Thermodynamics of Enzyme-Catalyzed Reactions: Part 4. Lyases

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Equilibrium constants and enthalpy changes for reactions catalyzed by the lyase class of enzymes have been compiled. For each reaction the following information is given: the reference for the data; the reaction studied; the name of the enzyme used and its Enzyme Commission number; the method of measurement; the conditions of measurement (temperature, pH, ionic strength, and the buffer(s) and cofactor(s) used); the data and an evaluation of it; and, sometimes, commentary on the data and on any corrections which have been applied to it or any calculations for which the data have been used. The data from 106 references have been examined and evaluated. Chemical Abstract Service registry numbers are given for the substances involved in these various reactions. There is a cross reference between the substances and the Enzyme Commission numbers of the enzymes used to catalyze the reactions in which the substances participate. © *1995 American Institute of Physics and American Chemical Society.*

Key words: apparent equilibrium constants; enthalpies of reaction; enzyme-catalyzed reactions; evaluated data; lyases; transformed thermodynamic properties.

Contents

1. Introduction

This article is a continuation of the first three reviews in this series[1–3] that dealt, respectively, with the thermodynamics of the reactions catalyzed by the oxidoreductases, transferases, and hydrolases. These are the first three classes of enzymes classified by the Nomenclature Committee of the International Union of Biochemistry.[4] In the current review a critical compilation of thermodynamic data is provided for the reactions catalyzed by the fourth class of enzymes—the lyases. These reactions play significant roles in metabolic processes such as glycolysis, the glyoxylic pathway, and the Kreb's or citric acid cycle. There is also interest in many of these reactions due to their importance in the utilization of biomass; an example here is the production of succinic acid from glucose. The data presented herein is limited to equilibrium and calorimetric measurements performed on these reactions under *in vitro* conditions. The thermodynamic quantities that are generally given are apparent equilibrium constants K' and calorimetrically determined enthalpies of reaction $\Delta_r H$(cal). Apparent equilibrium constants calculated from kinetic data are also tabulated. If the change in binding of hydrogen ion $\Delta_r N(H^+)$ in a biochemical reaction is known, the standard transformed enthalpy of reaction $\Delta_r H'^\circ$ can be calculated from the calorimetrically determined enthalpy of reaction.[5] Equilibrium constants K and standard molar enthalpies of reaction $\Delta_r H^\circ$ for chemical reference reactions are also given if they have been reported in the literature. The standard transformed enthalpy of reaction $\Delta_r H'^\circ$ can be used to calculate the temperature dependence of apparent equilibrium constants K' in the same way that the standard enthalpy of reaction $\Delta_r H^\circ$ is used to calculate the temperature dependence of the equilibrium constant K.

The data are presented in the same format as in Parts 1 to 3.[1–3] Thus, the following information is given for each entry in this review: the reference for the data; the biochemical reaction studied; the recommended name[4] of the enzyme used and its Enzyme Commission number; the method of measurement; the conditions of measurement (temperature, pH, ionic strength, and the buffer(s) and cofactor(s) used); the data and its evaluation; and, sometimes, commentary on the data and on any corrections that have been applied or any calculations for which the data have been used. The absence of a piece of information indicates that it was not found in the cited paper. The arrangement of the data, its evaluation, and the thermodynamic conventions have been discussed previously.[1] One should note that equilibrium constants should be expressed as dimensionless quantities. However, the numerical value obtained for the equilibrium constant of an unsymmetrical reaction will depend upon the measure of composition and standard concentration selected for the reactants and products. Thus, for the chemical reaction

$$A(aq)=B(aq)+C(aq), \qquad (1)$$

$K_c=c(B)c(C)/\{c(A)c^\circ\}$, $K_m=m(B)m(C)/\{m(A)m^\circ\}$, and $K_x=x(B)x(C)/x(A)$. Here, c, m, and x are, respectively, concentration, molality, and mole fraction, $c^\circ=1$ mol dm^{-3}, and $m^\circ=1$ mol kg^{-1}. The equilibrium constant expressed in terms of mole fractions is automatically dimensionless. Similar definitions and considerations apply to the apparent equilibrium constant K'. The symbols used in this review are given in the Glossary (see Section 8).

The subjective evaluation of the data in this review consisted of the assignment of a rating: A (high quality), B (good), C (average), or D (low quality). In making these assignments we considered the various experimental details which were provided in the study. These details include the method of measurement, the number of data points determined, and the extent to which the effects of varying temperature, pH, and ionic strength were investigated. A low rating was generally given when few details of the investigation were reported. For example, in many of the papers cited, the major aim of the study was the isolation and purification of the enzyme of interest. Thus, the equilibrium data

were obtained as only a small part of an investigation to characterize many of the properties of that enzyme and the reaction it catalyzes.

This effort has been given additional impetus by the recent completion of the IUBMB–IUPAC document "Recommendations for Nomenclature and Tables in Biochemical Thermodynamics".[6] The work described in this review paper has also been accepted by the Thermodynamics Commission (1.2) and by the Steering Committee on Biophysical Chemistry of IUPAC as a project of particular timeliness and importance. The project has therefore been conducted under the auspices of these bodies, has been endorsed by them, and has been written to be consistent with recommended IUPAC nomenclature.

2. Some Aspects and Uses of Thermodynamic Data on Biochemical Reactions

While a full discussion of the applications of thermodynamic data would be beyond the scope of this review, it seems useful to indicate briefly the utility of the information presented. A primary motivation for performing thermodynamic studies on biochemical reactions is to determine the position of equilibrium of the reaction(s) studied as well as to establish definitely the substrates that participate in the biochemical reaction(s). This information is concisely summarized in terms of the apparent equilibrium constants given herein. These apparent equilibrium constants can be conveniently used to calculate the extent of reaction under the stated set of conditions and therefore are very useful to engineers concerned with the optimization of product yield in bioreactors. The enthalpy changes accompanying these reactions are also required and determine how much heating or cooling is required to maintain a bioreactor at its proper temperature. To perform this calculation one must know both the standard transformed enthalpy of reaction $\Delta_r H'^\circ$, the change in binding of the hydrogen ion $\Delta_r N(H^+)$, and the enthalpy of protonation of the buffer(s) in the bioreactor. In general, both $\Delta_r H'^\circ$ and $\Delta_r N(H^+)$ are functions of temperature, pH, ionic strength, and the concentration of free metal ion(s).

Apparent equilibrium constants obtained from studies of *in vitro* systems can also be used to calculate the position of equilibrium in metabolic processes involving several reactions. Glycolysis is probably the best example of an enzymatic process where data are available and for which such calculations have been performed.[7,8] The results of these calculations can then be compared with information on the concentrations of the various substrates obtained from the analysis of *in vivo* systems. This comparison can provide valuable insight into the chemical machinery of living systems.

For many biochemical reactions, the apparent equilibrium constant is a function of temperature, pH, pX, and ionic strength. Therefore, when performing Hess' Law and thermochemical cycle calculations, it is necessary that the data for all of the reactions in such a calculation refer to the same set of conditions. The dependencies of apparent equilibrium constants and standard transformed enthalpies of reaction on the conditions of reaction can be very complex. Also, the reduction of such results to a common standard state generally requires auxiliary information on the binding of protons and metal ions to the various reactants as well as information on or assumptions about the activity coefficients of the species in solution. These types of calculations have been performed by Kuby and Noltmann,[9] Alberty,[10,11] Guynn, Gelberg, and Veech,[12] Langer *et al.*,[13] Goldberg and Tewari,[14] and others.

For some reactions, none of the reactants or products in a given biochemical reaction have ionizable groups or bind metal ions under the conditions of the study. In such a case, and when there are no hydrogen or metal ions as reactants in the chemical reference reaction, the thermodynamic quantities for the chemical reference reaction correspond directly to the transformed thermodynamic quantities for the overall biochemical reaction. For example, the biochemical reaction for the hydrolysis of sucrose to D-glucose and D-fructose is:

$$\text{sucrose(aq)} + H_2O(l) = \text{D-glucose(aq)} + \text{D-fructose(aq)}. \quad (1)$$

A chemical reference reaction involving specific species is:

$$\text{sucrose}^0\text{(aq)} + H_2O(l) = \text{D-glucose}^0\text{(aq)} + \text{D-fructose}^0\text{(aq)}. \quad (2)$$

Here, the charges of the reference species have been specified to distinguish these species from the biochemical reactants which, in principle, can consist of a mixture of pseudoisomer species.[8] Since the extent of ionization of these sugars for pH<10 is negligible, sucrose^0, D-glucose^0, and D-fructose^0 are the predominant species and for pH<10, $K'(1)=K(2)$, $\Delta_r H'^\circ(1)=\Delta_r H^\circ(2)$, and $\Delta_r G'^\circ(1)=\Delta_r G^\circ(2)$. Also, since $\Delta_r N(H^+)=0$ for reaction (2), $\Delta_r H(\text{cal})=\Delta_r H'^\circ(2)$.

Tables of standard formation properties[15] have proven to be a useful way of generalizing upon and presenting thermodynamic data for many chemical substances. However, tables of this type have been prepared for only limited classes of biochemical substances.[16–18] It has recently been shown[19] how it is possible to prepare tables of standard transformed formation properties for biochemical reactants (i.e., sums of species) as distinct from standard formation properties for individual biochemical species. The adenosine 5′-triphosphate series was used as a prototype for this purpose. Thus, it appears likely and desirable that several different types of thermodynamic tables will eventually appear in the literature. Clearly, the larger the scope of such tables, the more useful they are for calculating thermodynamic quantities for reactions which have not been the subject of a direct investigation.

3. Acknowledgments

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5. Table of Equilibrium Constants and Enthalpies of Reaction

5.1 Enzyme: phospho*enol*pyruvate carboxykinase (GTP) (EC 4.1.1.32)

ITP(aq)+oxaloacetate(aq)+H_2O(l)=IDP(aq)+phospho*enol*pyruvate(aq)+carbon dioxide(aq)

T/K	pH	K'_c
303.15	7.6	≈12

Reference: 54UTT/KUR
Method: chromatography and enzymatic assay
Buffer: acetate (0.050 mol dm^{-3})
pH: 7.6
Cofactor(s): $MnCl_2$ (0.002 mol dm^{-3})
Evaluation: C

The apparent equilibrium constant given here was calculated from the data given in Utter and Kurahashi's Table VIII.

ITP(aq)+oxaloacetate(aq)+H_2O(l)=IDP(aq)+phospho*enol*pyruvate(aq)+carbon dioxide(ac

T/K	pH	$c(MnCl_2)$/mol dm^{-3}	I_c/mol dm^{-3}	K'_c
298.15	7.80	0.0020	0.1	1.7
298.15	7.06	0.0025	0.1	0.50
298.15	7.03	0.0025	0.1	0.71

Reference: 66WOO/DAV
Method: spectrophotometry and enzymatic assay
Buffer: Tris (0.010 mol dm^{-3})+HCl
pH: 7.03–7.80
Cofactor(s): $MnCl_2$
Evaluation: A

Wood *et al.* also calculated K_c=4.5E-8 at T=298.15 K and I=0.1 mol dm^{-3} for the chemical reference reaction: ITP^{4-}(aq)+oxaloacetate^{2-}(aq)= IDP^{3-}(aq)+phospho*enol*pyruvate^{3-}(aq)+HCO_3^-(aq)+H^+(aq).

5.2. Enzyme: phospho*enol*pyruvate carboxykinase (diphosphate) (EC 4.1.1.38)

diphosphate(aq)+oxaloacetate(aq)+H_2O(l)=phosphate(aq)+phospho*enol*-pyruvate(aq)+carbon dioxide(aq)

T/K	pH	I_c/mol dm^{-3}	K'_c
298.15	6.5	0.1	0.013

Reference: 66WOO/DAV
Method: spectrophotometry and enzymatic assay
Buffer: carbonate+bicarbonate
pH: 6.5
Cofactor(s): $MgCl_2$ (0.0024 mol dm^{-3})
Evaluation: A

5.3. Enzyme: ribulose-biphosphate carboxylase (EC 4.1.1.39)

D-ribulose, 1,5-biphosphate(aq)+carbon dioxide(aq)=2 3-phospho-D-glycerate(aq)

T/K	pH	Buffer	$\Delta_r H$(cal)/kJ mol^{-1}
298.15	8.0	Tris+HCl	−61.1
298.15	8.0	triethanolamine	−43.1

Reference: 56KIT/HOR
Method: microcalorimetry
Buffer: Tris (0.1 mol dm^{-3})+HCl and triethanolamine
pH: 8.0
Evaluation: C

The temperature is assumed to be 298.15 K. After correction for the enthalpies of buffer protonation, Kitzinger *et al.* calculated $\Delta_r H'^{\circ}$ (T=298.15 K, pH=8.0)=−20.1 kJ mol^{-1}.

5.4. Enzyme: ketotetraose-phosphate aldolase (EC 4.1.2.2)

erythrulose 1-phosphate(aq)=formaldehyde(aq)+glycerone phosphate(aq)

T/K	pH	K'_c
301.15	7.4	4.3E-4

Reference: 54CHA
Method: radioactivity
Buffer: NH_4OH
pH: 7.4
Cofactor(s): $MgCl_2$ (0.075 mol dm^{-3})
Evaluation: B

The apparent equilibrium constant given here was calculated from the data given in Charalampous' Table III.

5.5. Enzyme: deoxyribose-phosphate aldolase (EC 4.1.2.4)

2-deoxy-D-ribose 5-phosphate(aq)=D-glyceraldehyde 3-phosphate(aq) + acetaldehyde(aq)

T/K	pH	K'_c
310.15	6.3	2.35E-4

Reference: 60PRI/HOR
Method: enzymatic assay, chemical analysis, and spectrophotometry
Buffer: malcate (0.025 mol dm^{-3})
pH: 6.3
Evaluation: B

2-deoxy-D-ribose 5-phosphate(aq)=D-glyceraldehyde 3-phosphate(aq) +acetaldehyde(aq)

T/K	pH	K'_c
295.15	7.5	2.5E-4

Reference: 67GRO
Method: spectrophotometry
Buffer: Tris (0.005 mol dm^{-3})
pH: 7.5
Evaluation: B

5.6. Enzyme: fructose-biphosphate aldolase (EC 4.1.2.13)

5,6-dideoxyfructose 1-phosphate(aq)=glycerone phosphate(aq) +propionaldehyde(aq)

T/K	pH	K'_c
310.15	7.0	6.9E-4

Reference: 55LEH/SIC
pH: 7.0
Evaluation: C

D-fructose 1,6-bisphosphate(aq)=glycerone phosphate(aq) +D-glyceraldehyde 3-phosphate(aq)

T/K	pH	K'_c
301.15	7.2	6.0E-5
311.15	7.2	1.19E-4
311.15	7.33	1.22E-4
321.15	7.2	2.34E-4

Reference: 40HER/GOR
Buffer: borate (0.8 mol dm^{-3})
pH: 7.2–7.33
Evaluation: C

Herbert *et al.* also calculated $\Delta_r H'^\circ$ ($\bar{T}$=311 K, pH=7.2)=55 kJ mol^{-1}.

D-fructose 1,6-bisphosphate(aq)=glycerone phosphate(aq) +D-glyceraldehyde 3-phosphate(aq)

T/K	pH	K'_c
303.15	7	8.0E-5
311.15	7	1.5E-4
313.15	7	1.1E-4
333.15	7	4.5E-4

Reference: 43MEY/JUN
Method: chemical analysis and polarimetry
pH: 7
Evaluation: B

These measurements were performed in the absence of a buffer but near pH=7. From the temperature dependence of the apparent equilibrium constant we calculate $\Delta_r H'^\circ$ ($\bar{T}$=318 K, pH≈7)≈48 kJ mol^{-1}.

