4b. Thermodynamic Symbols, Definitions, and Equations

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4b-1. Simple Systems. A simple system is defined as one of constant mass whose equilibrium states are described with the aid of only three thermodynamic coordinates, one of which is the kelvin temperature. The simple systems most often used are listed in Tables 4b-1 and 4b-2, and the rules for converting any equation holding for a hydrostatic system into the analogous equation for another simple system are given in Table 4b-7. Tables 4b-3 to 4b-6 contain the most useful thermodynamic equations involving first derivatives only. Table 4b-8 refers to phase transitions.

TABLE 4b-1. THERMODYNAMIC SYSTEMS AND COORDINATES

System	Intensive coordinate		Extensive coordinate	
Hydrostatic system	Pressure	P	Volume	V
Stretched wire	Tension	$\mathcal{F}$	Length	L
Surface film	Surface tension	$\mathcal{S}$	Area	A
Electric cell	Emf	$\mathcal{E}$	Charge	Z
Capacitor	Electric intensity	E	Polarization	P'
Magnetic substance	Magnetic intensity	$\mathcal{H}$	Magnetization	M

TABLE 4b-2. WORK DONE BY THERMODYNAMIC SYSTEMS

System	Intensive quantity (generalized force)	Extensive quantity (generalized displacement)	Work
Hydrostatic system	P in N/m²	V in m³	$P\,dV$ in J
Stretched wire	$\mathcal{F}$ in N	L in m	$-\mathcal{F}\,dL$ in J
Surface film	$\mathcal{S}$ in dynes/cm	A in cm²	$-\mathcal{S}\,dA$ in ergs
Electric cell	$\mathcal{E}$ in V	Z in C	$-\mathcal{E}\,dZ$ in J
Capacitor	E in N/C	P' in C · m	$-E\,dP'$ in J
Magnetic substance	$\mathcal{H}$ in A/m	M in Wb · m	$-\mathcal{H}\,dM$ in J

TABLE 4b-3. DEFINITIONS AND SYMBOLS FOR THERMAL QUANTITIES

Thermal quantity	Symbol	Definition
Heat..	Q	
Internal energy................................	U	
Entropy..	S	
Enthalpy (also called heat content, heat function, total heat)...............................	H	$U + PV$
Helmholtz function (also called free energy and work function, with symbol A used)...............	F	$U - TS$
Gibbs function (also called free energy, free enthalpy, thermodynamic potential, with symbol F used)....	G	$H - TS$
Volume expansivity (coefficient of volume expansion).	β	$\dfrac{1}{V}\left(\dfrac{\partial V}{\partial T}\right)_P$
Isothermal bulk modulus.........................	B	$-V\left(\dfrac{\partial P}{\partial V}\right)_T$
Adiabatic bulk modulus..........................	B_S	$-V\left(\dfrac{\partial P}{\partial V}\right)_S$
Isothermal compressibility.......................	k	$-\dfrac{1}{V}\left(\dfrac{\partial V}{\partial P}\right)_T$
Adiabatic compressibility........................	k_S	$-\dfrac{1}{V}\left(\dfrac{\partial V}{\partial P}\right)_S$
Heat capacity at constant volume................	C_V	$\left(\dfrac{dQ}{dT}\right)_V = T\left(\dfrac{\partial S}{\partial T}\right)_V$
Heat capacity at constant pressure...............	C_P	$\left(\dfrac{dQ}{dT}\right)_P = T\left(\dfrac{\partial S}{\partial T}\right)_P$
Ratio of heat capacities.........................	γ	$\dfrac{C_P}{C_V}$
Joule coefficient................................	η	$\left(\dfrac{\partial T}{\partial V}\right)_U$
Joule-Thomson (Kelvin) coefficient..............	μ	$\left(\dfrac{\partial T}{\partial P}\right)_H$
Linear expansivity..............................	α	$\dfrac{1}{L}\left(\dfrac{\partial L}{\partial T}\right)_{\mathscr{F}}$
Isothermal Young's modulus......................	Y	$\dfrac{L}{A}\left(\dfrac{\partial \mathscr{F}}{\partial L}\right)_T$
Adiabatic Young's modulus......................	Y_S	$\dfrac{L}{A}\left(\dfrac{\partial \mathscr{F}}{\partial L}\right)_S$

