frac{d\Delta G^0}{dT} = -\Delta S^0 \qquad (P = \text{constant}) \qquad (4.50)$$

Substituting $\Delta G^0 = -RT \ln K$ into the equation gives

$$-R \ln K - RT\frac{d \ln K}{dT} = -\Delta S^0$$

or

$$-RT\frac{d \ln K}{dT} = -\Delta S^0 + R \ln K$$

Multiplying both sides by T, we obtain

$$-RT^2\frac{d \ln K}{dT} = -T\Delta S^0 + RT \ln K$$

$RT \ln K$ is equal to $-\Delta G^0$; therefore,

$$\begin{aligned} -RT^2\frac{d \ln K}{dT} &= -T\Delta S^0 - \Delta G^0 \\ &= -T\Delta S^0 - (\Delta H^0 - T\Delta S^0) \\ &= -\Delta H^0 \qquad (P = \text{constant}) \qquad (4.51) \end{aligned}$$

We can write Eq. (4.51) in an alternate form by noting that $d(1/T) = -dT/T^2$

$$\frac{d \ln K}{d\left(\frac{1}{T}\right)} = -\frac{\Delta H^0}{R} \qquad (P = \text{constant})$$

or, in partial derivative form,

$$\left[\frac{\partial (\ln K)}{\partial\left(\frac{1}{T}\right)}\right]_P = -\frac{\Delta H^0}{R} \qquad (4.52$$

--- van't Hoff equation

- **When ΔH^o is approximately a constant over the temperature range of interest (less than 25°C), van't Hoff equation is integrated:**

$$\int_{K_1}^{K_2} d \ln K = -\frac{\Delta H^0}{R}\int_{T_1}^{T_2} d\frac{1}{T}$$

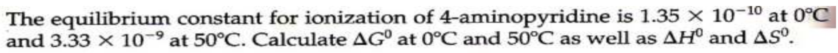
or

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

----- Eq. 4.53

- **This equation is often used to calculate an equilibrium constant K_2 at T_2 when K_1 and the standard enthalpy of the reaction ΔH^o are known**
- **From the equilibrium constant measured at 2 different temperatures, the enthalpy change can be calculated**

Example:



The equilibrium constant for ionization of 4-aminopyridine is 1.35×10^{-10} at 0°C and 3.33×10^{-9} at 50°C. Calculate ΔG^0 at 0°C and 50°C as well as ΔH^0 and ΔS^0.

C

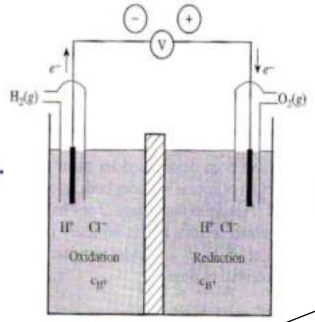
Galvanic Cells

Left electrode, oxidation takes place, electron being produced:

L

R

Right electrode, reduction takes place, electron being removed:



$$H_2(g, P_{H_2}) \longrightarrow 2H^+(c_{H^+}) + 2e^-$$

$$2e^- + \frac{1}{2}O_2(g, P_{O_2}) + 2H^+(c_{H^+}) \longrightarrow H_2O(l)$$

Boundary bet'n 2 different phases

Salt bridge or porous barrier

$$\mathrm{Pt} \,|\, H_2(g, P_{H_2}) \,|\, H^+(c_{H^+}) \,||\, H^+(c_{H^+}) \,|\, O_2(g, P_{O_2}) \,|\, \mathrm{Pt}$$

- **The cell reaction for this cell is the sum of the two half reactions written above, and balanced, so that the electron cancel in the cell reaction:**

$$H_2(g) + \frac{1}{2}O_2(g) \longrightarrow H_2O(l)$$

Standard Electrode Potentials

- **Reversible voltages have been determined for many reactions at standard conditions**
- **Each reaction includes both oxidation and reduction half-reaction**
- **We define the voltage of one half reaction as 0, all other reaction can be obtained relative to this arbitrary choice**
- **The chemist chose the reduction of H^+ to H_2 gas under standard condition, to have a standard electrode potential of 0:**

$$\mathrm{H^+}(a = 1) + e^- \longrightarrow \frac{1}{2}\mathrm{H_2}(g, P = 1\ \mathrm{atm}) \qquad \mathscr{E}^0 = 0.000\ \mathrm{V}$$