D-fructose 1,6-bisphosphate(aq)=glycerone phosphate(aq) +D-glyceraldehyde 3-phosphate(aq)

T/K	pH	K'_c
310.15	7.0	1.18E-4

Reference: 55LEH/SIC
pH: 7.0
Evaluation: C

D-fructose 1,6-bisphosphate(aq)=glycerone phosphate(aq) +D-glyceraldehyde 3-phosphate(aq)

T/K	pH	K'_c
311.15	7.1	9.3E-5

Reference: 64LOW/PAS
Method: fluorimetry
Buffer: imidazole (0.020 mol dm^{-3})
pH: 7.1
Cofactor(s): $MgCl_2$ (0.005 mol dm^{-3})
Evaluation: A

D-fructose 1,6-bisphosphate(aq)=glycerone phosphate(aq)
+D-glyceraldehyde 3- phosphate(aq)

$\frac{T}{K}$	pH	$\frac{c(MgCl_2)}{mol\ dm^{-3}}$	K'_c
311.15	≈6.7	0.005	9.9E-5
311.15	≈6.7	0.050	5.6E-5

Reference: 69VEE/RAI
Method: spectrophotometry
Buffer: sodium phosphate (0.010 mol dm^{-3})
pH: 6.35–7.12
Cofactor(s): $MgCl_2$
Evaluation: A

D-fructose 1,6-bisphosphate(ag)=glycerone phosphate(aq)
+D-glyceraldehyde 3-phosphate(aq)

$\frac{T}{K}$	pH	K'_c
282.15	8.8	6.4E-5
296.15	8.8	3.90E-4
303.15	8.8	6.10E-4
313.15	8.8	5.20E-4

Reference: 75KUR/KON
Buffer: Tris+acetate
pH: 8.8
Evaluation: C

From the temperature dependence of the apparent equilibrium constant we calculate $\Delta_r H'^\circ$ ($\bar{T}$=298 K, pH=8.8)≈53 kJ mol^{-1}.

D-fructose 1-phosphate(aq)=D-glyceraldehyde(aq)
+glycerone phosphate(aq)

$\frac{T}{K}$	$\frac{\Delta_r H(cal)}{kJ\ mol^{-1}}$
298.15	−60.2

Reference: 36MEY/SCH
Method: calorimetry
Buffer: phosphate
Evaluation: C

Meyerhof and Schulz also performed measurements using the racemic mixture of D- and L-glyceraldehyde. The result was $\Delta_r H$(cal)=−63.2 kJ mol^{-1}. The pH was not reported.

D-fructose 1-phosphate(aq)=D-glyceraldehyde(aq)
+glycerone phosphate(aq)

$\frac{T}{K}$	pH	K'_c
310.15	7.0	2.8E-6

Reference: 55LEH/SIC
pH: 7.0
Evaluation: C

D-fructose 1-phosphate(aq)=D-glyceraldehyde(aq)
+glycerone phosphate(aq)

$\frac{T}{K}$	pH	K'_c
282.15	8.8	2.1E-6
296.15	8.8	4.1E-6
303.15	8.8	6.2E-6
313.15	8.8	2.8E-6

Reference: 75KUR/KON
Buffer: Tris+acetate
pH: 8.8
Evaluation: C

From the temperature dependence of the apparent equilibrium constant we calculate $\Delta_r H'^\circ$ ($\bar{T}$=298 K, pH=8.8)≈11 kJ mol^{-1}.

methylerythrulose 1-phosphate(aq)=acetaldehyde(aq)
+glycerone phosphate(aq)

$\frac{T}{K}$	K'_c
273.15	0.0021
293.15	0.0029
313.15	0.0067

Reference: 36MEY/LOH
Method: chemical analysis
Buffer: phosphate
Evaluation: C

The approximate values of the apparent equilibrium constants given here were calculated from the results given in Meyerhof *et al.*'s Tables I and II. The pH was not reported.

D-fructose 1,6-bisphosphate(aq)=2 glycerone phosphate(aq)

$\frac{T}{K}$	pH	K'_c
266.15	7	0.00018
273.15	7	0.00030
293.15	7	0.0015
333.15	7	0.013
343.15	7	0.022

Reference: 34MEY/LOH
Method: spectrophotometry
pH: ≈7
Evaluation: C

From the temperature dependence of K'_c we calculate $\Delta_r H'^\circ$ ($\bar{T}$=255 K, pH=7)=47 kJ mol^{-1}.

D-fructose 1,6-bisphosphate(aq)=2 glycerone phosphate(aq)

$\frac{T}{K}$	pH	Salt	$\frac{c(\text{salt})}{\text{mol dm}^{-3}}$	K'_c
273.15	7	none	···	0.00032
293.15	7	none	···	0.0015
313.15	7	none	···	0.0064
333.15	7	none	···	0.019
293.15	7	NaCl	0.043	0.0011
293.15	7	NaCl	0.21	0.00075
293.15	7	NaCl	0.90	0.00047
293.15	7	Na_2SO_4	0.2	0.00055
293.15	7	$MgCl_2$	0.06	0.00035
293.15	7	$MgCl_2$	0.12	0.00035
293.15	7	$MgCl_2$	0.24	0.00035
273.15	7	$MgCl_2$	0.12	0.000071
293.15	7	$MgCl_2$	0.12	0.00029
333.15	7	$MgCl_2$	0.12	0.0012
273.15	7	$MgCl_2$	0.006	0.00014
293.15	7	$MgCl_2$	0.06	0.00037
293.15	7	$MgCl_2$	0.031	0.00031
293.15	7	$MgCl_2$	0.012	0.00051
293.15	7	$MgCl_2$	0.006	0.00064
293.15	7	$MgCl_2$	0.0025	0.0011
293.15	7	$MgCl_2$	0.0012	0.0014
313.15	7	$MgCl_2$	0.031	0.0014
313.15	7	$MgCl_2$	0.012	0.0020
313.15	7	$MgCl_2$	0.006	0.0025
313.15	7	$MgCl_2$	0.0012	0.0056
333.15	7	$MgCl_{22}$	0.031	0.0046
333.15	7	$MgCl_2$	0.012	0.0056
333.15	7	$MgCl_2$	0.006	0.0082
333.15	7	$MgCl_2$	0.0012	0.015

Reference: 35MEY
Method: spectrophotometry
pH: ≈7
Evaluation: C

Triose-phosphate isomerase (EC 5.3.1.1) was also present. The pH was not well controlled in this study. From the temperature dependence of the apparent equilibrium constant we calculate $\Delta_r H'^\circ$ ($\bar{T}$=303 K, pH≈7)=52 kJ mol^{-1}.

D-fructose 1,6-bisphosphate(aq)=2 glycerone phosphate(aq)

$\frac{T}{K}$	$\frac{\Delta_r H(\text{cal})}{\text{kJ mol}^{-1}}$
293.15	58
313.15	64

Reference: 35MEY/LOH
Method: calorimetry
Buffer: phosphate
Evaluation: C

Triose-phosphate isomerase (EC 5.3.1.1) was also present.

D-fructose 1,6-bisphosphate(aq)=2 glycerone phosphate(aq)

$\frac{T}{K}$	pH	K'_c
278.15	9.0	4.35E-4
298.15	9.0	1.82E-3
313.15	9.0	6.37E-3

Reference: 41UTT/WER
Method: chemical analysis
Buffer: glycine+NaOH
pH: 9.0
Cofactor(s): $MgCl_2$
Evaluation: B

Triose-phosphate isomerase (EC 5.3.1.1) was also present. From the temperature dependence of the apparent equilibrium constant we calculate $\Delta_r H'^\circ$ ($\bar{T}$=296 K, pH=9.0)≈55 kJ mol^{-1}.

D-fructose 1,6-bisphosphate (ag)=2 glycerone phosphate(aq)

$\frac{T}{K}$	pH	K'_c
303.15	7	0.0020
311.15	7	0.0024
313.15	7	0.0030
333.15	7	0.011

Reference: 43MEY/JUN
Method: chemical analysis and polarimetry
pH: 7
Evaluation: B

Triose-phosphate isomerase (EC 5.3.1.1) was also present. These measurements were performed in the absence of a buffer but near pH=7. From the temperature dependence of the apparent equilibrium constant we calculate $\Delta_r H'^\circ$ ($\bar{T}$=318 K, pH≈7)=50 kJ mol^{-1}

5.7. Enzyme: 2-dehydro-3-deoxyphosphogluconate aldolase (EC 4.1.2.14)

6-phospho-2-dehydro-3-deoxy-D-gluconate(aq)=pyruvate(aq) +D-glyceraldehyde 3-phosphate(aq)

$\frac{T}{K}$	pH	K'_c
298.15	6.8	1.6E-3

Reference: 62DOU/SHU
pH: 6.8
Evaluation: C

Few details were given in this Proceedings abstract.

6-phospho-2-dehydro-3-deoxy-D-gluconate(aq)=pyruvate(aq) +D-glyceraldehyde 3-phosphate(aq)

$\frac{T}{K}$	pH	K'_c
298.15	8.0	≈0.0012

Reference: 64MEL/WOO
Method: spectrophotometry and radioactivity
Buffer: imidazole
pH: 8.0
Evaluation: C

5.8. Enzyme: L-fuculose-phosphate aldolase (EC 4.1.2.17)

L-fuculose 1-phosphate(aq)=glycerone phosphate(aq) +(*S*)-lactaldehyde(aq)

$\frac{T}{K}$	pH	K'_c
310.15	7.2	4.6E-4

Reference: 62GHA/HEA
Method: spectrophotometry
Buffer: Tris (0.05 mol dm^{-3})
pH: 7.2
Evaluation: C

5.9. Enzyme: 2-dehydro-3-deoxy-L-pentonate aldolase (EC 4.1.2.18)

2-dehydro-3-deoxy-D-fuconate(aq)=pyruvate(aq)+(*S*)-lactaldehyde(aq)

$\frac{T}{K}$	pH	K'_c
301.15	7.5	1.2E-4

Reference: 72DAH/AND
Method: enzymatic assay and spectrophotometry
Buffer: Hepes (0.012 mol dm^{-3})
pH: 7.5
Cofactor(s):$MnCl_2$ (0.0038 mol dm^{-3})
Evaluation: B

2-dehydro-3-deoxy-L-pentonate(aq)=pyruvate(aq)+glycolaldehyde(aq)

$\frac{T}{K}$	pH	K'_c
301.15	7.4	3.7E-4

Reference: 69DAH/AND
Method: enzymatic assay and spectrophotometry
Buffer: Hepes (0.015 mol dm^{-3})
pH: 7.4
Cofactor(s): $MnCl_2$ (0.005 mol dm^{-3})
Evaluation: B

5.10. Enzyme: rhamnulose-1-phosphate aldolase (EC 4.1.2.19)

L-rhamnulose 1-phosphate(aq)=glycerone phosphate(aq)
+(*S*)-lactaldehyde(aq)

$\frac{T}{K}$	pH	K'_c
310.15	7.5	0.083

Reference: 65CHI/FEI
Method: spectrophotometry
Buffer: glycylglycine
pH: 7.5
Evaluation: C

5.11. Enzyme: 2-dehydro-3-deoxy-6-phosphogalactonate aldolase (EC 4.1.2.21)

2-dehydro-3-deoxy-D-galactonate 6-phosphate(aq)=pyruvate(aq)
+D-glyceraldehyde 3-phosphate(aq)

$\frac{T}{K}$	pH	K'_c
298.15	6.8	3.7E-3

Reference: 62DOU/SHU
Method: spectrophotometry
pH: 6.8
Evaluation: C

Few details were given in this Proceedings abstract. Also see [66SHU].

5.12. Enzymes: D-arabino-3-hexulose phosphate formaldehyde lyase (EC 4.1.2.0)

D-arabino-3-hexulose 6-phosphate(aq)=D-ribulose 5-phosphate(aq)
+formaldehyde(aq)

$\frac{T}{K}$	pH	K'_c
303.15	7.0	4.0E-5

Reference: 74FER/STR
Method: enzymatic assay and spectrophotometry
Buffer: phosphate (0.05 mol dm^{-3})
pH: 7.0
Cofactor(s): $MgCl_2$ (0.005 mol dm^{-3})
Evaluation: B

5.13. Enzyme: isocitrate lyase (EC 4.1.3.1)

isocitrate(aq)=succinate(aq)+glyoxylate(aq)

$\frac{T}{K}$	pH	K'_c
300.15	7.6	0.029

Reference: 56SMI/STA
Method: chemical analysis and enzymatic assay
Buffer: Tris (0.05 mol dm^{-3})
pH: 7.6
Cofactor(s): $MgCl_2$ (0.002 mol dm^{-3})
Evaluation: B

isocitrate(aq)=succinate(aq)+glyoxylate(aq)

$\frac{T}{K}$	pH	K'_c
300.15	7.6	0.029

Reference: 57SMI/GUN
Method: spectrophotometry
Buffer: Tris (0.067 mol dm^{-3})
pH: 7.6
Cofactor(s): $MgCl_2$ (0.002 mol dm^{-3})
Evaluation: B

isocitrate(aq)=succinate(aq)+glyoxylate(aq)

$\frac{T}{K}$	pH	K'_c
303.15	7.7	0.0023

Reference: 71WIL/ROC
Method: spectrophotometry
Buffer: Mops (0.10 mol dm^{-3})+NaOH
pH: 7.7
Cofactor(s): $MgCl_2$ (0.003 mol dm^{-3})
Evaluation: B

Williams *et al.* also obtained K' (T=303.15 K, pH=7.7)≈0.0016 from kinetic data.

5.14 Enzyme: malate synthase (EC 4.1.3.2)

(*S*)-malate(aq)+CoA(aq)=acetyl-CoA(aq)+H_2O(l)+glyoxylate(aq)

$\frac{T}{K}$	pH	K'
298.15	8.5	29

Reference: 62GOL/WAG
Method: spectrophotometry
Buffer: Tris (0.04 mol dm^{-3})
pH: 8.5
Cofactor(s): $MgCl_2$ (0.006 mol dm^{-3})
Evaluation: C

Goldman *et al.* report $\{K'c(H_2O)\}^{-1}=0.00063$. The apparent equilibrium constant given here was calculated from this result.