TABLE 4b-4. THERMODYNAMIC EQUATIONS FOR A HYDROSTATIC
SYSTEM OF CONSTANT MASS

First law of thermodynamics:

$$Q = U_2 - U_1 + W$$

$$dQ = dU + dW \tag{4b-1}$$

Second law of thermodynamics:

$$dQ = T\,dS \tag{4b-2}$$

Third law of thermodynamics:

$$\lim_{T \to 0} \Delta S_T = 0 \tag{4b-3}$$

$$dU = T\,dS - P\,dV \tag{4b-4}$$

$$dH = T\,dS + V\,dP \tag{4b-5}$$

$$dF = -S\,dT - P\,dV \tag{4b-6}$$

$$dG = -S\,dT + V\,dP \tag{4b-7}$$

Maxwell's equations:

$$\left(\frac{\partial T}{\partial V}\right)_S = -\left(\frac{\partial P}{\partial S}\right)_V \tag{4b-8}$$

$$\left(\frac{\partial T}{\partial P}\right)_S = \left(\frac{\partial V}{\partial S}\right)_P \tag{4b-9}$$

$$\left(\frac{\partial S}{\partial V}\right)_T = \left(\frac{\partial P}{\partial T}\right)_V \tag{4b-10}$$

$$\left(\frac{\partial S}{\partial P}\right)_T = -\left(\frac{\partial V}{\partial T}\right)_P \tag{4b-11}$$

Basic thermodynamic equations:

$$C_V = \left(\frac{\partial U}{\partial T}\right)_V = T\left(\frac{\partial S}{\partial T}\right)_V = -T\left(\frac{\partial P}{\partial T}\right)_V\left(\frac{\partial V}{\partial T}\right)_S \tag{4b-12}$$

$$C_P = \left(\frac{\partial H}{\partial T}\right)_P = T\left(\frac{\partial S}{\partial T}\right)_P = T\left(\frac{\partial V}{\partial T}\right)_P\left(\frac{\partial P}{\partial T}\right)_S \tag{4b-13}$$

$$T\,dS = C_V\,dT + T\left(\frac{\partial P}{\partial T}\right)_V dV = C_V\,dT + \frac{\beta T}{k}\,dV \tag{4b-14}$$

$$T\,dS = C_P\,dT - T\left(\frac{\partial V}{\partial T}\right)_P dP = C_P\,dT - V\beta T\,dP \tag{4b-15}$$

$$T\,dS = C_V\left(\frac{\partial T}{\partial P}\right)_V dP + C_P\left(\frac{\partial T}{\partial V}\right)_P dV = \frac{C_V k}{\beta}\,dP + \frac{C_P}{\beta V}\,dV \tag{4b-16}$$

$$\left(\frac{\partial C_V}{\partial V}\right) = T\left(\frac{\partial^2 P}{\partial T^2}\right)_V \tag{4b-17}$$

$$\left(\frac{\partial C_P}{\partial P}\right)_T = -T\left(\frac{\partial^2 V}{\partial T^2}\right)_P \tag{4b-18}$$

$$C_P - C_V = T\left(\frac{\partial P}{\partial T}\right)_V\left(\frac{\partial V}{\partial T}\right)_P = -T\left(\frac{\partial V}{\partial T}\right)_P^2\left(\frac{\partial P}{\partial V}\right)_T = \frac{TV\beta^2}{k} \tag{4b-19}$$

$$\gamma = \frac{C_P}{C_V} = \frac{(\partial P/\partial V)_S}{(\partial P/\partial V)_T} = \frac{k}{k_S} \tag{4b-20}$$

$$\mu = \left(\frac{\partial T}{\partial P}\right)_H = \frac{1}{C_P}\left[T\left(\frac{\partial V}{\partial T}\right)_P - V\right] = \frac{V}{C_P}(\beta T - 1) \tag{4b-21}$$

$$\eta = \left(\frac{\partial T}{\partial V}\right)_U = -\frac{1}{C_V}\left[T\left(\frac{\partial P}{\partial T}\right)_V - P\right] = -\frac{1}{C_V}\left(\frac{\beta T}{k} - P\right) \tag{4b-22}$$

TABLE 4b-5. FIRST DERIVATIVES OF T, P, V, AND S

$$\left(\frac{\partial T}{\partial P}\right)_V = \frac{k}{\beta}$$

$$\left(\frac{\partial T}{\partial P}\right)_S = \frac{V\beta T}{C_P} = \frac{(\gamma - 1)k}{\gamma\beta}$$

$$\left(\frac{\partial T}{\partial V}\right)_P = \frac{1}{V\beta}$$

$$\left(\frac{\partial T}{\partial V}\right)_S = -\frac{\beta T}{C_V k} = -\frac{\gamma - 1}{V\beta}$$

$$\left(\frac{\partial T}{\partial S}\right)_P = \frac{T}{C_P}$$

$$\left(\frac{\partial T}{\partial S}\right)_V = \frac{T}{C_V}$$

$$\left(\frac{\partial P}{\partial T}\right)_V = \frac{\beta}{k}$$

$$\left(\frac{\partial P}{\partial T}\right)_S = \frac{C_P}{V\beta T} = \frac{\gamma\beta}{(\gamma - 1)k}$$

