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The Herington Test for Thermodynamic Consistency

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The Herington test for thermodynamic consistency is examined in detail and shown to be incorrect. New expressions are proposed for the cases where information on heats of mixing is or is not available.

The Gibbs–Duhem equation imposes a general coupling among the partial properties of the components in a mixture and is generally the basis of most methods to test their thermodynamic consistency. Its general form is (Van Ness, 1964)

$$\sum x_i d \ln \gamma_i = -\frac{\Delta V}{RT} dP + \frac{\Delta H}{RT^2} dT \quad (1)$$

where ΔV and ΔH represent respectively the molar volume of mixing and molar enthalpy of mixing.

At constant temperature and pressure eq 1 may be written, for a binary system

$$x_1 \frac{d \ln \gamma_1}{dx_1} + x_2 \frac{d \ln \gamma_2}{dx_1} = 0 \quad (2)$$

Equation 2 is the basis of the so-called point-to-point test for thermodynamic consistency, but it is of little use since data are normally measured at either constant temperature or constant pressure. In its integrated form it becomes

$$\int_0^1 \ln \frac{\gamma_1}{\gamma_2} dx_1 = 0 \quad (3)$$

Equation 3—not applicable to the case of vapor–liquid equilibrium—means that if we plot $\ln \gamma_1/\gamma_2$ vs x_1 , the areas above (A) and below (B) the x -axis must be equal (Figure 1). This is the so-called area of Redlich–Kister test (1948), in which it is assumed that the volume and heat effects of mixing are negligible. In most isothermal cases the volume of mixing can be safely neglected and the thermodynamic consistency test performed according to the Redlich–Kister method. This is not the case for isobaric nonisothermal data for which

$$\int_0^1 \ln \frac{\gamma_1}{\gamma_2} dx_1 = \int_{T_2^\circ}^{T_1^\circ} \frac{\Delta H}{RT^2} dT = I \quad (4)$$

the right-hand-side integral of eq 4 cannot be neglected, and its evaluation requires data on the variation of the heat of mixing with temperature and composition. For consistent data, the value of I represents the difference between areas A and B caused by heat of mixing effects, as well as the experimental error.

Experimental information on the variation of the heat of mixing with temperature and composition is rarely available, and to overcome this difficulty Herington (1951) proposed an empirical test that estimates the value of the right-hand-side integral in eq 4 by using as the only parameter the total boiling-point range of the mixture.

As a first approximation, Herington assumes that the heat of mixing is a function of x_1 solely and independent of temperature over the temperature range covered by the isobaric data. Under this limitation eq 4 can be integrated to give

$$\int_0^1 \ln \frac{\gamma_1}{\gamma_2} dx_1 = \frac{\Delta H_a [T_1^\circ - T_2^\circ]}{RT_1^\circ T_2^\circ} \quad (5)$$

where ΔH_a represents the average value of the heat of

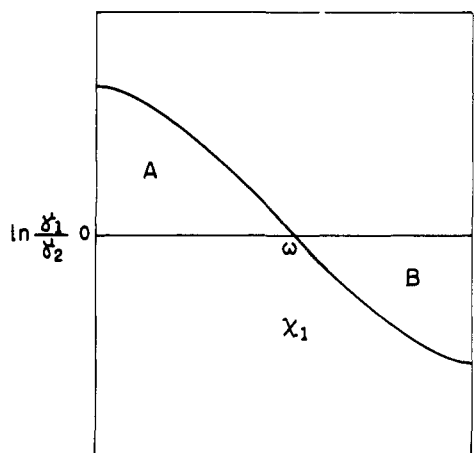


Figure 1. Plot of eq 6.

mixing in the total concentration range and T_1° and T_2° represent the boiling points of pure components 1 and 2 at the operating pressure. Herington then replaces ΔH_a by ΔH_m , the maximum (minimum) value of the heat of mixing in the concentration range, and the product $(T_1^\circ T_2^\circ)$ by T_i^2 where T_i is the lowest boiling point expressed in kelvin. If an azeotrope is present, the difference $|T_1^\circ - T_2^\circ|$ is replaced by $(T_{\max}^\circ - T_{\min}^\circ)$, the maximum difference in boiling points.