5.15 Enzyme: *N*-acetylneuraminate lyase (EC 4.1.3.3)

N-acetylneuraminate(aq)=*N*-acetyl-D-mannosamine(aq)+pyruvate(aq)

$\frac{T}{K}$	pH	K'_c
310.15	7.1	0.064

Reference: 60COM/ROS
Method: spectrophotometry
Buffer: phosphate (0.1 mol dm^{-3})
pH: 7.1
Evaluation: C

5.16. Enzyme: citrate *(pro-3S)*-lyase (EC 4.1.3.6)

citrate(aq)=acetate(aq)+oxaloacetate(aq)

$\frac{T}{K}$	pH	K'_c
300.15	7.6	0.64

Reference: 56SMI/STA
Method: chemical analysis
Buffer: Tris (0.05 mol dm^{-3})
pH: 7.6
Cofactor(s): $MnSO_4$ (0.002 mol dm^{-3})
Evaluation: B

citrate(aq)=acetate(aq)+oxaloacetate(aq)

$\frac{T}{K}$	pH	K'_c
303.15	7.0	0.0637

Reference: 63HAR/COL
Method: spectrophotometry
Buffer: phosphate (0.13 mol dm^{-3})
pH: 7.0
Cofactor(s): Mg^{2+}
Evaluation: C

citrate(aq)=acetate(aq)+oxaloacetate(aq)

$\frac{T}{K}$	pH	$\frac{c(Mg^{2+})}{mol\ dm^{-2}}$	$\frac{I_c}{mol\ dm^{-3}}$	K'_c
298.15	8.4	0.00031	0.1	0.118
298.15	8.4	0.00032	0.1	0.138
298.15	8.4	0.00061	0.1	0.0592
298.15	8.4	0.00062	0.1	0.123
298.15	8.4	0.00063	0.1	0.0986
298.15	8.4	0.00063	0.1	0.0739
298.15	8.4	0.00069	0.1	0.0640
298.15	8.4	0.00101	0.1	0.0667
298.15	8.4	0.00136	0.1	0.0430
298.15	8.4	0.00165	0.1	0.0457
298.15	8.4	0.00378	0.1	0.0293
298.15	8.4	0.00609	0.1	0.0218
298.15	8.4	0.00855	0.1	0.0159
298.15	8.4	0.00858	0.1	0.0178
298.15	8.4	0.00892	0.1	0.0176
298.15	8.4	0.00932	0.1	0.0243
298.15	8.4	0.00966	0.1	0.0251
298.15	8.4	0.01097	0.1	0.0184

Reference: 65TAT/DAT
Method: chemical analysis and spectrophotometry
Buffer: triethanolamine+HCl
pH: 8.4
Cofactor(s): $MgCl_2$
Evaluation: A

Tate and Datta also calculated $K_c=0.325$ at $T=298.15$ K, $I_c=0.1$ mol dm^{-3} for the chemical reference reaction: $citrate^{3-}$(aq)= $acetate^{-}$(aq)+$oxaloacetate^{2-}$(aq).

citrate(aq)=acetate(aq)+oxaloacetate(aq)

$\frac{T}{K}$	pH	$\frac{c(MgSO_4)}{mol\ dm^{-3}}$	$\frac{I_c}{mol\ dm^{-3}}$	K'_c
311.15	7.0	0.010	0.25	0.168
311.15	7.0	0.00508	0.25	0.314
311.15	7.0	0.00201	0.25	0.592
311.15	7.0	0.00102	0.25	0.909
311.15	7.0	0.000116	0.25	0.877

Reference: 73GUY/GEL
Method: spectrophotometry
Buffer: potassium phosphate (0.025 mol dm^{-3})
pH: 7.0
Cofactor(s): $MgSO_4$
Evaluation: A

5.17. Enzyme: citrate *(si)*-synthase (EC 4.1.3.7)

oxaloacetate(aq)+acetyl-CoA(aq)+H_2O(l)=citrate(aq)+CoA(aq)

$\frac{T}{K}$	pH	$\frac{c(MgSO_4)}{mol\ dm^{-3}}$	$\frac{I_c}{mol\ dm^{-3}}$	K'
311.15	6.39	2.77E-3	0.25	0.290E6
311.15	6.42	2.77E-3	0.25	0.418E6
311.15	6.52	2.77E-3	0.25	0.409E6
311.15	6.75	2.77E-3	0.25	0.697E6
311.15	6.79	2.77E-3	0.25	0.595E6
311.15	6.82	2.77E-3	0.25	0.773E6
311.15	6.91	2.77E-3	0.25	0.733E6
311.15	7.05	2.77E-3	0.25	1.14E6
311.15	7.20	2.77E-3	0.25	1.23E6
311.15	7.22	2.77E-3	0.25	1.80E6
311.15	7.28	2.77E-3	0.25	1.73E6
311.15	7.10	0.01E-3	0.25	1.03E6
311.15	7.10	0.10E-3	0.25	1.09E6
311.15	7.09	1.00E-3	0.25	1.29E6
311.15	7.06	10.0E-3	0.25	3.11E6
311.15	7.00	20.0E-3	0.25	5.40E6
311.15	6.94	30.0E-3	0.25	6.75E6
311.15	6.81	2.77E-3	0.25	1.31E6
311.15	7.11	2.77E-3	0.25	2.26E6
311.15	7.08	2.77E-3	0.25	1.53E6
311.15	7.35	2.77E-3	0.25	2.42E6
311.15	6.36	2.77E-3	0.25	0.992E6
311.15	6.82	2.77E-3	0.25	1.34E6

Reference: 73GUY/GEL
Method: spectrophotometry
Buffer: potassium phosphate (0.025 mol dm^{-3})
pH: 6.39–7.28
Cofactor(s): $MgSO_4$
Evaluation: A

Guynn *et al.* also calculated K' (T=311.15 K, pH=7.0, $c(Mg^{2+})$=0, I=0.25 mol dm^{-3})=(2.24±0.11)E6.

(*S*)-malate(aq)+acetyl-CoA(aq)+NAD(aq)+H_2O(l)=citrate(aq)+CoA(aq)+NADH(aq)

$\frac{T}{K}$	pH	K'
295.15	6.25	0.480
295.15	7.20	10.8
295.15	7.60	101
295.15	8.20	599
295.15	8.70	5610

Reference: 52STE/OCH
Method: spectrophotometry
Buffer: potassium phosphate (0.025 mol dm^{-3})
pH: 6.25–8.70
Cofactor(s): $MgCl_2$ (0.003 mol dm^{-3})
Evaluation: B

Malate dehydrogenase (EC 1.1.1.37) was also present. The results given by Stern *et al.* in their Table III and Fig. 3 included the concentration of water as 55.5 mol dm^{-3}. The apparent equilibrium constants given here have been adjusted so that the activity of water is unity.

5.18. Enzyme: ATP citrate*(pro-3S)*-lyase (EC 4.1.3.8)

ATP(aq)+citrate(aq)+CoA(aq)=ADP(aq)+phosphate(aq)+acetyl-CoA(aq)+oxaloacetate(aq)

$\frac{T}{K}$	pH	K'_c
298.15	8.1	≈1.2

Reference: 67PLO/CLE
Method: radioactivity and paper chromatography
Buffer: Tris+HCl
pH: 8.1
Cofactor(s): $MgCl_2$
Evaluation: C

5.19. Enzyme: 4-hydroxy-2-oxoglutarate aldolase (EC 4.1.3.16)

4-hydroxy-2-oxoglutarate(aq)=pyruvate(aq)+glyoxylate(aq)

$\frac{T}{K}$	pH	K'_c
310.15	7.5	≈0.0037

Reference: 63KUR/FUK
Method: spectrophotometry
Buffer: potassium phosphate (0.075 mol dm^{-3})
pH: 7.5
Evaluation: C

The apparent equilibrium constant was calculated from the results given in Huratomi and Fukunaga's Table III. The apparent equilibrium constant they calculated (K'=0.73) appears to be in error.

4-hydroxy-2-oxoglutarate(aq)=pyruvate(aq)+glyoxylate(aq)

$\frac{T}{K}$	pH	K'_c
310.15	8.4	0.012

Reference: 64MAI/DEK
Method: spectrophotometry
Buffer: Tris (0.1 mol dm^{-3})+HCl
pH: 8.4
Cofactor(s): $MgCl_2$ (0.005 mol dm^{-3})
Evaluation: C

The apparent equilibrium constant given here is based on the percentages of the various substrates reported by Maitra and Dekker. Note that the apparent equilibrium constant calculated by Maitra and Dekker is in error by a factor of 1000.

4-hydroxy-2-oxoglutarate(aq)=pyruvate(aq)+glyoxylate(aq)

$\frac{T}{K}$	pH	K'_c
310.15	8.4	0.010

Reference: 67ROS/ADA
Method: enzymatic assay, spectrophotometry, and chemical analysis
Buffer: Tris (0.013 mol dm^{-3})
pH: 8.4
Evaluation: B

The apparent equilibrium constant given here was calculated from the data given in Rosso and Adams' Table III on the assumption that the total volume of solution in an experiment was 1.0 cm^3.

5.20. Enzyme: citramalate lyase (EC 4.1.3.22)

(*S*)-2-methylmalate(aq)=acetate(aq)+pyruvate(aq)

$\frac{T}{\mathrm{K}}$	pH	K'_c
298.15	7.4	8.3

Reference: 67BAR
Method: spectrophotometry
Buffer: potassium phosphate (0.05 mol dm^{-3})
pH: 7.4
Cofactor(s): $MgCl_2$ (0.050 mol dm^{-3})
Evaluation: C

(*S*)-2-methylmalate(aq)=acetate(aq)+pyruvate(aq)

$\frac{T}{\mathrm{K}}$	pH	$\frac{I_c}{\mathrm{mol\ dm^{-3}}}$	K'_c
298.15	7.4	0.845	0.151
298.15	7.4	0.648	0.212
298.15	7.4	0.399	0.188
298.15	7.4	0.306	0.207
298.15	7.4	0.212	0.211

Reference: 87BUC/MIL
Method: enzymatic assay and spectrophotometry
Buffer: phosphate (0.050 mol dm^{-3})
pH: 7.4
Cofactor(s): $MgCl_2$
Evaluation: A

Buckel and Miller also calculated $K_c=0.32$ at $T=298.15$ K and $I=0$ for the chemical reference reaction: (*S*)-2-methylmalate^{2-}(aq)= acetate$^-$(aq)+pyruvate$^-$(aq).

5.21. Enzyme: malyl-CoA lyase (EC 4.1.3.24)

(*R*,*S*)-malyl-CoA(aq)=acetyl-CoA(aq)+glyoxylate(aq)

$\frac{T}{\mathrm{K}}$	pH	K'_c
303.15	7.4	0.0029

Reference: 73HER
Buffer: Tris (0.05 mol dm^{-3})+HCl
pH: 7.4
Evaluation: B

5.22. Enzyme: 2,3-dimethylmalate lyase (EC 4.1.3.32)

2,3-dimethylmalate(aq)=propanoate(aq)+pyruvate(aq)

$\frac{T}{\mathrm{K}}$	pH	K'_c
298.15	8.0	0.50

Reference: 79PIR/LIL
Method: gas chromatography and spectrophotometry
Buffer: Tris (0.10 mol dm^{-3})
pH: 8.0
Cofactor(s): $MgCl_2$ (0.002 mol dm^{-3})
Evaluation: B

It is not clear which optical isomer of 2,3-dimethylmalate is the active one, although the (2*R*,3*S*) form seems likely.

5.23. Enzyme: tryptophanase (EC 4.1.99.1)

L-tryptophan(aq)+H_2O(l)=indole(aq)+pyruvate(aq)+ammonia(aq)

$\frac{T}{\mathrm{K}}$	pH	$\frac{I_m}{\mathrm{mol\ kg^{-1}}}$	K'_m
287.45	7.98	0.727	0.83E-4
287.45	7.98	0.726	0.89E-4
292.15	7.90	0.726	1.37E-4
292.15	7.91	0.725	1.54E-4
298.15	7.76	0.723	2.35E-4
298.15	7.77	0.722	2.28E-4
298.15	7.84	1.47	2.40E-4
298.15	7.85	1.47	2.77E-4
298.15	7.89	0.494	2.12E-4
298.15	7.97	0.494	2.22E-4
298.15	7.93	0.933	2.65E-4
298.15	7.93	0.934	2.61E-4
298.15	8.85	0.491	2.59E-4
298.15	8.85	0.491	2.23E-4
304.25	7.71	0.721	4.24E-4
304.25	7.71	0.721	3.59E-4
310.15	7.81	0.720	5.98E-4
310.15	7.81	0.720	5.71E-4
316.15	7.94	0.697	9.59E-4
316.15	7.92	0.703	10.1E-4

Reference: 94TEW/GOL
Method: HPLC
Buffer: potassium phosphate (0.10 mol kg^{-1})
pH: 7.76–8.85
Cofactor(s): pyridoxal 5-phosphate
Evaluation: A

Tewari and Goldberg also calculated $K_c=(1.05\pm0.13)$E-4, $\Delta_r G°=(22.71\pm0.33)$ kJ mol^{-1}, $\Delta_r H°=(62.0\pm2.3)$ kJ mol^{-1}, and $\Delta_r S°=(132\pm8)$ J K^{-1} mol^{-1} at $T=298.15$ K and $I=0$ for the chemical reference reaction: L-tryptophan(aq)+H_2O(l)=indole(aq) +pyruvate$^-$(aq) +NH_4^+(aq).

L-tryptophan(aq)+H_2O(l)=indole(aq)+pyruvate(aq)+ammonia(aq)

T/K	pH	I_m/mol kg^{-1}	$\Delta_r H$(cal)/kJ mol^{-1}
298.15	7.82	0.30	63.2

Reference: 94TEW/GOL
Method: calorimetry
Buffer: potassium phosphate (0.10 mol kg^{-1})
pH: 7.82
Evaluation: A

Tewari and Goldberg also calculated $\Delta_r H°=(62.0\pm2.3)$ kJ mol^{-1} at $T=298.15$ K and $I=0$ for the chemical reference reaction: L-tryptophan(aq)+H_2O(l)=indole(aq)+pyruvate$^-$(aq)+NH_4^+(aq).