$$\left(\frac{\partial P}{\partial V}\right)_T = -\frac{1}{Vk}$$

$$\left(\frac{\partial P}{\partial V}\right)_S = -\frac{\gamma}{Vk}$$

$$\left(\frac{\partial P}{\partial S}\right)_T = -\frac{1}{V\beta}$$

$$\left(\frac{\partial P}{\partial S}\right)_V = \frac{\beta T}{C_V k} = \frac{\gamma - 1}{V\beta}$$

$$\left(\frac{\partial V}{\partial T}\right)_P = V\beta$$

$$\left(\frac{\partial V}{\partial T}\right)_S = -\frac{C_V k}{\beta T} = -\frac{V\beta}{\gamma - 1}$$

$$\left(\frac{\partial V}{\partial P}\right)_T = -Vk$$

$$\left(\frac{\partial V}{\partial P}\right)_S = -\frac{Vk}{\gamma}$$

$$\left(\frac{\partial V}{\partial S}\right)_T = \frac{k}{\beta}$$

$$\left(\frac{\partial V}{\partial S}\right)_P = \frac{V\beta T}{C_P} = \frac{(\gamma - 1)k}{\gamma\beta}$$

$$\left(\frac{\partial S}{\partial T}\right)_V = \frac{C_V}{T}$$

$$\left(\frac{\partial S}{\partial T}\right)_P = \frac{C_P}{T}$$

$$\left(\frac{\partial S}{\partial P}\right)_T = -V\beta$$

$$\left(\frac{\partial S}{\partial P}\right)_V = \frac{C_V k}{\beta T} = \frac{V\beta}{\gamma - 1}$$

$$\left(\frac{\partial S}{\partial V}\right)_P = \frac{C_P}{V\beta T} = \frac{\gamma\beta}{(\gamma - 1)k}$$

$$\left(\frac{\partial S}{\partial V}\right)_T = \frac{\beta}{k}$$

TABLE 4b-6. First Derivatives of U, H, F, and G with Respect to T, P, V, and S

Internal energy U	Enthalpy H	Helmholtz function F	Gibbs function G
$\left(\dfrac{\partial U}{\partial T}\right)_P = C_P - PV\beta$	$\left(\dfrac{\partial H}{\partial T}\right)_P = C_P$	$\left(\dfrac{\partial F}{\partial T}\right)_P = -S - PV\beta$	$\left(\dfrac{\partial G}{\partial T}\right)_P = -S$
$\left(\dfrac{\partial U}{\partial T}\right)_V = C_V$	$\left(\dfrac{\partial H}{\partial T}\right)_V = C_V + \dfrac{V\beta}{k}$	$\left(\dfrac{\partial F}{\partial T}\right)_V = -S$	$\left(\dfrac{\partial G}{\partial T}\right)_V = -S + \dfrac{V\beta}{k}$
$\left(\dfrac{\partial U}{\partial T}\right)_S = \dfrac{PC_V k}{\beta T} = \dfrac{PV\beta}{\gamma-1}$	$\left(\dfrac{\partial H}{\partial T}\right)_S = \dfrac{C_P}{\beta T}$	$\left(\dfrac{\partial F}{\partial T}\right)_S = \begin{cases} -S + \dfrac{PV\beta}{\gamma-1} \\[2mm] -S + \dfrac{PC_V k}{\beta T} \end{cases}$	$\left(\dfrac{\partial G}{\partial T}\right)_S = \begin{cases} -S + \dfrac{C_P}{\beta T} \\[2mm] -S + \dfrac{V\gamma\beta}{(\gamma-1)k} \end{cases}$
$\left(\dfrac{\partial U}{\partial P}\right)_T = -V\beta T + VkP$	$\left(\dfrac{\partial H}{\partial P}\right)_T = V(1 - \beta T) = -C_P\mu$	$\left(\dfrac{\partial F}{\partial P}\right)_T = PVk$	$\left(\dfrac{\partial G}{\partial P}\right)_T = V$
$\left(\dfrac{\partial U}{\partial P}\right)_V = \dfrac{C_V k}{\beta} = \dfrac{V\beta T}{\gamma-1}$	$\left(\dfrac{\partial H}{\partial P}\right)_V = V + \dfrac{C_V k}{\beta}$	$\left(\dfrac{\partial F}{\partial P}\right)_V = -\dfrac{Sk}{\beta}$	$\left(\dfrac{\partial G}{\partial P}\right)_V = -\dfrac{Sk}{\beta} + V$
$\left(\dfrac{\partial U}{\partial P}\right)_S = \dfrac{PVk}{\gamma}$	$\left(\dfrac{\partial H}{\partial P}\right)_S = V$	$\left(\dfrac{\partial F}{\partial P}\right)_S = \begin{cases} -\dfrac{SV\beta T}{C_P} + \dfrac{PVk}{\gamma} \\[2mm] -\dfrac{Sk(\gamma-1)}{\gamma\beta} + \dfrac{PVk}{\gamma} \end{cases}$	$\left(\dfrac{\partial G}{\partial P}\right)_S = \begin{cases} -\dfrac{SV\beta T}{C_P} + V \\[2mm] -\dfrac{S(\gamma-1)k}{\gamma\beta} + V \end{cases}$
$\left(\dfrac{\partial U}{\partial V}\right)_T = \dfrac{\beta T}{k} - P$	$\left(\dfrac{\partial H}{\partial V}\right)_T = \dfrac{\beta T}{k} - \dfrac{1}{k}$	$\left(\dfrac{\partial F}{\partial V}\right)_T = -P$	$\left(\dfrac{\partial G}{\partial V}\right)_T = -\dfrac{1}{k}$