- **The Standard reduction electrode potentials at 25°C given in the table were obtained relative to this choice**
- **To calculate the standard potential and therefore the standard free energy for a chemical reaction from the table, it is necessary to combine the appropriate potentials for the half-reactions**
- **The value of ξ^o_{cell} is ξ^o for the reduction half-cell (R) minus the ξ^o for the oxidation half-cell reaction (L)**

Standard reduction electrode potentials at 25°C

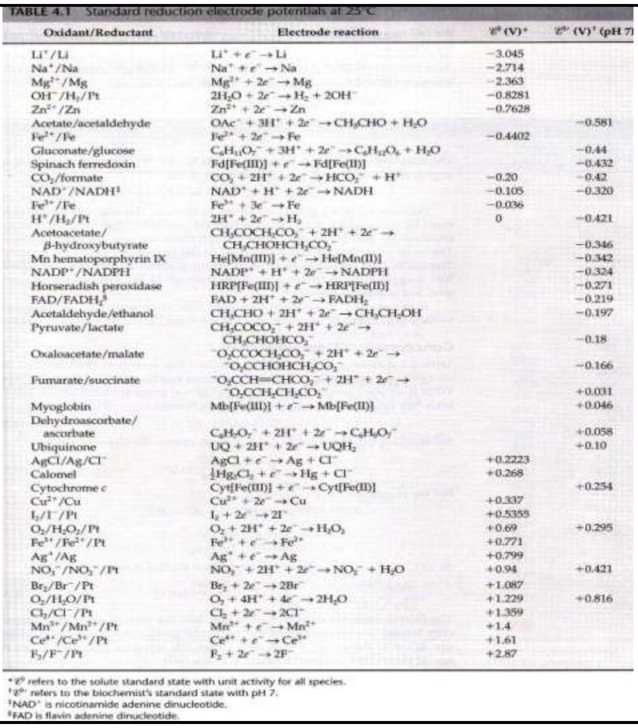


TABLE 4.1 Standard reduction electrode potentials at 25°C

Oxidant/Reductant	Electrode reaction	$\mathscr{E}^0$ (V)*	$\mathscr{E}^{0\prime}$ (V)† (pH 7
Li^+/Li	$Li^+ + e^- \rightarrow Li$	−3.045	
Na^+/Na	$Na^+ + e^- \rightarrow Na$	−2.714	
Mg^{2+}/Mg	$Mg^{2+} + 2e^- \rightarrow Mg$	−2.363	
$OH^-/H_2/Pt$	$2H_2O + 2e^- \rightarrow H_2 + 2OH^-$	−0.8281	
Zn^{2+}/Zn	$Zn^{2+} + 2e^- \rightarrow Zn$	−0.7628	
Acetate/acetaldehyde	$OAc^- + 3H^+ + 2e^- \rightarrow CH_3CHO + H_2O$		−0.581
Fe^{2+}/Fe	$Fe^{2+} + 2e^- \rightarrow Fe$	−0.4402	
Gluconate/glucose	$C_6H_{11}O_7^- + 3H^+ + 2e^- \rightarrow C_6H_{12}O_6 + H_2O$		−0.44
Spinach ferredoxin	$Fd[Fe(III)] + e^- \rightarrow Fd[Fe(II)]$		−0.432
CO_2/formate	$CO_2 + 2H^+ + 2e^- \rightarrow HCO_2^- + H^+$	−0.20	−0.42
$NAD^+/NADH$[‡]	$NAD^+ + H^+ + 2e^- \rightarrow NADH$	−0.105	−0.320
Fe^{3+}/Fe	$Fe^{3+} + 3e^- \rightarrow Fe$	−0.036	
$H^+/H_2/Pt$	$2H^+ + 2e^- \rightarrow H_2$	0	−0.421
Acetoacetate/ β-hydroxybutyrate	$CH_3COCH_2CO_2^- + 2H^+ + 2e^- \rightarrow CH_3CHOHCH_2CO_2^-$		−0.346
Mn hematoporphyrin IX	$He[Mn(III)] + e^- \rightarrow He[Mn(II)]$		−0.342
$NADP^+/NADPH$	$NADP^+ + H^+ + 2e^- \rightarrow NADPH$		−0.324
Horseradish peroxidase	$HRP[Fe(III)] + e^- \rightarrow HRP[Fe(II)]$		−0.271
$FAD/FADH_2$[§]	$FAD + 2H^+ + 2e^- \rightarrow FADH_2$		−0.219
Acetaldehyde/ethanol	$CH_3CHO + 2H^+ + 2e^- \rightarrow CH_3CH_2OH$		−0.197
Pyruvate/lactate	$CH_3COCO_2^- + 2H^+ + 2e^- \rightarrow CH_3CHOHCO_2^-$		−0.18