5.24. Enzyme: fumurate hydratase (EC 4.2.1.2)

fumarate(aq)+H_2O(l)=(*S*)-malate(aq)

T/K	pH	K'
298.15	6.81	3.1
298.15	7.12	3.3

Reference: 31BOR/SCH
Method: electrochemistry
pH: 6.81–7.12
Evaluation: C

fumurate(aq)+H_2O(l)=(*S*)-malate(aq)

T/K	pH	K'
278.15	6.8	8.4
288.15	6.8	6.5
298.15	6.8	5.1
311.15	6.8	3.8
327.15	6.8	2.1

Reference: 34JAC
Method: polarimetry
Buffer: barbital
pH: 6.8
Evaluation: C

From the temperature dependence of the apparent equilibrium constant we calculate $\Delta_r H'°$ ($T=303$ K, pH=6.8)=−21 kJ mol^{-1}.

fumurate(aq)+H_2O(l)=(*S*)-malate(aq)

T/K	pH	K'
293.15	7.4	4.57
303.15	7.4	3.54
313.15	7.4	3.17
323.15	7.4	2.65

Reference: 40KRE/SMY
Method: manometry
Buffer: phosphate (0.1 mol dm^{-3})
pH: 7.4
Evaluation: B

From the temperature dependence of the apparent equilibrium constant we calculate $\Delta_r H'°$ ($T=308$ K, pH=7.4)=−14 kJ mol^{-1}.

fumurate(aq)+H_2O(l)=(*S*)-malate(aq)

T/K	pH	$\Delta_r H'°$/kJ mol^{-1}
297.45	6.8	−16.0

Reference: 45OHL
Method: calorimetry
Buffer: barbital
pH: 6.8
Evaluation: B

This same result was reported later by Ohlmeyer [46OHL] in a separate publication.

fumurate(aq)+H_2O(l)=(*S*)-malate(aq)

T/K	pH	K'
288.3	7.29	4.86
292.8	7.29	4.48
298.5	7.29	4.07
303.0	7.29	3.64
308.1	7.29	3.31
313.4	7.29	3.13
318.3	7.29	2.79
323.3	7.29	2.46

Reference: 48SCO/POW
Method: chemical analysis
Buffer: phosphate
pH: 7.29
Evaluation: B

The apparent equilibrium constants given here were taken from Scott and Powell's Fig. 2. Scott and Powell calculated $\Delta_r H'°$ ($T=305$ K, pH =7.29)=−14.9 kJ mol^{-1} from the temperature dependence of the apparent equilibrium constant.

fumurate(aq)=H_2O(l)=(*S*)-malate(aq)

$\frac{T}{K}$	pH	Buffer	$\frac{I_c}{mol\ dm^{-3}}$	K'
298.15	7.3	phosphate	0.0011	4.28
298.15	7.3	phosphate	0.010	4.37
298.15	7.3	phosphate	0.049	4.44
298.15	7.3	phosphate	0.100	4.59
298.15	7.3	phosphate	0.25	4.87
298.15	4.06	?	0.05	9.49
298.15	5.00	?	0.05	5.66
298.15	5.05	?	0.05	4.66
298.15	6.00	?	0.05	4.55
298.15	6.01	?	0.05	4.42
298.15	6.06	?	0.05	4.47
298.15	7.99	?	0.05	4.31
298.15	8.00	?	0.05	4.35
298.15	9.01	?	0.05	4.43
313.0	7.30	phosphate (0.05 mol dm^{-3})	0.10	3.11
313.0	7.30	phosphate (0.05 mol dm^{-3})	0.10	3.13
308.3	7.30	phosphate (0.05 mol dm^{-3})	0.10	3.81
308.3	7.30	phosphate (0.05 mol dm^{-3})	0.10	3.72
307.7	7.30	phosphate (0.05 mol dm^{-3})	0.10	4.01
307.6	7.30	phosphate (0.05 mol dm^{-3})	0.10	3.97
307.5	7.30	phosphate (0.05 mol dm^{-3})	0.10	4.00
307.5	7.30	phosphate (0.05 mol dm^{-3})	0.10	3.93
307.3	7.30	phosphate (0.05 mol dm^{-3})	0.10	3.97
304.1	7.30	phosphate (0.05 mol dm^{-3})	0.10	4.68
304.1	7.30	phosphate (0.05 mol dm^{-3})	0.10	4.74
303.6	7.30	phosphate (0.05 mol dm^{-3})	0.10	4.69
303.6	7.30	phosphate (0.05 mol dm^{-3})	0.10	4.85
294.1	7.30	phosphate (0.05 mol dm^{-3})	0.10	4.88
294.1	7.30	phosphate (0.05 mol dm^{-3})	0.10	4.82
293.4	7.30	phosphate (0.05 mol dm^{-3})	0.10	4.99
293.3	7.30	phosphate (0.05 mol dm^{-3})	0.10	5.04
291.2	7.30	phosphate (0.05 mol dm^{-3})	0.10	5.70
291.2	7.30	phosphate (0.05 mol dm^{-3})	0.10	5.54
290.8	7.30	phosphate (0.05 mol dm^{-3})	0.10	5.68
290.8	7.30	phosphate (0.05 mol dm^{-3})	0.10	5.61
277.8	7.30	phosphate (0.05 mol dm^{-3})	0.10	7.22
277.8	7.30	phosphate (0.05 mol dm^{-3})	0.10	7.37
307.5	4.91	acetate (0.20 mol dm^{-3})	0.10	5.94
295.2	4.91	acetate (0.20 mol dm^{-3})	0.10	6.34
292.6	4.91	acetate (0.20 mol dm^{-3})	0.10	6.69
292.6	4.91	acetate (0.20 mol dm^{-3})	0.10	6.88
290.8	4.91	acetate (0.20 mol dm^{-3})	0.10	7.01
290.8	4.91	acetate (0.20 mol dm^{-3})	0.10	7.08
290.8	4.91	acetate (0.20 mol dm^{-3})	0.10	7.20
290.6	4.91	acetate (0.20 mol dm^{-3})	0.10	7.36
290.6	4.91	acetate (0.20 mol dm^{-3})	0.10	7.51
277.9	4.91	acetate (0.20 mol dm^{-3})	0.10	8.14

Reference: 53BOC/ALB
Method: spectrophotometry
Buffer: phosphate and acetate
pH: 4.06–9.01
Evaluation: A

The results given here were taken from Bock and Alberty's Figs. 1 to 3. From the temperature dependence of the apparent equilibrium constant, Bock and Alberty calculated $\Delta_r H'^\circ$ ($\bar{T}$=294 K, pH=7.3, I_c=0.1 mol dm^{-3})=−(16.6±0.4) kJ mol^{-1} and $\Delta_r H'^\circ$ ($\bar{T}$=293 K, pH=4.91, I_c=0.1 mol dm^{-3})=−(10.0±1.7) kJ mol^{-1}.

fumurate(aq)+H_2O(l)=(*S*)-malate(aq)

$\frac{T}{K}$	pH	K'
298.15	7.4	4.43

Reference: 53KRE
Method: polarimetry and manometry
Buffer: carbonate+bicarbonate
pH: 7.4
Evaluation: A

fumurate(aq)+H_2O(l)=(*S*)-malate(aq)

$\frac{T}{K}$	pH	K'
275.8	7.30	6.31
276.9	6.35	6.31
277.0	6.35	6.31
277.2	6.35	6.31
282.3	6.35	5.68
283.5	7.30	5.50
284.0	6.35	5.50
286.1	6.35	5.30
288.2	6.35	5.01
288.2	7.30	4.86
291.9	6.35	4.57
292.6	7.30	4.47
292.8	6.35	4.57
296.7	6.35	4.21
298.1	7.30	3.98
298.7	6.35	3.98
299.2	6.35	4.01
302.5	7.30	3.63
303.0	6.35	3.78
303.0	6.35	3.63
307.8	7.30	3.21
309.9	6.35	3.21
310.7	6.35	3.09
311.7	6.35	3.09

Reference: 53MAS
Method: spectrophotometry
Buffer: phosphate (0.067 mol dm^{-3})
pH: 6.35–7.30
Evaluation: A

The apparent equilibrium constants given here were taken from Massey's Fig. 1. Masey also calculated $\Delta_r H'^\circ$ ($\bar{T}$=294 K, pH≈6.6)=−15.1 kJ mol^{-1} from the temperature dependence of the apparent equilibrium constant.

fumarate(aq)+H_2O(l)=(*S*)-malate(aq)

$\frac{T}{K}$	K'
298.15	4.45

Reference: 69BEN
Method: calorimetry
Evaluation: C

This result is based on unpublished data of Kitzinger and Hems. There is very little information given about the measurement.

fumarate(aq)+H_2O(l)=(*S*)-malate(aq)

T/K	$\Delta_r H$(cal)/kJ mol^{-1}
298.15	−15.5

Reference: 69BEN
Method: calorimetry
Evaluation: C

This result is based on unpublished data of Kitzinger and Hems. There is very little information given about the measurement.

fumarate(aq)+H_2O(l)=(*S*)-malate(aq)

T/K	pH	K'
298.15	8.2	6.2

Reference: 69WAN/BAR
Method: spectrophotometry
Buffer: Tris (0.050 mol dm^{-3})+HCl
pH: 8.2
Evaluation: C

fumarate(aq)+H_2O(l)=(*S*)-malate(aq)

T/K	pH	K'
298.15	8.0	4.25

Reference: 80COO/BLA
Method: spectrophotometry
Buffer: Tris (0.1 mol dm^{-3})+HCl
pH: 8.0
Evaluation: B

fumarate(aq)+H_2O(l)=(*S*)-malate(aq)

T/K	pH	I_m/mol kg^{-1}	K'
298.15	7.30	0.00048	4.25
298.15	7.63	0.0035	4.16
298.15	7.99	0.0055	4.14
309.41	7.99	0.0055	3.28
320.05	7.99	0.0055	2.66

Reference: 85GAJ/GOL
Method: gas chromatography
Buffer: Tris+HCl
pH: 7.30–7.99
Evaluation: A

Gajewski *et al.* also calculated $K=4.20$, $\Delta_r G°=-3.56$ kJ mol^{-1}, $\Delta_r H°=-15.7$ kJ mol^{-1}, and $\Delta_r C_p°=-36$ J K^{-1} mol^{-1} at $T=298.15$ K and $I=0$ for the chemical reference reaction: fumarate^{2-}(aq)+H_2O(l)=(*S*)- malate^{2-}(aq).

fumarate(aq)+H_2O(l)=(*S*)-malate(aq)

T/K	pH	I_m/mol kg^{-1}	$\Delta_r H$(cal)/kJ mol^{-1}
298.15	7.92	0.33	−16.12
298.15	8.24	0.41	−16.27
298.15	7.80	0.44	−16.26
298.15	8.04	0.56	−16.40
298.15	8.11	0.78	−16.82
313.15	7.98	0.32	−16.48
313.15	7.99	0.51	−16.84
313.15	8.03	0.76	−17.12
320.15	8.06	0.42	−16.94
320.15	8.11	0.60	−17.27
320.15	8.14	0.76	−17.44

Reference: 85GAJ/GOL
Method: calorimetry
Buffer: Tris+HCl
pH: 7.80–8.24
Evaluation: A

The calorimetric enthalpies of reaction given here were calculated from the results given in Gajewski *et al.*'s Tables 3 and 4.

fumarate(aq)+H_2O(l)=(*S*)-malate(aq)

T/K	pH	K'
298.15	7.6	4.3

Reference: 92KER/KER
Method: spectrophotometry
Buffer: potassium phosphate (0.05 mol dm^{-3})
pH: 7.2
Evaluation: C

5.25. Enzyme: aconitate hydratase (EC 4.2.1.3)

citrate(aq)=*cis*-aconitate(aq)+H_2O(l)

T/K	pH	K'
298.15	6.8	0.048

Reference: 43KRE/EGG
Method: polarimetry and manometry
Buffer: phosphate
pH: 6.8
Evaluation: B

The apparent equilibrium constant given here was calculated from the percentages of the substrates in solution.

citrate(aq)=*cis*-aconitate(aq)+H_2O(l)

$\frac{T}{K}$	pH	K'
298.15	7.4	0.032

Reference: 53KRE
Method: polarimetry and manometry
Buffer: carbonate+bicarbonate
pH: 7.4
Evaluation: A

The apparent equilibrium constant given here was calculated from the percentages of the substrates in solution.

citrate(aq)=*cis*-aconitate(aq)+H_2O(l)

$\frac{T}{K}$	pH	Solvent	K'
298.15	7.4	H_2O	0.046
298.15	7.4	D_2O	0.042

Reference: 66THO/NAN
Method: spectrophotometry
Buffer: Tris (0.033 mol dm^{-3})+HCl
pH: 7.4
Cofactor(s): $MgSO_4$ (0.003 mol dm^{-3})
Evaluation: C

The apparent equilibrium constant given here was calculated from the percentages of the various substrates given in Thomson *et al.*'s Table II.

isocitrate(aq)=*cis*-aconitate(aq)+H_2O(l)

$\frac{T}{K}$	pH	K'
311.15	1.4	0.69

Reference: 43KRE/EGG
Method: polarimetry
Buffer: phosphate
pH: 6.8
Evaluation: B

The apparent equilibrium constant given here was calculated from the percentages of the substrates in solution.

isocitrate(aq)=*cis*-aconitate(aq)+H_2O(l)

$\frac{T}{K}$	pH	K'
298.15	7.4	0.47

Reference: 53KRE
Method: polarimetry and manometry
Buffer: carbonate+bicarbonate
pH: 7.4
Evaluation: A

The apparent equilibrium constant given here was calculated from the percentages of the substrates in solution.

isocitrate(aq)=*cis*-aconitate(aq)+H_2O(l)

$\frac{T}{K}$	pH	Solvent	K'
298.15	7.4	H_2O	0.55
298.15	7.4	D_2O	0.44

Reference: 66THO/NAN
Method: spectrophotometry
Buffer: Tris (0.033 mol dm^{-3})+HCl
pH: 7.4
Cofactor(s): $MgSO_4$ (0.003 mol dm^{-3})
Evaluation: C

The apparent equilibrium constant given here was calculated from the percentages of the various substrates given in Thomson *et al.*'s Table II.

isocitrate(aq)=citrate(aq)

$\frac{T}{K}$	pH	K'
298.15	6.8	14.4

Reference: 43KRE/EGG
Method: polarimetry and manometry
Buffer: phosphate
pH: 6.8
Evaluation: B

The apparent equilibrium constant given here was calculated from the percentages of the substrates in solution.

isocitrate(aq)=citrate(aq)

$\frac{T}{K}$	pH	K'
298.15	7.4	14.7

Reference: 53KRE
Method: polarimetry and manometry
Buffer: carbonate+bicarbonate
pH: 7.4
Evaluation: A

The apparent equilibrium constant given here was calculated from the percentages of the substrates in solution.

isocitrate(aq)=citrate(aq)

$\frac{T}{K}$	pH	Solvent	K'
298.15	7.4	H_2O	11.8
298.15	7.4	D_2O	10.3

Reference: 66THO/NAN
Method: spectrophotometry
Buffer: Tris (0.033 mol dm^{-3})+HCl
pH: 7.4
Cofactor(s): $MgSO_4$ (0.003 mol dm^{-3})
Evaluation: C

The apparent equilibrium constant given here was calculated from the percentages of the various substrates given in Thomson *et al.*'s Table II.

isocitrate(aq)=citrate(aq)

T/K	pH	$c(MgSO_4)$/mol dm^{-3}	$c(CaCl_2)$/mol dm^{-3}	K'
310.15	7.3	0	0	7.5
310.15	7.3	0.00065	0	14
310.15	7.3	0.0011	0	18
310.15	7.3	0.0016	0	25
310.15	7.3	0.0021	0	35
310.15	7.3	0.0031	0	35
310.15	7.3	0.0050	0	33
310.15	7.3	0.050	0	28
310.15	7.3	0	0.00065	11
310.15	7.3	0	0.0011	15
310.15	7.3	0	0.0016	17
310.15	7.3	0	0.0021	19
310.15	7.3	0	0..031	25
310.15	7.3	0	0.0050	26
310.15	7.3	0	0.050	30

Reference: 67ENG/DEN
Method: spectrophotometry
Buffer: triethanolamine (0.1 mol dm^{-3})+HCl
pH: 7.3
Cofactor(s): $MgSO_4$ and $CaCl_2$
Evaluation: B

The apparent equilibrium constants given here were taken from England *et al.*'s Fig. 1.

isocitrate(aq)=citrate(aq)

T/K	pH	$c(Na^+)$/mol dm^{-3}	$c(MgCl_2)$/mol dm^{-3}	I_c/mol dm^{-3}	K'
298.15	7.5	0	0	0.10	9.31
298.15	7.5	0.080	0	0.10	12.2
310.15	7.5	0.080	0	0.10	10.8
298.15	7.5	0.022	0	0.044	11.4
298.15	7.5	0.048	0	0.070	11.6
298.15	7.5	0.130	0	0.15	12.7
298.15	7.5	0	0.001	0.10	21.3
298.15	7.5	0	0.002	0.10	36.1
298.15	7.5	0	0.003	0.10	46.1
298.15	7.5	0	0.004	0.10	52.5
298.15	7.5	0	0.007	0.10	64.8
298.15	7.5	0	0.010	0.10	69.0
298.15	7.5	?	0.001	0.044	27.6
298.15	7.5	?	0.002	0.044	48.3
298.15	7.5	?	0.004	0.044	66.8
298.15	7.5	?	0.008	0.044	77.7
298.15	7.5	?	0.0005	0.070	16.4
298.15	7.5	?	0.001	0.070	23.3
298.15	7.5	?	0.002	0.070	37.9
298.15	7.5	?	0.004	0.070	54.5
298.15	7.5	?	0.006	0.070	63.8
298.15	7.5	?	0.008	0.070	67.3
298.15	7.5	?	0.001	0.15	21.5
298.15	7.5	?	0.002	0.15	31.2
298.15	7.5	?	0.004	0.15	46.8
298.15	7.5	?	0.008	0.15	59.7