TABLE 4b-6. FIRST DERIVATIVES OF U, H, F, AND G WITH RESPECT TO T, P, V, AND S (Continued)

Internal energy U	Enthalpy H	Helmholtz function F	Gibbs function G
$\left(\dfrac{\partial U}{\partial V}\right)_P = \dfrac{C_P}{V\beta} - P = \dfrac{\gamma\beta T}{(\gamma-1)k} - P$	$\left(\dfrac{\partial H}{\partial V}\right)_P = \dfrac{C_P}{V\beta}$	$\left(\dfrac{\partial F}{\partial V}\right)_P = -\dfrac{S}{V\beta} - P$	$\left(\dfrac{\partial G}{\partial V}\right)_P = -\dfrac{S}{V\beta}$
$\left(\dfrac{\partial U}{\partial V}\right)_S = -P$	$\left(\dfrac{\partial H}{\partial V}\right)_S = -\dfrac{\gamma}{k}$	$\left(\dfrac{\partial F}{\partial V}\right)_S = \begin{cases}\dfrac{S\beta T}{C_V k} - P \\[2mm] \dfrac{S(\gamma-1)}{V\beta} - P\end{cases}$	$\left(\dfrac{\partial G}{\partial V}\right)_S = \begin{cases}\dfrac{S\beta T}{C_V k} - \dfrac{\gamma}{k} \\[2mm] \dfrac{S(\gamma-1)}{V\beta} - \dfrac{\gamma}{k}\end{cases}$
$\left(\dfrac{\partial U}{\partial S}\right)_T = T - \dfrac{Pk}{\beta}$	$\left(\dfrac{\partial H}{\partial S}\right)_T = T - \dfrac{1}{\beta}$	$\left(\dfrac{\partial F}{\partial S}\right)_T = -\dfrac{Pk}{\beta}$	$\left(\dfrac{\partial G}{\partial S}\right)_T = \dfrac{1}{\beta}$
$\left(\dfrac{\partial U}{\partial S}\right)_P = \begin{cases}T - \dfrac{PV\beta T}{C_P} \\[2mm] T - \dfrac{(\gamma-1)Pk}{\gamma\beta}\end{cases}$	$\left(\dfrac{\partial H}{\partial S}\right)_P = T$	$\left(\dfrac{\partial F}{\partial S}\right)_P = \begin{cases}-\dfrac{ST}{C_P} - \dfrac{PV\beta T}{C_P} \\[2mm] -\dfrac{ST}{C_P} - \dfrac{Pk(\gamma-1)}{\gamma\beta}\end{cases}$	$\left(\dfrac{\partial G}{\partial S}\right)_P = -\dfrac{ST}{C_P}$
$\left(\dfrac{\partial U}{\partial S}\right)_V = T$	$\left(\dfrac{\partial H}{\partial S}\right)_V = T + \dfrac{\gamma-1}{\beta}$	$\left(\dfrac{\partial F}{\partial S}\right)_V = -\dfrac{ST}{C_V}$	$\left(\dfrac{\partial G}{\partial S}\right)_V = \begin{cases}-\dfrac{ST}{C_V} + \dfrac{V\beta T}{C_V k} \\[2mm] -\dfrac{ST}{C_V} + \dfrac{V(\gamma-1)}{V\beta}\end{cases}$

TABLE 4b-7. CONVERSION FROM HYDROSTATIC TO OTHER SYSTEMS

System	Replacement for P	Replacement for V
Stretched wire.............	$-\mathcal{F}$	L
Surface film...............	$-\mathscr{A}$	A
Electric cell...............	$-\mathcal{E}$	Z
Capacitor.................	$-E$	P'
Magnetic substance........	$-\mathcal{H}$	M

TABLE 4b-8. PHASE TRANSITIONS

First-order transition from 1 to 2

$$L_{1\to 2} = \text{latent heat} = H_2 - H_1 = T(S_2 - S_1)$$

$$\frac{dP}{dT} = \frac{L_{1\to 2}}{T(V_2 - V_1)} \qquad \text{(Clapeyron's equation)}$$

$$\frac{dL_{1\to 2}}{dT} = C_{P2} - C_{P1} + [V_2(1 - \beta_2 T) - V_1(1 - \beta_1 T)]\frac{dP}{dT}$$