Oxaloacetate/malate	$^-O_2CCOCH_2CO_2^- + 2H^+ + 2e^- \rightarrow {}^-O_2CCHOHCH_2CO_2^-$		−0.166
Fumarate/succinate	$^-O_2CCH{=}CHCO_2^- + 2H^+ + 2e^- \rightarrow {}^-O_2CCH_2CH_2CO_2^-$		+0.031
Myoglobin	$Mb[Fe(III)] + e^- \rightarrow Mb[Fe(II)]$		+0.046
Dehydroascorbate/ ascorbate	$C_6H_6O_7^- + 2H^+ + 2e^- \rightarrow C_6H_8O_7^-$		+0.058
Ubiquinone	$UQ + 2H^+ + 2e^- \rightarrow UQH_2$		+0.10
$AgCl/Ag/Cl^-$	$AgCl + e^- \rightarrow Ag + Cl^-$	+0.2223	
Calomel	$\frac{1}{2}Hg_2Cl_2 + e^- \rightarrow Hg + Cl^-$	+0.268	
Cytochrome *c*	$Cyt[Fe(III)] + e^- \rightarrow Cyt[Fe(II)]$		+0.254
Cu^{2+}/Cu	$Cu^{2+} + 2e^- \rightarrow Cu$	+0.337	
$I_2/I^-/Pt$	$I_2 + 2e^- \rightarrow 2I^-$	+0.5355	
$O_2/H_2O_2/Pt$	$O_2 + 2H^+ + 2e^- \rightarrow H_2O_2$	+0.69	+0.295
$Fe^{3+}/Fe^{2+}/Pt$	$Fe^{3+} + e^- \rightarrow Fe^{2+}$	+0.771	
Ag^+/Ag	$Ag^+ + e^- \rightarrow Ag$	+0.799	
$NO_3^-/NO_2^-/Pt$	$NO_3^- + 2H^+ + 2e^- \rightarrow NO_2^- + H_2O$	+0.94	+0.421
$Br_2/Br^-/Pt$	$Br_2 + 2e^- \rightarrow 2Br^-$	+1.087	
$O_2/H_2O/Pt$	$O_2 + 4H^+ + 4e^- \rightarrow 2H_2O$	+1.229	+0.816
$Cl_2/Cl^-/Pt$	$Cl_2 + 2e^- \rightarrow 2Cl^-$	+1.359	
$Mn^{3+}/Mn^{2+}/Pt$	$Mn^{3+} + e^- \rightarrow Mn^{2+}$	+1.4	
$Ce^{4+}/Ce^{3+}/Pt$	$Ce^{4+} + e^- \rightarrow Ce^{3+}$	+1.61	
$F_2/F^-/Pt$	$F_2 + 2e^- \rightarrow 2F^-$	+2.87	

*$\mathscr{E}^0$ refers to the solute standard state with unit activity for all species.

†$\mathscr{E}^{0\prime}$ refers to the biochemist's standard state with pH 7.

‡NAD^+ is nicotinamide adenine dinucleotide.

§FAD is flavin adenine dinucleotide.

Example: To find ξ^o_{cell} and ΔG of the reaction:

$$\mathrm{Zn}(s) + \mathrm{Cu}^{2+}(a = 1) \longrightarrow \mathrm{Zn}^{2+}(a = 1) + \mathrm{Cu}(s)$$

- **The half-reactions and the potentials are:**

$$\begin{array}{ll} \mathrm{Cu}^{2+}(a = 1) + 2e^- \longrightarrow \mathrm{Cu}(s) & \mathscr{E}^0 = +0.337\ \mathrm{V} \\ \mathrm{Zn}(s) \longrightarrow \mathrm{Zn}^{2+}(a = 1) + 2e^- & \mathscr{E}^0 = -(-0.763\ \mathrm{V}) \\ \hline & \mathscr{E}^0_{\mathrm{cell}} = +1.100\ \mathrm{V} \end{array}$$