Reference: 69BLA
Method: spectrophotometry
Buffer: triethanolamine
pH: 7.5
Cofactor(s): $MgCl_2$
Evaluation: A

The results given here were taken from Blair's Tables 1 and 2 and Fig. 2.

isocitrate(aq)=citrate(aq)

T/K	pH	$c(MgCl_2)$/mol dm^{-3}	K'
311.15	7.07	0	9.89
311.15	7.07	0.009	9.92
311.15	7.07	0.047	10.0
311.15	7.07	0.094	11.0
311.15	7.07	0.230	12.2
311.11	7.07	0.470	13.9
311.15	7.07	0.700	16.1
311.15	7.07	0.930	18.0
311.15	7.07	2.30	28.8
311.15	7.07	3.60	37.2
311.15	7.07	4.50	43.6
311.15	7.07	6.90	47.0
311.15	7.07	8.50	46.0
311.15	7.07	10.0	52.3
311.15	7.07	12.3	57.9
311.15	7.07	0.000	9.83
311.15	7.07	0.047	10.6
311.15	7.07	0.700	17.1
311.15	7.07	2.30	28.8
311.15	7.07	6.90	47.5
311.15	6.64	0.000	9.51
311.15	6.64	0.047	10.3
311.15	6.64	0.700	15.8
311.15	6.64	2.30	29.5
311.15	6.64	6.90	46.0
311.15	7.45	0.000	9.48
311.15	7.45	0.047	9.95
311.15	7.45	0.700	14.8
311.15	7.45	2.30	27.6
311.15	7.45	6.90	46.6

Reference: 73VEL/GUY
Method: enzymatic assay and fluorometry
Buffer: phosphate
pH: 6.64–7.45
Cofactor(s): $MgCl_2$
Evaluation: A

5.26. Enzyme: 3-dehydroquinate dehydratase (EC 4.2.1.10)

3-dehydroquinate(aq)=3-dehydroshikimate(aq)+H_2O(l)

T/K	pH	K'
302.15	7.4	15

Reference: 54MIT/DAV
Method: spectrophotometry
Buffer: potassium phosphate (0.033 mol dm^{-3})
pH: 7.4
Evaluation: C

5.27. Enzyme: phosphopyruvate hydratase (EC 4.2.1.11)

2-phospho-D-glycerate(aq)=phospho*enol*pyruvate(aq)+H_2O(l)

$\frac{T}{K}$	K'
273.15	0.33
293.15	0.39
313.15	0.54
333.15	0.70

Reference: 34LOH/MEY
Method: chemical analysis
Evaluation: C

The pH was not reported.

2-phospho-D-glycerate(aq)=phospho*enol*pyruvate(aq)+H_2O(l)

$\frac{T}{K}$	K'
301.15	2.3

Reference: 35AKA
Evaluation: C

The pH was not reported.

2-phospho-D-glycerate(aq)=phospho*enol*pyruvate(aq)+H_2O(l)

$\frac{T}{K}$	pH	K'
293.15	7.34	1.43

Reference: 41WAR/CHR
Method: spectrophotometry
Buffer: bicarbonate and phosphate
pH: 7.34
Cofactor(s): $MgSO_4$
Evaluation: C

2-phospho-D-glycerate(aq)=phospho*enol*pyruvate(aq)+H_2O(l)

$\frac{T}{K}$	K'
297.15	2.9

Reference: 49MEY/OES
Method: chemical analysis and radioactivity
Buffer: bicarbonate
Cofactor(s): Mg^{2+}
Evaluation: C

The pH was not reported.

2-phospho-D-glycerate(aq)=phospho*enol*pyruvate(aq)+H_2O(l)

$\frac{T}{K}$	pH	$\frac{c(MgSO_4)}{mol\ dm^{-3}}$	$\frac{c(MnSO_4)}{mol\ dm^{-3}}$	$\frac{c(KCl)}{mol\ dm^{-3}}$	K'
288.0	7.5	0.008	0	0.4	3.54
299.5	7.5	0.008	0	0.4	4.55
307.5	7.5	0.008	0	0.4	5.28
298.15	6.0	0.001	0	0	2.50
298.15	6.5	0.001	0	0	3.50
298.15	7.0	0.001	0	0	4.29
298.15	7.5	0.001	0	0	4.68
298.15	8.0	0.001	0	0	5.00
298.15	8.5	0.001	0	0	5.15
298.15	6.0	0.01	0	0	2.65
298.15	6.5	0.01	0	0	3.40
298.15	7.0	0.01	0	0	3.92
298.15	7.5	0.01	0	0	4.29
298.15	8.0	0.01	0	0	4.41
298.15	8.5	0.01	0	0	4.52
298.15	6.00	0	0.001	0	2.35
298.15	6.50	0	0.001	0	3.19
298.15	6.88	0	0.001	0	3.48
298.15	7.28	0	0.001	0	3.89
298.15	8.08	0	0.001	0	4.20
298.15	5.92	0	0.002	0	2.12
298.15	6.50	0	0.002	0	2.91
298.15	6.90	0	0.002	0	3.51
298.15	7.28	0	0.002	0	3.48
298.15	8.08	0	0.002	0	3.80
298.15	5.92	0	0.005	0	2.32
298.15	6.50	0	0.005	0	2.84
298.15	6.90	0	0.005	0	3.16
298.15	7.28	0	0.005	0	3.19
298.15	8.08	0	0.005	0	3.27
298.15	6.03	0.008	0	0.4	2.63
298.15	6.04	0.008	0	0.4	2.83
298.15	6.08	0.008	0	0.4	2.45
298.15	6.08	0.008	0	0.4	2.76
298.15	6.13	0.008	0	0.4	2.76
298.15	6.13	0.008	0	0.4	2.55
298.15	6.23	0.008	0	0.4	3.21
298.15	6.23	0.008	0	0.4	3.27
298.15	6.23	0.008	0	0.4	3.32
298.15	6.29	0.008	0	0.4	3.17
298.15	6.29	0.008	0	0.4	3.21
298.15	6.34	0.008	0	0.4	3.10
298.15	6.34	0.008	0	0.4	3.21
298.15	6.34	0.008	0	0.4	3.36
298.15	6.43	0.008	0	0.4	3.78
298.15	6.49	0.008	0	0.4	3.63
298.15	6.49	0.008	0	0.4	3.68
298.15	6.55	0.008	0	0.4	3.61
298.15	6.55	0.008	0	0.4	3.84
298.15	6.74	0.008	0	0.4	4.09
298.15	6.74	0.008	0	0.4	4.37
298.15	6.78	0.008	0	0.4	4.26
298.15	6.84	0.008	0	0.4	4.00
298.15	6.84	0.008	0	0.4	4.24
298.15	6.84	0.008	0	0.4	4.26
298.15	7.00	0.008	0	0.4	4.38
298.15	7.00	0.008	0	0.4	4.43
298.15	7.00	0.008	0	0.4	4.52
298.15	7.00	0.008	0	0.4	4.68
298.15	7.12	0.008	0	0.4	4.40
298.15	7.12	0.008	0	0.4	4.80
298.15	7.16	0.008	0	0.4	4.80
298.15	7.16	0.008	0	0.4	4.97
298.15	7.38	0.008	0	0.4	4.56
298.15	7.38	0.008	0	0.4	4.64
298.15	7.38	0.008	0	0.4	4.70

2-phospho-D-glycerate(aq)=phospho*enol*pyruvate(aq)+H_2O(l)—Continued

T/K	pH	$c(MgSO_4)$/mol dm^{-3}	$c(MnSO_4)$/mol dm^{-3}	c(KCl)/mol dm^{-3}	K'
298.15	7.38	0.008	0	0.4	5.00
298.15	7.46	0.008	0	0.4	4.68
298.15	7.46	0.008	0	0.4	4.82
298.15	7.46	0.008	0	0.4	4.86
298.15	7.85	0.008	0	0.4	4.71
298.15	7.85	0.008	0	0.4	5.25
298.15	7.88	0.008	0	0.4	5.06
298.15	7.88	0.008	0	0.4	5.10
298.15	7.88	0.008	0	0.4	5.25
298.15	7.88	0.008	0	0.4	5.92
298.15	7.94	0.008	0	0.4	5.15
298.15	7.94	0.008	0	0.4	5.25
298.15	8.25	0.008	0	0.4	4.97
298.15	8.25	0.008	0	0.4	5.05
298.15	8.25	0.008	0	0.4	5.08
298.15	8.25	0.008	0	0.4	5.25

Reference: 57WOL/BAL
Method: spectrophotometry
Buffer: imidazole (0.05 mol dm ^{3})
pH: 5.9 to 8.5
Cofactor(s): $MgSO_4$ and $MnSO_4$
Evaluation: A

The apparent equilibrium constants given here were taken from Wold and Ballou's Figs. 4–6 and Table IV. Wold and Ballou also calculated $K=6.3$ at $T=298.15$ K for the chemical reference reaction: 2-phospho-D-glycerate$^-$(aq) =phospho*enol*pyruvate$^-$(aq)+H_2O(l). From the temperature dependence of the apparent equilibrium constant we calculate $\Delta_rH'^\circ$ ($\bar{T}=298$ K, pH=7.5)=15 kJ mol^{-1}.

2-phospho-D-glycerate(aq)=phospho*enol*pyruvate(aq)+H_2O(l)

T/K	pH	K'
311.15	7.1	4.6

Reference: 64LOW/PAS
Method: fluorimetry
Buffer: imidazole (0.020 mol dm^{-3})
pH: 7.1
Cofactor(s): $MgCl_2$ (0.005 mol dm^{-3})
Evaluation: A

5.28. Enzyme: enoyl-CoA hydratase (EC 4.2.1.17)

(3*R*)-3-hydroxybutanoyl-CoA(aq)=*cis*-but-2-enoyl-CoA(aq)+H_2O(l)

T/K	pH	K'
298.15	7.5	0.18

Reference: 56STE/DEL
Method: spectrophotometry
Buffer: Tris
pH: 7.5
Evaluation: B

(3*S*)-3-hydroxybutanoyl-CoA(aq)=*trans*-but-2-enoyl-CoA(aq)+H_2O(l)

T/K	pH	K'
298.15	7.5	0.29

Reference: 56STE/DEL
Method: spectrophotometry
Buffer: Tris
pH: 7.5
Evaluation: C

(3*R*)-3-hydroxyhexanoyl-CoA(aq)=*cis*-hex-2-enoyl-CoA(aq)+H_2O(l)

T/K	pH	K'
298.15	7.5	0.20

Reference: 56STE/DEL
Method: spectrophotometry
Buffer: Tris
pH: 7.5
Evaluation: B

Stern and del Campillo reported $\{K'\cdot c(H_2O)\}^{-1}=0.0919$. The apparent equilibrium constant given here was calculated from this result.

(3*S*)-3-hydroxyhexanoyl-CoA(aq)=*trans*-hex-2-enoyl-CoA(aq)+H_2O(l)

T/K	pH	K'
298.15	7.5	0.66

Reference: 56STE/DEL
Method: spectrophotometry
Buffer: Tris
pH: 7.5
Evaluation: B

Stern and del Campillo reported $\{K'\cdot c(H_2O)\}^{-1}=0.0274$. The apparent equilibrium constant given here was calculated from this result.

5.29. Enzyme: tryptophan synthase (EC 4.2.1.20)

D-glyceraldehyde 3-phosphate(aq)+indole(aq)= 1-(indol-3-yl)glycerol 3-phosphate(aq)

T/K	pH	K'_c
298.15	7.8	≈2300

Reference: 76WEI/KIR
Method: spectrophotometry
Buffer: Tris (0.05 mol dm^{-3})
pH: 7.8
Evaluation: C

D-glyceraldehyde 3-phosphate(aq)+indole(aq)= 1-(indol-3-yl)glycerol 3-phosphate(aq)

T/K	pH	Δ_rH(cal)/kJ mol^{-1}
298.15	7.5	−54.0

Reference: 85WIE/HIN
Method: calorimetry and spectrophotometry
Buffer: sodium diphosphate (0.1 mol dm^{-3})
pH: 7.5
Evaluation: A

indole(aq)+L-serine(aq)=L-tryptophan(aq)+H_2O(l)

$\frac{T}{K}$	pH	Buffer	$\frac{\Delta_r H(\text{cal})}{\text{kJ mol}^{-1}}$
283.15	7.5	sodium diphosphate (0.1 mol dm^{-3})	78.7
298.15	7.5	sodium diphosphate (0.1 mol dm^{-3})	80.3
298.15	7.5	Tris (0.2 mol dm^{-3})	81.2
308.15	7.5	sodium diphosphate (0.1 mol dm^{-3})	80.6

Reference: 85WIE/HIN
Method: calorimetry and spectrophotometry
Buffer: sodium diphosphate (0.1 mol dm^{-3}) and Tris (0.2 mol dm^{-3})
pH: 7.5
Cofactor(s): pyridoxal 5-phosphate
Evaluation: A

This reaction is catalyzed by the β_2 subunit of tryptophan synthase. Since the calorimetrically determined reaction enthalpies $\Delta_r H(\text{cal})$ were the same (within experimental error) in both diphosphate and Tris buffers at pH=7.5, the change in binding of hydrogen ion $\Delta_r N(H^+)$ in this biochemical reaction is zero and $\Delta_r H(\text{cal})=\Delta_r H'^\circ$. From the temperature dependence of $\Delta_r H'^\circ$, we calculate $\Delta_r C_p'^\circ$ ($\bar{T}$=296 K, pH=7.5)≈76 J K^{-1} mol^{-1}.

1-(indol-3-yl)glycerol 3-phosphate(aq)+L-serine(aq)=L-tryptophan(aq)+D-glyceraldehyde 3-phosphate(aq)+H_2O(l)

$\frac{T}{K}$	pH	$\frac{\Delta_r H(\text{cal})}{\text{kJ mol}^{-1}}$
298.15	7.5	−13.4

Reference: 85WIE/HIN
Method: calorimetry and spectrophotometry
Buffer: sodium diphosphate (0.1 mol dm^{-3})
pH: 7.5
Evaluation: A

L-serine(aq)=pyruvate(aq)+ammonia(aq)

$\frac{T}{K}$	pH	$\frac{\Delta_r H(\text{cal})}{\text{kJ mol}^{-1}}$
308.15	7.5	−7.3

Reference: 85WIE/HIN
Method: calorimetry
Buffer: sodium diphosphate (0.1 mol dm^{-3})
pH: 7.5
Evaluation: A

This reaction is catalyzed by the β_2 subunit of tryptophan synthase.