Second-order transition from 1 to 2

$$\frac{dP}{dT} = \frac{C_{P2} - C_{P1}}{TV(\beta_2 - \beta_1)}$$
$$\frac{dP}{dT} = \frac{\beta_2 - \beta_1}{k_2 - k_1} \qquad \text{(Ehrenfest's equations)}$$

Lambda transition

Let P'_λ represent the slope of the PT curve at the λ point, and let S'_λ represent the slope of the ST curve at the λ point. At a temperature T, a *small amount* above or below T_λ,

$$\frac{C_P}{T} = S'_\lambda + V\beta P'_\lambda$$

If V'_λ is the slope of the VT curve at T_λ,

$$\frac{C_V}{T} = S'_\lambda - \frac{\beta}{k} V'_\lambda$$

$$\beta = \frac{V'_\lambda}{V} - kP'_\lambda$$

TABLE 4b-9. EQUATIONS FOR SYSTEMS OF VARIABLE
COMPOSITION AND VARIABLE MASS

Consider a system which is a homogeneous mixture of any number of constituents 1, 2, ... , k, . . . with n_1 moles of substance 1, n_2 moles of substance 2, etc., at a uniform temperature T, a uniform pressure P, and a volume V. The chemical potential of the kth constituent is

$$\mu_k = \left(\frac{\partial U}{\partial n_k}\right)_{S,V,\,\text{other }n\text{'s}} \tag{4b-23}$$

$$\mu_k = \left(\frac{\partial H}{\partial n_k}\right)_{S,P,\,\text{other }n\text{'s}} \tag{4b-24}$$

$$\mu_k = \left(\frac{\partial A}{\partial n_k}\right)_{T,V,\,\text{other }n\text{'s}} \tag{4b-25}$$

$$\mu_k = \left(\frac{\partial G}{\partial n_k}\right)_{T,P,\,\text{other }n\text{'s}} \tag{4b-26}$$

$$dU = T\,dS - P\,dV + \Sigma\mu_k\,dn_k \tag{4b-27}$$

$$dH = T\,dS + V\,dP + \Sigma\mu_k\,dn_k \tag{4b-28}$$

$$dA = -S\,dT - P\,dV + \Sigma\mu_k\,dn_k \tag{4b-29}$$

$$dG = -S\,dT + V\,dP + \Sigma\mu_k\,dn_k \tag{4b-30}$$

$$G = U + PV - TS = \Sigma n_k\mu_k \tag{4b-31}$$

$$-S\,dT + V\,dP = \Sigma n_k\,d\mu_k \tag{4b-32}$$

4b-2. Equations for Ideal Gas Reactions. Assume a mixture of four reacting substances whose chemical symbols are A, B, C, and D, where A and B are the initial constituents (reactants) and C and D the final constituents (products), the reaction being represented by

$$aA + bB \rightleftharpoons cC + dD$$
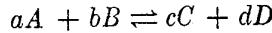
Four substances are chosen only for convenience; the equations to be developed can easily be applied to reactions in which any number of substances participate. The lower-case letters a, b, c, and d are the *stoichiometric coefficients,* which are always positive integers or fractions.

If we start with arbitrary amounts of *both* initial and final constituents and imagine the reaction to proceed completely to the right, at least one of the initial constituents, say A, will completely disappear. Then it is possible to find a positive number n_0 such that the original number of moles of each of the initial constituents is expressed in the form

$$n_A\,(\text{original}) = n_0 a$$
$$n_B\,(\text{original}) = n_0 b + i_B$$

where i_B is a constant representing the number of moles of B that cannot combine. If we imagine the reaction to proceed completely to the left, at least one of the final constituents, say C, will completely disappear. In this event, another positive number n_0' can be found such that the original number of moles of each final constituent is expressed in the form

$$n_C\,(\text{original}) = n_0' c$$
$$n_D\,(\text{original}) = n_0' d + i_D$$

If the reaction is imagined to proceed completely to the left, there is the maximum amount possible of each initial constituent and the minimum amount of each final constituent. Thus,

$$n_A\,(\text{max}) = (n_0 + n_0')a \qquad n_C\,(\text{min}) = 0$$
$$n_B\,(\text{max}) = (n_0 + n_0')b + i_B \qquad n_D\,(\text{min}) = i_D$$

If the reaction is imagined to proceed completely to the right, there is the minimum amount possible of each initial constituent and the maximum amount of each final constituent. Thus,

$$n_A\,(\text{min}) = 0 \qquad n_C\,(\text{max}) = (n_0 + n_0')c$$
$$n_B\,(\text{min}) = i_B \qquad n_D\,(\text{max}) = (n_0 + n_0')d + i_D$$

Suppose the reaction proceeds partially either to the right or to the left to such an extent that there are n_A moles of A, n_B moles of B, n_C moles of C, and n_D moles of D present at a given moment. We define the *degree of reaction* ϵ in terms of any one of the initial constituents, say A, as the fraction

$$\epsilon = \frac{n_A \text{ (max)} - n_A}{n_A \text{ (max)} - n_A \text{ (min)}}$$