- **Using formulas stated before, ΔG can be calculated:** $\Delta G^o = -\,nF\xi^o_{cell}$

$$\Delta G^0 = -2.20\ \mathrm{eV} = -212\ \mathrm{kJ}$$

Notes:

- **The Table gives reduction potential, thus the sign of the potential must be changed for the oxidation half-cell reaction**
- **The voltages must not be multiplied by 2 even though there are 2 electrons involved.**
- ***n* will be considered only when calculating *G***
- **If ξ is negative, standard free energy is positive, thus the reaction does not occur *spontaneously***

Concentration Dependence of ξ

To find the free energies at random concentrations:

- **Given** $\Delta G = \Delta G^0 + RT \ln Q$
- **Since** $\Delta G\ (\mathrm{J}) = -n\mathscr{E}F$
- **Therefore** $\mathscr{E} = \mathscr{E}^0 - \dfrac{RT}{nF} \ln Q$ **--- this is a Nernst Equation**
- **For the reaction** $a\mathrm{A} + b\mathrm{B} \longrightarrow c\mathrm{C} + d\mathrm{D}$

$$Q = \frac{(a_{\mathrm{C}})^c (a_{\mathrm{D}})^d}{(a_{\mathrm{A}})^a (a_{\mathrm{B}})^b}$$

- **The Nernst Equation can be written as:**

$$\mathscr{E} = \mathscr{E}^0 - \frac{0.0591}{n} \log Q$$

- **The Nernst Equation can be used to calculate the voltage and Gibbs free energy for any concentration of reactants and products in a cell**
- **At equilibrium $\Delta G = 0$; therefore $\xi = 0$, thus, the standard potential gives the equilibrium constant for the reaction in the cell:**