5.30. Enzyme: maleate hydratase (EC 4.2.1.31)

(*R*)-malate(aq)=maleate(aq)+H_2O(l)

$\frac{T}{K}$	pH	$\frac{I_c}{\text{mol dm}^{-3}}$	K'
298.15	7.0	0.1	4.88E-4

Reference: 93WER/TWE
Method: HPLC
Buffer: potassium phosphate (0.025 mol dm^{-3})
pH: 7.0
Evaluation: B

(*R*)-malate(aq)=maleate(aq)+H_2O(l)

$\frac{T}{K}$	pH	Buffer	$\frac{I_c}{\text{mol dm}^{-3}}$	K'
298.15	6.50	potassium phosphate (0.10 mol dm^{-3})+Hepes (0.10 mol dm^{-3})+NaOH	0.10	7.41E-4
298.15	7.00	potassium phosphate (0.20 mol dm^{-3})+NaOH	0.10	4.88E-4
298.15	7.50	potassium phosphate (0.10 mol dm^{-3})+Hepers (0.10 mol dm^{-3})+NaOH	0.10	4.46E-4
298.15	8.00	potassium phosphate (0.10 mol dm^{-3})+Hepes (0.10 mol dm^{-3})+NaOH	0.10	4.28E-4
298.15	8.50	potassium phosphate (0.10 mol dm^{-3})+Hepes (0.10 mol dm^{-3})+NaOH	0.10	4.17E-4
288.3	7.00	potassium phosphate (0.20 mol dm^{-3})+NaOH	0.10	4.39E-4
292.9	7.00	potassium phosphate (0.20 mol dm^{-3})+NaOH	0.10	5.00E-4
297.8	7.00	potassium phosphate (0.20 mol dm^{-3})+NaOH	0.10	5.58E-4
302.9	7.00	potassium phosphate (0.20 mol dm^{-3})+NaOH	0.10	6.24E-4
307.9	7.00	potassium phosphate (0.20 mol dm^{-3})+NaOH	0.10	7.20E-4
313.2	7.00	potassium phosphate (0.20 mol dm^{-3})+NaOH	0.10	8.11E-4

Reference: 93WER/TWE2
Method: HPLC
Buffer: {potassium phosphate (0.20 mol dm^{-3})+NaOH} and {potassium phosphate (0.10 mol dm^{-3})+Hepes (0.10 mol dm^{-3})+NaOH}
pH: 7.0
Evaluation: B

The apparent equilibrium constants given here were taken from van der Werf *et al.*'s Figs. 2 and 3. From the temperature dependence of K' van der Werf *et al.* calculated $\Delta_r H'^\circ$ ($\bar{T}$=301 K, pH=7.0)=18.1 kJ mol^{-1}. They also calculated K=0.000419 at T=298.15 K for the chemical reference reaction: (*R*)-malate^{2-}(aq)=maleate^{2-}(aq)+H_2O(l).

5.31. Enzyme: *(S)*-2-methymalate dehydratase (EC 4.2.1.34)

(*S*)-2-methylmalate(aq)=2-methylfumarate(aq)+H_2O(l)

T/K	pH	K'
298.15	8.2	0.17

Reference: 69WAN/BAR
Method: spectrophotometry
Buffer: Tris (0.050 mol dm^{-3})+HCl
pH: 8.2
Evaluation: C

5.32. Enzyme: *(R)*-2-methylmalate dehydratase (EC 4.2.1.35)

(*R*)-2-methylmalate(aq)=2-methylmaleate(aq)+H_2O(l)

T/K	pH	I_c/mol dm^{-3}	K'
298.15	7.0	0.1	0.0962

Reference: 93WER/TWE
Method: HPLC
Buffer: potassium phosphate (0.025 mol dm^{-3})
pH: 7.0
Evaluation: B

(*R*)-2-methylmalate(aq)=2-methylmaleate(aq)+H_2O(l)

T/K	pH	Buffer	I_c/mol dm^{-3}	K'
298.15	6.00	potassium phosphate (0.10 mol dm^{-3})+Hepes (0.10 mol dm^{-3})+NaOH	0.10	0.0153
298.15	6.50	potassium phosphate (0.10 mol dm^{-3})+Hepes (0.10 mol dm^{-3})+NaOH	0.10	0.0105
298.15	7.00	potassium phosphate (0.20 mol dm^{-3})+NaOH	0.10	0.00962
298.15	7.50	potassium phosphate (0.10 mol dm^{-3})+Hepes (0.10 mol dm^{-3})+NaOH	0.10	0.00945
298.15	8.00	potassium phosphate (0.10 mol dm^{-3})+Hepes (0.10 mol dm^{-3})+NaOH	0.10	0.00929
298.15	8.50	potassium phosphate (0.10 mol dm^{-3})+Hepes (0.10 mol dm^{-3})+NaOH	0.10	0.00917
283.5	7.00	potassium phosphate (0.20 mol dm^{-3})+NaOH	0.10	0.00553
288.1	7.00	potassium phosphate (0.20 mol dm^{-3})+NaOH	0.10	0.00675
292.5	7.00	potassium phosphate (0.20 mol dm^{-1})+NaOH	0.10	0.00758
298.2	7.00	potassium phosphate (0.20 mol dm^{-3})+NaOH	0.10	0.00864
302.8	7.00	potassium phosphate (0.20 mol dm^{-3})+NaOH	0.10	0.0103
307.9	7.00	potassium phosphate (0.20 mol dm^{-3})+NaOH	0.10	0.0119
313.2	7.00	potassium phosphate (0.20 mol dm^{-3})+NaOH	0.10	0.0144

Reference: 93WER/TWE2
Method: HPLC
Buffer: {potassium phosphate (0.20 mol dm^{-3})+NaOH} and {potassium phosphate (0.10 mol dm^{-3})+Hepes (0.10 mol dm^{-3})+NaOH}
pH: 7.0
Evaluation: B

The apparent equilibrium constants given here were taken from van der Werf *et al.*'s Figs. 2 and 3. From the temperature dependence of K' van der Werf *et al.* calculated $\Delta_r H'^\circ(\bar{T}=298$ K, pH=7.0)=22.6 kJ mol^{-1}. They also calculated $K=0.00909$ at $T=298.15$ K for the chemical reference reaction: (*R*)-2-methylmalate^{2-}(aq)=2-methylmaleate^{2-}(aq)+H_2O(l).

5.33. Enzyme: D-glutamate cyclase (EC 4.2.1.48)

γ-fluoroglutamate(aq)=*cis*-D-4-fluoro-5-oxopyrrolidine-2-carboxylate(aq)+H_2O(l)

T/K	pH	K'
299.4	7.9	0.58
303.2	7.9	0.44
305.9	7.9	0.50
313.5	7.9	0.43

Reference: 71UNK/GOL
Method: spectrophotometry
Buffer: 2-methylimidazole (0.15 mol dm^{-3})+HCl
pH: 7.9
Cofactor(s): $MgSO_4$ (0.033 mol dm^{-3})
Evaluation: B

The apparent equilibrium constants given here were taken from Unkeless and Goldman's Table II and Fig. 4. Unkeless and Goldman also calculated $\Delta_r H'^\circ$ ($\bar{T}=307$ K, pH=7.9)=15.7 kJ mol^{-1} from the temperature dependence of the apparent equilibrium constant.

γ-fluoroglutamate(aq)=*trans*-D-4-fluoro-5-oxopyrrolidine-2-carboxylate(aq)+H_2O(l)

T/K	pH	K'
303.15	7.9	2

Reference: 71UNK/GOL
Method: spectrophotometry
Buffer: 2-methylimidazole (0.15 mol dm^{-3})+HCl
pH: 7.9
Cofactor(s): $MgSO_4$ (0.033 mol dm^{-3})
Evaluation: B

D-glutamate(aq)=5-oxo-D-proline(aq)+H_2O(l)

T/K	pH	K'
310.15	8.3	16

Reference: 63MEI/BUK
Method: chromatography and radioactivity
Buffer: Tris (0.17 mol dm^{-3})+HCl
pH: 8.3
Cofactor(s): $MgCl_2$ (0.033 mol dm^{-3})
Evaluation: B

D-glutamate(aq)=5-oxo-D-proline(aq)+H_2O(l)

$\frac{T}{K}$	pH	K'
293.4	7.9	24.3
302.3	7.9	27.0
303.2	7.9	26.8
310.9	7.9	30.3

Reference: 71UNK/GOL
Method: spectrophotometry
Buffer: 2-methylimidazole (0.15 mol dm^{-3})+HCl
pH: 7.9
Cofactor(s): $MgSO_4$ (0.033 mol dm^{-3})
Evaluation: B

The apparent equilibrium constants given here were taken from Unkeless and Goldman's Table II and Fig. 4. Unkeless and Goldman also calculated $\Delta_t H'^\circ$ ($\bar{T}$=320 K, pH=7.9)=9.6 kJ mol^{-1} from the temperature dependence of the apparent equilibrium constant.

5.34. Enzyme: urocanate hydratase (EC 4.2.1.49)

urocanate(aq)+H_2O(l)=4,5-dihydro-4-oxo-5-imidazolepropanoate(aq)

$\frac{T}{K}$	pH	K'
277.15	7.5	35.5
288.15	7.5	49.1
293.15	7.5	58.2
298.15	7.5	69.8
310.15	7.5	91.2

Reference: 75COH/LYN
Method: spectrophotometry
Buffer: potassium phosphate (0.025 mol dm^{-3})
pH: 7.5
Evaluation: A

Cohn *et al.* also calculated $\Delta_t H'^\circ$ ($\bar{T}$=294 K, pH=7.5)=21.8 kJ mol^{-1} from the temperature dependence of K'.

5.35. Enzyme: crotonyl-[acyl-carrier-protein] hydratase (EC 4.2.1.58)

(3*R*)-3-hydroxybutanoyl-[acyl-carrier protein] (aq)=
but-2-enoyl-[acyl-carrier protein] (aq)+H_2O(l)

$\frac{T}{K}$	pH	K'
298.15	8.5	≈0.32

Reference: 68MIZ/WEE
Method: enzymatic assay and spectrophotometry
Buffer: Tris (0.11 mol dm^{-3})+HCl
pH: 8.5
Evaluation: C

5.36. Enzyme: dimethylmaleate hydratase (EC 1.4.2.1.85)

(2*R*,3*S*)-2,3-dimethylmalate(aq)=dimethylmaleate(aq)+H_2O(l)

$\frac{T}{K}$	pH	K'
308.15	7.0	0.43

Reference: 84KOL/EGG
Method: spectrophotometry
Buffer: phosphate (0.10 mol dm^{-3})
pH: 7.0
Evaluation: B

(2*R*,3*S*)-2,3-dimethylmalate(aq)=dimethylmaleate(aq)+H_2O(l)

$\frac{T}{K}$	pH	$\frac{I_c}{mol\ dm^{-3}}$	K'
298.15	7.0	0.1	0.089

Reference: 93WER/TWE
Method: HPLC
Buffer: potassium phosphate (0.025 mol dm^{-3})
pH: 7.0
Evaluation: B

5.37. Enzyme: 3-hydroxybutyryl-CoA dehyratase (EC 4.2.1.a)

DL-3-hydroxybutanoyl-CoA(aq)=*trans*-but-2-enoyl-CoA(aq)+H_2O(l)

$\frac{T}{K}$	pH	K'
308.15	7.4	0.28

Reference: 85COO/PRA
Method: spectrophotometry and HPLC
Buffer: Tris (0.10 mol dm^{-3})+HCl
pH: 7.4
Evaluation: C

Cook *et al.* reported $\{K' \cdot c(H_2O)\}^{-1}$=0.0638. The apparent equilibrium constant given here was calculated from this result. Also see data given under EC 4.2.1.17.

5.38. Enzyme: aspartate ammonia-lyase (EC 4.3.1.1)

L-aspartate(aq)=fumarate(aq)+ammonia(aq)

$\frac{T}{K}$	pH	K'_c
310.15	7.4	≈0.04

Reference: 26QUA/WOO
Method: chemical analysis
Buffer: phosphate
pH: 7.4
Evaluation: C

L-aspartate(aq)=fumarate(aq)+ammonia(aq)

$\frac{T}{K}$	pH	K_c'
310.15	7.4	0.01

Reference: 29WOO
Method: chemical analysis and polarimetry
Buffer: phosphate
pH: 7.4
Evaluation: B

L-aspartate(aq)=fumarate(aq)+ammonia(aq)

$\frac{T}{K}$	pH	K_c'
278.15	7.0	0.0024
310.15	7.0	0.0076

Reference: 35JAC/TAP
Method: polarimetry and chemical analysis
Buffer: barbital
pH: 7.0
Evaluation: C

L-aspartate(aq)=fumarate(aq)+ammonia(aq)

$\frac{T}{K}$	pH	K_c'
310.15	6.8	0.023

Reference: 55WIL/MCI
Method: chemical analysis
Buffer: phosphate (0.05 mol dm^{-3})
pH: 6.8
Evaluation: C

L-aspartate(aq)=fumarate(aq)+ammonia(aq)

$\frac{T}{K}$	pH	K_c'
302.15	7.0	0.010
312.15	7.0	0.022

Reference: 61WIL/WIL
Method: chemical analysis
Buffer: phosphate (0.10 mol dm^{-3})
pH: 7.0
Evaluation: B

L-aspartate(aq)=fumarate(aq)+ammonia(aq)

$\frac{T}{K}$	K_c'
310.15	0.020

Reference: 65SEK/SUN
Evaluation: C

The value of the apparent equilibrium constant (forward direction of the reaction) we calculate from the data given in Sekijo *et al.*'s Table 10 differs from the value calculated by Sekijo *et al.*

L-aspartate(aq)=fumarate(aq)+ammonia(aq)

$\frac{T}{K}$	pH	$\frac{I_m}{\text{mol dm}^{-3}}$	K_m'
278.05	7.0	0.1	0.00215
288.45	7.0	0.1	0.00307
300.55	7.0	0.1	0.00511
309.45	7.0	0.1	0.00673
309.45	5.7	0.1	0.0071
309.45	7.0	0.1	0.0067
309.45	7.7	0.1	0.0064
309.45	7.0	0.10	0.0067
309.45	7.0	0.30	0.0091
309.45	7.0	0.52	0.0098
309.45	7.0	0.73	0.0098

Reference: 68BAD/MIL
Method: amino acid analysis, Conway diffusion, and UV absorption
Buffer: Hepes, Mes, Tris, and phosphate
pH: 5.7–7.0
Cofactor(s): $MgSO_4$
Evaluation: A

Several of the apparent equilibrium constants given here were taken from Bada and Miller's Figs. 1 and 3. Bada and Miller also calculated $K_m=0.00230$, $\Delta_r H°=26.9$ kJ mol^{-1}, $\Delta_r S°=39.7$ J K^{-1} mol^{-1}, and $\Delta_r C_p°=-117$ J K^{-1} mol^{-1} at $T=298.15$ K and $I_m=0.1$ mol kg^{-1} for the chemical reference reaction: L-aspartate$^-$(aq)=fumarate^{2-}(aq) $+NH_4^+$(aq).

L-aspartate(aq)=fumarate(aq)+ammonia(aq)

$\frac{T}{K}$	pH	K_m'
286.15	7.43	0.00331
292.15	7.39	0.00374
298.25	7.37	0.00471
304.25	7.33	0.00559
310.15	7.30	0.00507
310.25	7.29	0.00669
310.15	7.24	0.00854
316.25	7.35	0.00763

Reference: 86GOL/GAJ
Method: HPLC
Buffer: phosphate
pH: 7.25–7.43
Evaluation: A

Goldberg *et al.* also calculated $K_m=(0.00148\pm0.0001)$, $\Delta_r H°=(24.5\pm1.0)$ kJ mol^{-1}, and $\Delta_r C_p°=-(147\pm100)$ J K^{-1} mol^{-1} at $T=298.15$ K and $I=0$ for the chemical reference reaction: L-aspartate$^-$(aq)=fumarate^{2-}(aq)+NH_4^+(aq).