It follows that $\epsilon = 0$ when the reaction is completely to the left and $\epsilon = 1$ when it is completely to the right. Expressing n_A (max) and n_A (min) in terms of the constants that determine the original amounts, we get

$$\epsilon = \frac{(n_0 + n_0')a - n_A}{(n_0 + n_0')a}$$

or
$$n_A = (n_0 + n_0')a(1 - \epsilon)$$

The number of moles of each of the constituents is given, therefore, by the expressions

$$n_A = (n_0 + n_0')a(1 - \epsilon) \qquad n_C = (n_0 + n_0')c\epsilon$$
$$n_B = (n_0 + n_0')b(1 - \epsilon) + i_B \qquad n_D = (n_0 + n_0')d\epsilon + i_D$$

Since all the n's are functions of ϵ only, it follows that in a homogeneous mixture, all the mole fractions are functions of ϵ only. Consider, for example, a vessel containing n_0 moles of water vapor only, with no hydrogen or oxygen present. If dissociation occurs until the degree of dissociation is ϵ, then the n's and the x's (mole fractions) are functions of ϵ as shown in Table 4b-10.

TABLE 4b-10. $H_2O \rightleftharpoons H_2 + \frac{1}{2}O_2$

Constituent	Stoichio-metric coefficient	Number of moles n	Mole fraction x
$A = H_2O$	$a = 1$	$n_A = n_0(1 - \epsilon)$	$x_A = \dfrac{1 - \epsilon}{1 + \epsilon/2}$
$C = H_2$	$c = 1$	$n_C = n_0\epsilon$	$x_C = \dfrac{\epsilon}{1 + \epsilon/2}$
$D = O_2$	$d = \frac{1}{2}$	$n_D = n_0\epsilon/2$	$x_D = \dfrac{\epsilon/2}{1 + \epsilon/2}$
		$\Sigma n = n_0(1 + \epsilon/2)$	

In the case of a mixture of four reacting *ideal* gases in equilibrium, the *equilibrium constant* K is given by the *law of mass action*,

$$\frac{(x_C)^c \cdot (x_D)^d}{(x_A)^a \cdot (x_B)^b} P^{c+d-a-b} = K$$

Since each x is a function of ϵ, K is a function of P and the equilibrium value of ϵ, the function being different for each reaction. The values of K as functions of P and ϵ for all possible reactions among two, three, or four constituents, with stoichiometric coefficients taking on the value 1, 2, or 3, are given in Table 4b-11.