$$\mathscr{E}^0 = \frac{RT}{nF} \ln K \qquad K = 10^{n\mathscr{E}^0/0.0591}$$

----At 25°C

Ionization Constants and Enthalpies of Ionization at 25°C

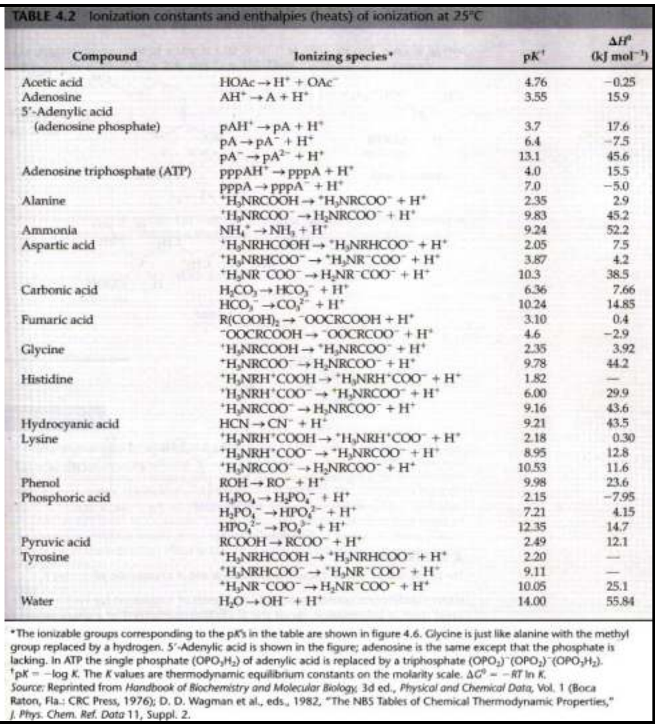


TABLE 4.2 Ionization constants and enthalpies (heats) of ionization at 25°C

Compound	Ionizing species*	pK†	ΔH^0 (kJ mol^{-1})
Acetic acid	$HOAc \rightarrow H^+ + OAc^-$	4.76	−0.25
Adenosine	$AH^+ \rightarrow A + H^+$	3.55	15.9
5′-Adenylic acid (adenosine phosphate)	$pAH^+ \rightarrow pA + H^+$	3.7	17.6
	$pA \rightarrow pA^- + H^+$	6.4	−7.5
	$pA^- \rightarrow pA^{2-} + H^+$	13.1	45.6
Adenosine triphosphate (ATP)	$pppAH^+ \rightarrow pppA + H^+$	4.0	15.5
	$pppA \rightarrow pppA^- + H^+$	7.0	−5.0
Alanine	$^+H_3NRCOOH \rightarrow {}^+H_3NRCOO^- + H^+$	2.35	2.9
	$^+H_3NRCOO^- \rightarrow H_2NRCOO^- + H^+$	9.83	45.2
Ammonia	$NH_4^+ \rightarrow NH_3 + H^+$	9.24	52.2
Aspartic acid	$^+H_3NRHCOOH \rightarrow {}^+H_3NRHCOO^- + H^+$	2.05	7.5
	$^+H_3NRHCOO^- \rightarrow {}^+H_3NR^-COO^- + H^+$	3.87	4.2
	$^+H_3NR^-COO^- \rightarrow H_2NR^-COO^- + H^+$	10.3	38.5
Carbonic acid	$H_2CO_3 \rightarrow HCO_3^- + H^+$	6.36	7.66
	$HCO_3^- \rightarrow CO_3^{2-} + H^+$	10.24	14.85
Fumaric acid	$R(COOH)_2 \rightarrow {}^-OOCRCOOH + H^+$	3.10	0.4
	$^-OOCRCOOH \rightarrow {}^-OOCRCOO^- + H^+$	4.6	−2.9
Glycine	$^+H_3NRCOOH \rightarrow {}^+H_3NRCOO^- + H^+$	2.35	3.92
	$^+H_3NRCOO^- \rightarrow H_2NRCOO^- + H^+$	9.78	44.2
Histidine	$^+H_3NRH^+COOH \rightarrow {}^+H_3NRH^+COO^- + H^+$	1.82	—
	$^+H_3NRH^+COO^- \rightarrow {}^+H_3NRCOO^- + H^+$	6.00	29.9
	$^+H_3NRCOO^- \rightarrow H_2NRCOO^- + H^+$	9.16	43.6
Hydrocyanic acid	$HCN \rightarrow CN^- + H^+$	9.21	43.5
Lysine	$^+H_3NRH^+COOH \rightarrow {}^+H_3NRH^+COO^- + H^+$	2.18	0.30
	$^+H_3NRH^+COO^- \rightarrow {}^+H_3NRCOO^- + H^+$	8.95	12.8
	$^+H_3NRCOO^- \rightarrow H_2NRCOO^- + H^+$	10.53	11.6
Phenol	$ROH \rightarrow RO^- + H^+$	9.98	23.6
Phosphoric acid	$H_3PO_4 \rightarrow H_2PO_4^- + H^+$	2.15	−7.95
	$H_2PO_4^- \rightarrow HPO_4^{2-} + H^+$	7.21	4.15
	$HPO_4^{2-} \rightarrow PO_4^{3-} + H^+$	12.35	14.7
Pyruvic acid	$RCOOH \rightarrow RCOO^- + H^+$	2.49	12.1
Tyrosine	$^+H_3NRHCOOH \rightarrow {}^+H_3NRHCOO^- + H^+$	2.20	—
	$^+H_3NRHCOO^- \rightarrow {}^+H_3NR^-COO^- + H^+$	9.11	—
	$^+H_3NR^-COO^- \rightarrow H_2NR^-COO^- + H^+$	10.05	25.1
Water	$H_2O \rightarrow OH^- + H^+$	14.00	55.84

*The ionizable groups corresponding to the pK's in the table are shown in figure 4.6. Glycine is just like alanine with the methyl group replaced by a hydrogen. 5′-Adenylic acid is shown in the figure; adenosine is the same except that the phosphate is lacking. In ATP the single phosphate (OPO_3H_2) of adenylic acid is replaced by a triphosphate $(OPO_2)^-(OPO_2)^-(OPO_3H_2)$.

†pK = −log *K*. The *K* values are thermodynamic equilibrium constants on the molarity scale. $\Delta G^0 = -RT \ln K$.

Source: Reprinted from *Handbook of Biochemistry and Molecular Biology,* 3d ed., *Physical and Chemical Data,* Vol. 1 (Boca Raton, Fla.: CRC Press, 1976); D. D. Wagman et al., eds., 1982, "The NBS Tables of Chemical Thermodynamic Properties," *J. Phys. Chem. Ref. Data* 11, Suppl. 2.