L-aspartate(aq)=fumarate(aq)+ammonia(aq)

T/K	pH	I_m/mol kg^{-1}	$\Delta_r H'°$/kJ mol^{-1}
298.15	7.27	0.133	24.8
304.15	7.28	0.133	24.7
310.15	7.30	0.066	24.2
310.15	7.32	0.134	23.7
310.15	7.28	0.182	23.8
310.15	7.27	0.334	23.1

Reference: 86GOL/GAJ
Method: calorimetry
Buffer: phosphate
pH: 7.27–7.32
Evaluation: A

Goldberg *et al.* applied corrections for protonation of the buffer and for the side reaction of fumarate to malate to obtain the values of $\Delta_r H'°$ given here.

5.39. Enzyme: methylaspartate ammonia-lyase (EC 4.3.1.2)

L-*threo*-3-methylaspartate(aq)=2-methylfumarate(aq)+ammonia(aq)

T/K	pH	Buffer	K'_c
298.15	7.9	Tris (0.05 mol dm^{-3})+HCl	0.238
298.15	9.7	ethanolamine (0.05 mol dm^{-3})	0.306

Reference: 59BAR/SMY
Method: spectrophotometry
Buffer: {Tris (0.05 mol dm^{-3})+HCl} and ethanolamine (0.05 mol dm^{-3})
pH: 7.9–9.7
Cofactor(s): $MgCl_2$ (0.001 mol dm^{-3})
Evaluation: B

5.40. Enzyme: histidine ammonia-lyase (EC 4.3.1.3)

L-histidine(aq)=urocanate(aq)+ammonia(aq)

T/K	pH	K'_c
298.15	8.0	3

Reference: 67WIL/HIR
Method: spectrophotometry
Buffer: Tris (0.033 mol dm^{-3})+acetate
pH: 8.0
Cofactor(s): $MgSO_4$ (0.001 mol dm^{-3})
Evaluation: C

L-histidine(aq)=urocanate(aq)+ammonia(aq)

T/K	pH	K'_c
303.2	7.2	0.016
305.3	7.2	0.025
308.2	7.2	0.028
311.3	7.2	0.040
316.4	7.2	0.10

Reference: 73MCC/KOL
Method: spectrophotometry and thin layer chromatography
Buffer: phosphate (0.040 mol dm^{-3})
pH: 7.2
Evaluation: C

The apparent equilibrium constants given here were taken from McClard and Kolenbrander's Fig. 4. McClard and Kolenbrander also calculated $\Delta_r H'°$ (pH−7.2)−108 kJ mol^{-1} for this reaction from the temperature dependence of the apparent equilibrium constant. Larson *et al.* [93LAR/TEW] have pointed out that the results of McClard and Kolenbrander may be in error because equilibrium was not reached in their experiments.

L-histidine(aq)=urocanate(aq)+ammonia(aq)

T/K	pH	I_m/mol kg^{-1}	K'_m
298.25	8.41	0.167	3.01
298.25	8.70	0.145	2.35

Reference: 93LAR/TEW
Method: HPLC
Buffer: Tris (0.101 mol kg^{-1})+HCl
pH: 8.41–8.70
Evaluation: A

Larson *et al.* also calculated $K_m=(2.7\pm0.7)$, $\Delta_r G°=-(2.5\pm0.7)$ kJ mol^{-1}, $\Delta_r H°=(7.6\pm0.8)$ kJ mol^{-1}, and $\Delta_r S°=(34\pm4)$ J K^{-1} mol^{-1} at $T=298.15$ K and $I=0$ for the chemical reference reaction: L-histidine(aq)=urocanate$^-$(aq)+NH_4^+(aq).

L-histidine(aq)=urocanate(aq)+ammonia(aq)

T/K	pH	I_m/mol kg^{-1}	$\Delta_r H$(cal)/kJ mol^{-1}
298.15	8.15	0.30	9.24
310.15	8.15	0.29	9.44

Reference: 93LAR/TEW
Method: calorimetry
Buffer: phosphate
pH: 8.15
Evaluation: A

5.41. Enzyme: phenylalanine ammonia-lyase (EC 4.3.1.5)

L-phenylalanine(aq)=*trans*-cinnamate(aq)+ammonia(aq)

$\frac{T}{K}$	pH	Buffer	K'_c
303.15	6.8	potassium phosphate (0.13 mol dm^{-3})	6.0
303.15	6.8	potassium phosphate (0.08 mol dm^{-3})	4.7
303.15	6.8	potassium phosphate (0.08 mol dm^{-3})	5.7
303.15	6.8	potassium phosphate (0.12 mol dm^{-3})	5.2
303.15	6.8	potassium phosphate (0.12 mol dm^{-3})	6.1
303.15	6.8	potassium phosphate (0.08 mol dm^{-3})	5.9
303.15	6.8	potassium phosphate (0.08 mol dm^{-3})	7.4
303.15	6.8	potassium phosphate (0.19 mol dm^{-3})	7.9
303.15	6.8	potassium phosphate (0.19 mol dm^{-3})	7.9
303.15	6.8	potassium phosphate (0.12 mol dm^{-3})	8.0
303.15	6.8	potassium phosphate (0.08 mol dm^{-3})	7.4
303.15	8.5	sodium diphosphate (0.08 mol dm^{-3})	3.9
303.15	8.5	sodium diphosphate (0.08 mol dm^{-3})	5.4
303.15	8.5	sodium diphosphate (0.069 mol dm^{-3})	6.2
303.15	8.5	sodium diphosphate (0.084 mol dm^{-3})	5.4
303.15	8.5	sodium diphosphate (0.08 mol dm^{-3})	5.5
303.15	8.5	sodium diphosphate (0.08 mol dm^{-3})	6.6
303.15	8.5	sodium diphosphate (0.069 mol dm^{-3})	6.3
303.15	8.5	sodium diphosphate (0.084 mol dm^{-3})	6.2
303.15	8.5	sodium diphosphate (0.08 mol dm^{-3})	6.7

Reference: 68HAV/HAN
Method: chromatography
Buffer: sodium diphosphate and potassium phosphate
pH: 6.8–8.5
Evaluation: B

The apparent equilibrium constants given here were taken from Havir and Hansen's Fig. 2.

L-phenylalanine(aq)=*trans*-cinnamate(aq)+ammonia(aq)

$\frac{T}{K}$	pH	K'_m
285.65	7.68	1.54
292.15	7.62	2.09
298.05	7.69	2.47
304.45	7.62	3.11
309.95	6.98	3.61
309.95	7.25	3.74
309.95	7.71	3.46
309.95	7.39	3.70
309.95	7.28	3.58
316.45	7.23	4.48

Reference: 87TEW/GAJ
Method: HPLC
Buffer: Tris (0.1 mol dm^{-3})+HCl
pH: 7.0–7.7
Evaluation: A

Tewari *et al.* also calculated $K_m=(1.16\pm0.3)$ and $\Delta_r H°=(24.8\pm2.0)$ kJ mol^{-1} at $T=298.15$ K and $I=0$ for the chemical reference reaction: L-phenylalanine$^{\pm}$(aq)=*trans*cinnamate^{-}(aq)+NH_4^+(aq).

5.42. Enzyme: β-alanyl-CoA ammonia lyase (EC 4.3.1.6)

β-alanylpantetheine(aq)=acrylylpantetheine(aq)+ammonia(aq)

$\frac{T}{K}$	pH	K'_c
298.15	7.5	1.22E-6

Reference: 59VAG/EAR
Method: spectrophotometry
Buffer: triethanolamine (0.05 mol dm^{-3})+HCl
pH: 7.5
Evaluation: B

5.43. Enzyme: arginosuccinate lyase (EC 4.3.2.1)

N-(L-argino)succinate(aq)=fumarate(aq)+L-arginine(aq)

$\frac{T}{K}$	pH	K'_c
311.15	7.5	0.0114

Reference: 53RAT/ANS
Method: chemical analysis
Buffer: potassium phosphate (0.05 mol dm^{-3})
pH: 7.5
Evaluation: B

5.44. Enzyme: adenylosuccinate lyase (EC 4.3.2.2)

adenylosuccinate(aq)=fumarate(aq)+AMP(aq)

$\frac{T}{K}$	pH	K'_c
298.15	7.0	0.012

Reference: 55CAR/COH
Method: spectrophotometry
pH: 7.0
Evaluation: C

The temperature was assumed to be 298.15 K. This was a preliminary result.

adenylosuccinate(aq)=fumarate(aq)+AMP(aq)

$\frac{T}{K}$	pH	K'_c
308.15	6.0	0.0063
308.15	6.75	0.0074
308.15	7.0	0.0068

Reference: 56CAR/COH
Method: spectrophotometry
Buffer: sodium phosphate (0.05 mol dm^{-3})
pH: 6.0–7.0
Evaluation: B

N-(5-amino-1-β-D-ribosylimidazol-4-yl-carbonyl)-L-aspartic acid 5′-phosphate(aq)=fumarate(aq)+5-amino-1-β-D-ribosylimidazole-4-carboxamide 5′-phosphate(aq)

$\frac{T}{K}$	pH	K'_c
310.15	7.2	0.0023

Reference: 59MIL/LUK
Method: spectrophotometry, chromatography, and radioactivity
Buffer: phosphate (0.023 mol dm^{-3})
pH: 7.2
Evaluation: C

5.45. Enzyme: unreidoglycolate lyase (EC 4.3.2.3)

(-)-ureidoglycolate(aq)=glyoxylate(aq)+urea(aq)

$\frac{T}{K}$	pH	K'_c
303.15	8.4	0.15
303.15	8.8	0.14

Reference: 65GAU/WOL
Method: chemical analysis
Buffer: sodium barbital (0.040 mol dm^{-3})
pH: 8.4–8.8
Evaluation: C

(-)-ureidoglycolate(aq)=glyoxylate(aq)+urea(aq)

$\frac{T}{K}$	pH	K'_c
303.15	7.5	0.14

Reference: 67TRI/VOG
Method: polarimetry
Buffer: triethanolamine (0.07 mol dm^{-3})+HCl
pH: 7.5
Cofactor(s): $ZnSO_4$ (0.010 mol dm^{-3})
Evaluation: B

5.46. Enzyme: lactoylglutathione lyase (EC 4.4.1.5)

(*R*)-*S*-lactoylgluthathione(aq)=glutathione (reduced)(aq)+methylglyoxal(aq)

$\frac{T}{K}$	pH	K'_c
303.15	7.0	9.0E-5

Reference: 83SEL/MAN
Method: spectrophotometry
Buffer: sodium phosphate (0.1 mol dm^{-3})
pH: 7.0
Evaluation: C

The approximate value of the apparent equilibrium constant given here was obtained from kinetic data.

5.47. Enzyme: adenylate cyclase (EC 4.6.1.1)

ATP(aq)=adenosine 3′-5′-(cyclic)phosphate(aq)+diphosphate(aq)

$\frac{T}{K}$	pH	K'_c
298.15	7.3	0.065

Reference: 71HAY/GRE
Method: enzymatic assay
Buffer: Tris (0.0590 mol dm^{-3})+HCl
pH: 7.3
Cofactor(s): $MgSO_4$ (0.010 mol dm^{-3})
Evaluation: B

ATP(aq)=adenosine 3′,5′-(cyclic)phosphate(aq)+diphosphate(aq)

$\frac{T}{K}$	pH	K'_c
298.15	7.3	0.255

Reference: 71TAK/KUR
Method: chromatography, fluorometry, and radioactivity
Buffer: Tris (0.050 mol dm^{-3})+HCl
pH: 7.3
Cofactor(s): $MgSO_4$ (0.005 mol dm^{-3})
Evaluation: C

ATP(aq)=adenosine 3′,5′-(cyclic)phosphate(aq)+diphosphate(aq)

$\frac{T}{K}$	pH	K'_c
298.15	6.2	0.029
298.15	6.5	0.036
298.15	6.8	0.049
298.15	7.0	0.065
298.15	7.3	0.116
298.15	7.7	0.270

Reference: 74KUR/TAK
Method: fluorometry, spectrophotometry, and radioactivity
Buffer: Hepes (0.060 mol dm^{-3})+KOH
pH: 6.2–7.7
Cofactor(s): $MgSO_4$ (0.005 mol dm^{-3})
Evaluation: A

6. List of Substances with Chemical Abstract Service (CAS) Registry Numbers With Cross References to Enzyme Commission Numbers

Substance	CAS Registry Number[a]	Enzyme Commission Numbers
acetaldehyde	75-07-0	4.1.2.4, 4.1.2.13
acetate	64-19-7	4.1.3.6, 4.1.3.22
acetyl-coenzyme A	102029-73-2	4.1.3.2, 4.1.3.7, 4.1.3.8, 4.1.3.24
N-acetyl-D-mannosamine	3615-17-6	4.1.3.3
N-acetylneuraminate	131-48-6	4.1.3.3
cis-aconitate	585-84-2	4.2.1.3
acrylylpantetheine	4515-49-5	4.3.1.6
adenosine 3′,5′-(cyclic)phosphate	60-92-4	4.6.1.1
adenosine 5′-diphosphate	58-64-0	4.1.3.8
adenosine 5′-monophosphate	18422-05-4	4.3.2.2
adenosine 5′-triphosphate	56-65-5	4.1.3.8, 4.6.1.1
adenylosuccinate	19046-78-7	4.3.2.2
β-alanylpantetheine	110180-69-3	4.3.1.6
5-amino-1-β-D-ribosylimidazole-4-carboxamide 5′-phosphate	3031-94-5	4.3.2.2
N-(5-amino-1-β-D-ribosylimidazol-4-yl-carbonyl)-L-aspartic acid 5′-phosphate	3031-95-6	4.3.2.2
ammonia	1336-21-6	4.1.99.1, 4.2.1.20, 4.3.1.1, 4.3.1.2, 4.3.1.3, 4.3.1.5, 4.3.1.6
D-arabino-3-hexulose 6-phosphate	53010-97-2	4.1.2.a
L-arginine	74-79-3	4.3.2.1
N-(L-argino)succinate	2387-71-5	4.3.2.1
L-aspartate	56-84-8	4.3.1.1
but-2-enoyl-[acyl-carrier protein]	[b]	4.2.1.58
cis-but-2-enoyl-coenzyme A	6244-90-2	4.2.1.17
trans-but-2-enoyl-coenzyme A	102680-35-3	4.2.1.17, 4.2.1.a
carbon dioxide	124-38-9	4.1.1.32, 4.1.1.38, 4.1.1.39
trans-cinnamate	140-10-3	4.3.1.5
citrate	77-92-9	4.1.3.6, 4.1.3.7, 4.1.3.8, 4.2.1.3
coenzyme A	85-61-0	4.1.3.2, 4.1.3.7, 4.1.3.8
2-dehydro-3-deoxy-D-fuconate	35902-09-1	4.1.2.18
2-dehydro-3-deoxy-D-galactonate 6-phosphate	32120-43-7	4.1.2.21
2-dehydro-3-deoxy-L-pentonate	3495-27-0	4.1.2.18
3-dehydroquinate	10534-44-8	4.2.1.10
3-dehydroshikimate	2922-42-1	4.2.1.10
2-deoxy-D-ribose 5-phosphate	102916-66-5	4.1.2.4
5,6-dideoxyfructose 1-phosphate	29024-88-2	4.1.2.13
4,5-dihydro-4-oxo-5-imidazolepropanoate	17340-16-8	4.2.1.49
2,3-dimethylmalate	31519-20-7	4.1.3.32
(2*R*,3*S*)-2,3-dimethylmalate	73522-92-6	4.2.1.85
dimethylmaleate	624-48-6	4.2.1.85
diphosphate	2466-09-3	4.1.1.38, 4.6.1.1
erythrulose 1-phosphate	2547-10-6	4.1.2.2
γ-fluoroglutamate	2708-77-2	4.2.1.48
cis-D-4-fluoro-5-oxopyrrolidine-2-carboxylate	160705-72-6	4.2.1.48
trans-D-4-fluoro-5-oxopyrrolidine-2-carboxylate	160705-73-7	4.2.1.48
formaldehyde	50-00-0	4.1.2.2, 4.1.2.a
D-fructose 1,6-bisphosphate	488-69-7	4.1.2.13
D-fructose 1-phosphate	103213-46-3	4.1.2.13
L-fuculose 1-phosphate	92418-41-2	4.1.2.17
fumurate	110-17-8	4.2.1.2, 4.3.1.1, 4.3.2.1, 4.3.2.2
D-glutamate	6893-26-1	4.2.1.48
glutathione (reduced)	70-18-8	4.4.1.5
D-glyceraldehyde	453-17-8	4.1.2.13
D-glyceraldehyde 3-phosphate	142-10-9	4.1.2.4, 4.1.2.13, 4.1.2.14, 4.1.2.21, 4.2.1.20
glycerone phosphate	102783-56-2	4.1.2.2, 4.1.2.13, 4.1.2.17, 4.1.2.19
glycolaldehyde	23147-58-2	4.1.2.18
glyoxylate	298-12-4	4.1.3.1, 4.1.3.2, 4.1.3.16, 4.1.3.24, 4.3.2.3