TABLE 4b-11. EQUILIBRIUM CONSTANTS EXPRESSED AS FUNCTIONS OF P AND ϵ

Reaction	K	Reaction	K
$A \rightleftharpoons C$	$\dfrac{\epsilon}{1-\epsilon}$	$3A \rightleftharpoons 2C + 2D$	$\dfrac{16\epsilon^4 P}{27(1-\epsilon)^3(3+\epsilon)}$
$A \rightleftharpoons 2C$	$\dfrac{4\epsilon^2 P}{1-\epsilon^2}$	$3A \rightleftharpoons C + 3D$	$\dfrac{\epsilon^4 P}{(1-\epsilon)^3(3+\epsilon)}$
$A \rightleftharpoons 3C$	$\dfrac{27\epsilon^3 P^2}{(1-\epsilon)(1+2\epsilon)^2}$	$3A \rightleftharpoons 2C + 3D$	$\dfrac{4\epsilon^5 P^2}{(1-\epsilon)^3(3+2\epsilon)^2}$
$2A \rightleftharpoons C$	$\dfrac{\epsilon(2-\epsilon)}{4(1-\epsilon)^2 P}$	$A + B \rightleftharpoons C$	$\dfrac{\epsilon(2-\epsilon)}{(1-\epsilon)^2 P}$
$2A \rightleftharpoons 3C$	$\dfrac{27\epsilon^3 P}{4(2+\epsilon)(1-\epsilon)^2}$	$A + B \rightleftharpoons 2C$	$\dfrac{4\epsilon^2}{(1-\epsilon)^2}$
$3A \rightleftharpoons C$	$\dfrac{\epsilon(3-2\epsilon)^2}{27(1-\epsilon)^3 P^2}$	$A + B \rightleftharpoons 3C$	$\dfrac{27\epsilon^3 P}{(1-\epsilon)^2(2+\epsilon)}$
$3A \rightleftharpoons 2C$	$\dfrac{4\epsilon^2(3-\epsilon)}{27(1-\epsilon)^3 P}$	$A + 2B \rightleftharpoons C$	$\dfrac{\epsilon(3-2\epsilon)^2}{4(1-\epsilon)^3 P^2}$
$A \rightleftharpoons C + D$	$\dfrac{\epsilon^2 P}{1-\epsilon^2}$	$A + 2B \rightleftharpoons 2C$	$\dfrac{\epsilon^2(3-\epsilon)}{(1-\epsilon)^3 P}$
$A \rightleftharpoons C + 2D$	$\dfrac{4\epsilon^3 P^2}{(1-\epsilon)(1+2\epsilon)^2}$	$A + 2B \rightleftharpoons 3C$	$\dfrac{27\epsilon^3}{4(1-\epsilon)^3}$
$A \rightleftharpoons 2C + 2D$	$\dfrac{16\epsilon^4 P^3}{(1-\epsilon)(1+3\epsilon)^3}$	$2A + 2B \rightleftharpoons C$	$\dfrac{\epsilon(4-3\epsilon)^3}{16(1-\epsilon)^4 P^3}$
$A \rightleftharpoons C + 3D$	$\dfrac{27\epsilon^4 P^3}{(1-\epsilon)(1+3\epsilon)^3}$	$2A + 2B \rightleftharpoons 3C$	$\dfrac{27\epsilon^3(4-\epsilon)}{16(1-\epsilon)^4 P}$
$A \rightleftharpoons 2C + 3D$	$\dfrac{108\epsilon^5 P^4}{(1-\epsilon)(1+4\epsilon)^4}$	$A + 3B \rightleftharpoons C$	$\dfrac{\epsilon(4-3\epsilon)^3}{27(1-\epsilon)^4 P^3}$
$A \rightleftharpoons 3C + 3D$	$\dfrac{729\epsilon^6 P^5}{(1-\epsilon)(1+5\epsilon)^5}$	$A + 3B \rightleftharpoons 2C$	$\dfrac{4\epsilon^2(4-2\epsilon)^2}{27(1-\epsilon)^4 P^2}$
$2A \rightleftharpoons C + D$	$\dfrac{\epsilon^2}{4(1-\epsilon^2)}$	$A + 3B \rightleftharpoons 3C$	$\dfrac{\epsilon^3(4-\epsilon)}{(1-\epsilon)^4 P}$
$2A \rightleftharpoons C + 2D$	$\dfrac{\epsilon^3 P}{(1-\epsilon)^2(2+\epsilon)}$	$2A + 3B \rightleftharpoons C$	$\dfrac{\epsilon(5-4\epsilon)^4}{108(1-\epsilon)^5 P^4}$
$2A \rightleftharpoons C + 3D$	$\dfrac{27\epsilon^4 P^2}{16(1-\epsilon^2)^2}$	$2A + 3B \rightleftharpoons 2C$	$\dfrac{\epsilon^2(5-3\epsilon)^2}{27(1-\epsilon)^5 P^3}$
$2A \rightleftharpoons 2C + 3D$	$\dfrac{27\epsilon^5 P^3}{(1-\epsilon)^2(2+3\epsilon)^3}$	$2A + 3B \rightleftharpoons 3C$	$\dfrac{\epsilon^3(5-2\epsilon)^2}{4(1-\epsilon)^5 P^2}$
$2A \rightleftharpoons 3C + 3D$	$\dfrac{729\epsilon^6 P^4}{4(1-\epsilon)^2(2+4\epsilon)^4}$	$3A + 3B \rightleftharpoons C$	$\dfrac{\epsilon(6-5\epsilon)^5}{729(1-\epsilon)^6 P^5}$
$3A \rightleftharpoons C + D$	$\dfrac{\epsilon^2(3-\epsilon)}{27(1-\epsilon)^3 P}$	$3A + 3B \rightleftharpoons 2C$	$\dfrac{4\epsilon^2(6-4\epsilon)^4}{729(1-\epsilon)^6 P^4}$
$3A \rightleftharpoons C + 2D$	$\dfrac{4\epsilon^3}{27(1-\epsilon)^3}$	$A + B \rightleftharpoons C + D$	$\dfrac{\epsilon^2}{(1-\epsilon)^2}$

TABLE 4b-11. EQUILIBRIUM CONSTANTS EXPRESSED AS FUNCTIONS OF P AND ϵ (Continued)