6. List of Substances with Chemical Abstract Service (CAS) Registry Numbers With Cross References to Enzyme Commission Numbers—Continued

Substance	CAS Registry Number[a]	Enzyme Commission Numbers
H_2O	7732-18-5	4.1.1.32, 4.1.1.38, 4.1.3.2, 4.1.3.7, 4.1.99.1, 4.2.1.2, 4.2.1.3, 4.2.1.10, 4.2.1.11, 4.2.1.17, 4.2.1.20, 4.2.1.31, 4.2.1.34, 4.2.1.35, 4.2.1.48, 4.2.1.49, 4.2.1.58, 4.2.1.85, 4.2.1.a
cis-hex-2-enoyl-coenzyme A	160705-74-8	4.2.1.17
trans-hex-2-enoyl-coenzyme A	10018-93-6	4.2.1.17
L-histidine	71-00-1	4.3.1.3
(3*R*)-3-hydroxybutanoyl-[acyl-carrier protein]	[b]	4.2.1.58
DL-3-hydroxybutanoyl-coenzyme A	103404-51-9	4.2.1.a
(3*R*)-3-hydroxybutanoyl-coenzyme A	21804-29-5	4.2.1.17
(3*S*)-3-hydroxybutanoyl-coenzyme A	22138-45-0	4.2.1.17
(3*R*)-3-hydroxyhexanoyl-coenzyme A	117249-47-5	4.2.1.17
(3*S*)-3-hydroxyhexanoyl-coenzyme A	79171-47-4	4.2.1.17
4-hydroxy-2-oxoglutarate	1187-99-1	4.1.3.16
indole	120-72-9	4.1.99.1, 4.2.1.20
1-(indol-3-yl)glycerol 3-phosphate	4220-97-7	4.2.1.20
inosine 5′-diphosphate	81012-88-6	4.1.1.32
inosine 5′-triphosphate	35908-31-7	4.1.1.32
isocitrate	320-77-4	4.1.3.1, 4.2.1.3
(*S*)-lactaldehyde	3913-64-2	4.1.2.17, 4.1.2.18, 4.1.2.19
(*R*)-*S*-lactoylglutathione	41656-56-8	4.4.1.5
(*R*)-malate	636-61-3	4.2.1.31
(*S*)-malate	97-67-6	4.1.3.2, 4.1.3.7, 4.2.1.2
maleate	110-16-7	4.2.1.31
(*R*,*S*)-malyl-coenzyme A	2043-93-8	4.1.3.24
L-threo-3-methylaspartate	31571-69-4	4.3.1.2
methylerythrulose 1-phosphate	160705-75-9	4.1.2.13
2-methylfumarate	498-24-8	4.2.1.34, 4.3.1.2
methylglyoxal	78-98-8	4.4.1.5
(*R*)-2-methylmalate	6236-10-8	4.2.1.35
(*S*)-2-methylmalate	6236-09-5	4.1.3.22, 4.2.1.34
2-methylmaleate	498-23-7	4.2.1.35
β-nicotinamide-adenine dinucleotide (oxidized)	53-84-9	4.1.3.7
β-nicotinamide-adenine dinucleotide (reduced)	606-68-8	4.1.3.7
oxaloacetate	328-42-7	4.1.1.32, 4.1.1.38, 4.1.3.6, 4.1.3.7, 4.1.3.8
5-oxo-D-proline	4042-36-8	4.2.1.48
L-phenylalanine	63-91-2	4.3.1.5
phosphate	10049-21-5	4.1.1.38, 4.1.3.8
6-phospho-2-dehydro-3-deoxy-D-gluconate	27244-54-8	4.1.2.14
2-phospho-D-glycerate	70195-25-4	4.2.1.11
3-phospho-D-glycerate	80731-10-8	4.1.1.39
phospho*enol*pyruvate	4265-07-0	4.1.1.32, 4.1.1.38, 4.2.1.11
propanoate	79-09-04	4.1.3.32
propionaldehyde	123-38-6	4.1.2.13
pyruvate	127-17-3	4.1.2.14, 4.1.2.18, 4.1.2.21, 4.1.3.3, 4.1.3.16, 4.1.3.22, 4.1.3.32, 4.1.99.1, 4.2.1.20
L-rhamnulose 1-phosphate	444-09-7	4.1.2.19
D-ribulose 1,5-biphosphate	108321-97-7	4.1.1.39
D-ribulose 5-phosphate	108321-99-9	4.1.2.a
L-serine	56-45-1	4.2.1.20
succinate	110-15-6	4.1.3.1
L-tryptophan	73-22-3	4.1.99.1, 4.2.1.20
urea	57-13-6	4.3.2.3
(-)-ureidoglycolate	103192-53-6	4.3.2.3
urocanate	104-98-3	4.2.1.49, 4.3.1.3

[a]In some cases the CAS registry number refers to a salt of the substance.
[b]In the absence of an amino acid sequence, no CAS registry number is assigned to this substance.

7. Abbreviations

ADP	adenosine 5′-diphosphate
AMP	adenosine 5′-monophosphate
ATP	adenosine 5′-triphosphate
CoA	coenzyme A
Hepes	*N*-(2-hydroxyethyl)piperazine-*N*′-2-ethanesulfonic acid
IDP	inosine 5′-diphosphate
ITP	inosine 5′-triphosphate
Mes	2-(*N*-morpholino)ethanesulfonic acid
Mops	3-(*N*-morpholino)propanesulfonic acid
NAD	β-nicotinamide-adenine dinucleotide (oxidized)
NADH	β-nicotinamide-adenine dinucleotide (reduced)
Tris	tris(hydroxymethyl)aminomethane

8. Glossary of Symbols

Symbol	Name	Unit
c	concentration	mol dm^{-3}
c°	standard concentration ($c^\circ = 1$ mol dm^{-3})	mol dm^{-3}
$\Delta_r C_p^\circ$	standard heat capacity of reaction at constant pressure	J K^{-1} mol^{-1}
$\Delta_r G^\circ$	standard Gibbs energy of reaction	kJ mol^{-1}
$\Delta_r G'^\circ$	standard transformed Gibbs energy of reaction	kJ mol^{-1}
$\Delta_r H^\circ$	standard enthalpy of reaction	kJ mol^{-1}
$\Delta_r H'^\circ$	standard transformed enthalpy of reaction	kJ mol^{-1}
$\Delta_r H$(cal)	calorimetrically determined enthalpy of reaction	kJ mol^{-1}
I_c	ionic strength, concentration basis	mol dm^{-3}
I_m	ionic strength, molality basis	mol kg^{-1}
K	equilibrium constant[a]	dimensionless
K'	apparent equilibrium constant[a]	dimensionless
m	molality	mol kg^{-1}
m°	standard molality ($m^\circ = 1$ mol kg^{-1})	mol kg^{-1}
$\Delta_r N(H^+)$	change in binding of hydrogen ion in a biochemical reaction	dimensionless
pH	$-\log_{10}\{c(H^+)/c^\circ\}$[b]	dimensionless
pX	$-\log_{10}\{c(X)/c^\circ\}$	dimensionless
$\Delta_r S^\circ$	standard entropy of reaction	J K^{-1} mol^{-1}
T	thermodynamic temperature	K
x	mole fraction	dimensionless

[a]When needed, a subscript c, m, or x is added to these quantities to designate a concentration, molality, or mole fraction basis.

[b]This is an approximate definition. The IUPAC Green Book (I. Mills, T. Cvitaš, K. Homann, N. Kallay, and K. Kuchitsu, "Quantities, Units and Symbols in Physical Chemistry," Blackwell Scientific Publications, Oxford, 1993) contains a discussion of the operational definition of pH.

9. Reference Codes and References in the Table

26QUA/WOO Quastel, J. H.; Woolf, B.; Biochem. J.; **20**, 545 (1926).
29WOO Woolf, B.; Biochem. J.; **23**, 472 (1929).
31BOR/SCH Borsook, H.; Schott, H. F.; J. Biol. Chem.; **92**, 559 (1931).
34JAC Jacobsohn, K. P.; Biochem. Z.; **274**, 167 (1934).
34LOH/MEY Lohman, K.; Meyerhof, O.; Biochem. Z.; **273**, 60 (1934).
34MEY/LOH Meyerhof, O.; Lohmann, K.; Biochem. Z.; **271**, 89 (1934).
35AKA Akano, R.; Biochem. Z.; **280**, 110 (1935).
35JAC/TAP Jacobsohn, K. P.; Tapadinhas, J.; Biochem. Z.; **282**, 374 (1935).
35MEY Meyerhof, O.; Biochem. Z.; **277**, 77 (1935).
35MEY/LOH Meyerhof, O.; Lohman, K.; Biochem. Z.; **275**, 430 (1935).
36MEY/SCH Meyerhof, O.; Schulz, W.; Biochem. Z. **289**, 87 (1936).
36MEY/LOH Meyerhof, O.; Lohmann, K.; Schuster, Ph.; Biochem. Z.; **286**, 301 (1936).
40HER/GOR Herbert, D.; Gordon, H.; Subrahmanyan, V.; Green, D. E.; Biochem. J.; **34**, 1108 (1940).
40KRE/SMY Krebs, H. A.; Smyth, D. H.; Evans, E. A., Jr.; Biochem. J.; **34**, 1041 (1940).
41UTT/WER Utter, M. F.; Werkman, C. H.; J. Bacteriol.; **42**, 665 (1941).
41WAR/CHR Warburg, O.; Christian, W.; Biochem. Z.; **310**, 384 (1941).
43KRE/EGG Krebs, H. A.; Eggleston, L. V.; Biochim. J.; **37**, 334 (1943).
43MEY/JUN Meyerhof, O.; Junowicz Kocholaty, R.; J. Biol. Chem.; **149**, 71 (1943).
45OHL Ohlmeyer, P.; Hoppe-Seyler's Z. Physiol. Chem.; **282**, 37 (1945).
46OHL Ohlmeyer, P.; Z. Naturforsch.; **1**, 30 (1946).
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49MEY/OES Meyerhof, O.; Oesper, P.; J. Biol. Chem.; **179**, 1371 (1949).
52STE/OCH Stern, J. R.; Ochoa, S.; Lynen, F.; J. Biol. Chem.; **198**, 313 (1952).
53BOC/ALB Bock, R. M.; Alberty, R. A.; J. Am. Chem. Soc.; **75**, 1921 (1953).
53KRE Krebs, H. A.; Biochem. J.; **54**, 78 (1953).
53MAS Massey, V.; Biochem. J.; **53**, 72 (1953).
53RAT/ANS Ratner, S.; Anslow, W. P.; Jr.; Petrack, B.; J. Biol. Chem.; **204**, 115 (1953).
54CHA Charlampous, F. C.; J. Biol. Chem.; **211**, 249 (1954).
54MIT/DAV Mitsuhashi, S.; Davis, B. D.; Biochim. Biophys. Acta; **15**, 54 (1954).
54UTT/KUR Utter, M. F.; Kurahashi, K.; J. Biol. Chem.; **207**, 821 (1954).
55CAR/COH Carter, C. E.; Cohen, L. H.; J. Am. Chem. Soc.; **77**, 499 (1955).
55LEH/SIC Lehninger, A. L.; Sice, J.; Jensen, E. V.; Biochim. Biophys. Acta; **17**, 286 (1955).
55WIL/MCI Williams, V. R.; McIntyre, R. T.; J. Biol. Chem.; **217**, 467 (1955).
56CAR/COH Carter, C. E.; Cohen, L. H.; J. Biol. Chem.; **222**, 17 (1956).
56KIT/HOR Kitzinger, C.; Horecker, B. L.; Weisbach, A; Abstr. 20th Int. Physiol. Congress, Brussels (1956).
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56STE/DEL Stern, J. R.; del Campillo, A.; J. Biol. Chem.; **218**, 985 (1956).
57WOL/BAL Wold, F.; Ballou, C. E.; J. Biol. Chem.; **227**, 301 (1957).
57SMI/GUN Smith, R. A.; Gunsalus, I. C.; J. Biol. Chem.; **229**, 305 (1957).
59BAR/SMY Barker, H. A.; Smyth, R. D.; Wilson, R. M.; Weissbach, H.; J. Biol. Chem.; **234**, 320 (1959).
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63KUR/FUK Kuratomi, K.; Fukunaga, K.; Biochim. Biophys. Acta; **78**, 617 (1963).
63MEI/BUK Meister, A.; Bukenberger, M. W.; Strassburger, M.; Biochem. Z.; **338**, 217 (1963).
64LOW/PAS Lowry, O. H.; Passonneau, J. V.; J. Biol. Chem.; **239**, 31 (1964).
64MAI/DEK Maitra, U.; Dekker, E. E.; J. Biol. Chem.; **239**, 1485 (1964).
64MEL/WOO Meloche, H. P.; Wood, W. A.; J. Biol. Chem.; **239**, 3511 (1964).
65CHI/FEI Chiu, T. H.; Feingold, D. S.; Biochem. Biophys. Res. Commun.; **19**, 511 (1965).
65GAU/WOL Gaudy, E. T.; Wolfe, R. S.; J. Bacteriol.; **90**, 1531 (1965).
65SEK/SUN Sekijo, C.; Sunhara, N.; Iwakumo, S.; Hakko To Taisha; **2**, 139 (1965).
65TAT/DAT Tate, S. S.; Datta, S. P.; Biochem. J.; **94**, 470 (1965).
66SHU Shuster, C. W.; Methods Enzymol.; **9**, 524 (1966).
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69VEE/RAI Veech, R. L.; Raijman, L.; Dalziel, K.; Krebs, H. A.; Biochem. J.; **115**, 837 (1969).
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73VEL/GUY Veloso, D.; Guynn, R. W.; Oskarsson, M.; Veech, R. L.; J. Biol. Chem.; **248**, 4811 (1973).

74FER/STR Ferenci, T.; Strøm, T.; Quayle, J. R.; Biochem. J.; **144**, 477 (1974).

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