Reaction	K	Reaction	K
$A + B \rightleftharpoons C + 2D$	$\dfrac{4\epsilon^3 P}{(1 - \epsilon)^2(2 + \epsilon)}$	$A + 3B \rightleftharpoons C + 2D$	$\dfrac{4\epsilon^3(4 - \epsilon)}{27(1 - \epsilon)^4 P}$
$A + B \rightleftharpoons 2C + 2D$	$\dfrac{4\epsilon^4 P^2}{(1 - \epsilon)^2(1 + \epsilon)^2}$	$A + 3B \rightleftharpoons 2C + 2D$	$\dfrac{16\epsilon^4}{27(1 - \epsilon)^4}$
$A + B \rightleftharpoons C + 3D$	$\dfrac{27\epsilon^4 P^2}{4(1 - \epsilon)^2(1 + \epsilon)^2}$	$A + 3B \rightleftharpoons C + 3D$	$\dfrac{\epsilon^4}{(1 - \epsilon)^4}$
$A + B \rightleftharpoons 2C + 3D$	$\dfrac{108\epsilon^5 P^3}{(1 - \epsilon)^2(2 + 3\epsilon)^3}$	$A + 3B \rightleftharpoons 2C + 3D$	$\dfrac{4\epsilon^5 P}{(1 - \epsilon)^4(4 + \epsilon)}$
$A + B \rightleftharpoons 3C + 3D$	$\dfrac{729\epsilon^6 P^4}{16(1 - \epsilon)^2(1 + 2\epsilon)^4}$	$A + 3B \rightleftharpoons 3C + 3D$	$\dfrac{27\epsilon^6 P^2}{4(1 - \epsilon)^4(2 + \epsilon)^2}$
$A + 2B \rightleftharpoons C + D$	$\dfrac{\epsilon^2(3 - \epsilon)}{4(1 - \epsilon)^3 P}$	$2A + 3B \rightleftharpoons C + D$	$\dfrac{\epsilon^2(5 - 3\epsilon)^3}{108(1 - \epsilon)^5 P^3}$
$A + 2B \rightleftharpoons C + 2D$	$\dfrac{\epsilon^3}{(1 - \epsilon)^3}$	$2A + 3B \rightleftharpoons C + 2D$	$\dfrac{\epsilon^3(5 - 2\epsilon)^2}{27(1 - \epsilon)^5 P^2}$
$A + 2B \rightleftharpoons 2C + 2D$	$\dfrac{4\epsilon^4 P}{(1 - \epsilon)^3(3 + \epsilon)}$	$2A + 3B \rightleftharpoons 2C + 2D$	$\dfrac{4\epsilon^4(5 - \epsilon)}{27(1 - \epsilon)^5 P}$
$A + 2B \rightleftharpoons C + 3D$	$\dfrac{27\epsilon^4 P}{4(1 - \epsilon)^3(3 + \epsilon)}$	$2A + 3B \rightleftharpoons C + 3D$	$\dfrac{\epsilon^4(5 - \epsilon)}{4(1 - \epsilon)^5 P}$
$A + 2B \rightleftharpoons 2C + 3D$	$\dfrac{27\epsilon^5 P^2}{(1 - \epsilon)^3(3 + 2\epsilon)^2}$	$2A + 3B \rightleftharpoons 2C + 3D$	$\dfrac{\epsilon^5}{(1 - \epsilon)^5}$
$A + 2B \rightleftharpoons 3C + 3D$	$\dfrac{27\epsilon^6 P^3}{4(1 - \epsilon)^3(1 + \epsilon)^3}$	$2A + 3B \rightleftharpoons 3C + 3D$	$\dfrac{27\epsilon^6 P}{4(1 - \epsilon)^5(5 + \epsilon)}$
$2A + 2B \rightleftharpoons C + D$	$\dfrac{\epsilon^2(2 - \epsilon)^2}{4(1 - \epsilon)^4 P^2}$	$3A + 3B \rightleftharpoons C + D$	$\dfrac{16\epsilon^2(3 - 2\epsilon)^4}{729(1 - \epsilon)^6 P^4}$
$2A + 2B \rightleftharpoons C + 2D$	$\dfrac{\epsilon^3(4 - \epsilon)}{4(1 - \epsilon)^4 P}$	$3A + 3B \rightleftharpoons C + 2D$	$\dfrac{4\epsilon^3(2 - \epsilon)^3}{27(1 - \epsilon)^6 P^3}$
$2A + 2B \rightleftharpoons C + 3D$	$\dfrac{27\epsilon^4}{16(1 - \epsilon)^4}$	$3A + 3B \rightleftharpoons 2C + 2D$	$\dfrac{64\epsilon^4(3 - \epsilon)^2}{729(1 - \epsilon)^6 P^2}$
$2A + 2B \rightleftharpoons 2C + 3D$	$\dfrac{27\epsilon^5 P}{4(1 - \epsilon)^4(4 + \epsilon)}$	$3A + 3B \rightleftharpoons C + 3D$	$\dfrac{4\epsilon^4(3 - \epsilon)^2}{27(1 - \epsilon)^6 P^2}$
$2A + 2B \rightleftharpoons 3C + 3D$	$\dfrac{729\epsilon^6 P^2}{64(1 - \epsilon)^4(2 + \epsilon)^2}$	$3A + 3B \rightleftharpoons 2C + 3D$	$\dfrac{4\epsilon^5(6 - \epsilon)}{27(1 - \epsilon)^6 P}$
$A + 3B \rightleftharpoons C + D$	$\dfrac{4\epsilon^2(2 - \epsilon)^2}{27(1 - \epsilon)^4 P^2}$		