Equation 5 becomes

$$\int_0^1 \ln \frac{\gamma_1}{\gamma_2} dx_1 < \frac{\Delta H_m |T_1^\circ - T_2^\circ|}{RT_i^2} \quad (6)$$

According to Herington, the function on the right-hand side of inequality 6 will usually be several times larger than that on the left, particularly for systems which form azeotropes.

Let us now consider the total area Σ of the plot represented in Figure 1. From the relation

$$\Delta G^E = RT[x_1 \ln \gamma_1 + x_2 \ln \gamma_2] \quad (7)$$

we get

$$\frac{d(\Delta G^E/RT)}{dx_1} = \ln \frac{\gamma_1}{\gamma_2} \quad (8)$$

According to eq 8, the extreme value of ΔG^E (ΔG_m^E) occurs when $\gamma_1 = \gamma_2$ and $x_1 = \omega$. Integrating eq 8 from $x_1 = 0$ to $x_1 = \omega$, we get

$$A = \frac{\Delta G_m^E}{RT_\omega} \quad (9)$$

For consistent data $A = B$ so that the total area of the curve represented in Figure 1 is $|2\Delta G_m^E/RT_\omega|$.

Table 1. Parameters of the Herington Relation

	$(\Delta H/\Delta G^E)_{\max}$	$\%T_{\max}/T_{\min}$	$\Delta H_s/\Delta H_{\max}$		$(\Delta H/\Delta G^E)_{\max}$	$\%T_{\max}/T_{\min}$	$\Delta H_s/\Delta H_{\max}$
butanol + cyclohexane (13) ^a	0.0008	110.5	0.40	nitromethane + <i>m</i> -xylene (41)	1.6	110.1	0.71
2-butanol + cyclohexane (13)	0.0008	105.3	0.62	methanol + ethyl acetate (39)	1.6	103.7	0.54
tert-butanol + cyclohexane (13)	0.0011	100.5	0.47	TKEBS + benzene (53)	1.6		0.63
benzene + pyridine (29)	0.1	110.0	<i>b</i>	ethyl formate + EtOH (37)	1.6	107.4	0.67
cyclopentane + 2,3-dimethylbutane (30)	0.1	102.7	<i>b</i>	2-propanol + benzene (38)	1.7	100.6	0.71
dioxane + acetonitrile (11)	0.1	105.6		nitromethane + <i>o</i> -xylene (41)	1.8	111.5	0.67
chlorobenzene + pyridine (29)	0.2	104.2	0.60	nitromethane + <i>p</i> -xylene (41)	1.8	109.9	0.64
methanol + benzene (51)	0.3	104.6	0.55	nitromethane + benzene (41)	1.8	106.0	0.75
triethylamine + ethanol (7)	0.3	103.2	0.63	cyclohexane + 2,3-dimethylbutane (31)	1.8	110.5	0.63
propanol + water (25)	0.3	100.7	<i>b</i>	cyclohexane + carbon tetrachloride (62)	1.9	101.2	0.52
water + acetone (58)	0.3	113.3	<i>b</i>	hexane + hexadecane (55)	1.9	163.8	0.69
TKEBS ^c + cyclohexane (53)	0.3		0.69	heptane + hexadecane (55)	1.9	150.7	0.65
TKEBS + carbon tetrachloride (53)	0.4		0.50	decane + hexadecane (55)	1.9	125.2	0.67
acetic acid + water (14)	0.4	104.8	0.60	octane + hexadecane (55)	1.9	140.4	0.67
ethanol + methylcyclohexane (19)	0.5	106.4	0.53	triethylamine + water (7)	2.0	102.9	0.70
ethanol + cyclohexane (52)	0.5	100.7	0.74	perfluoromethylcyclohexane + methylcyclohexane (8)	2.1	107.1	0.68
carbon tetrachloride + chloroform (27)	0.6	104.6	0.67	ethyl acetate + EtOH (39)	2.1	100.3	0.70
methanol + carbon tetrachloride (51)	0.6	103.5	0.72	cyclohexane + methylpyrrolidine (4)	2.1		0.49
dioxolane + acetonitrile (6)	0.6		0.57	cyclohexane + methanol (61)	2.1	104.8	0.48
cyclopentane + cyclopentanol (20)	0.6	128.4	0.74	carbon tetrachloride + cyclohexane (47)	2.1	101.1	0.66
cyclooctane + cyclohexane (33)	0.6	116.2	<i>b</i>	ethyl formate + PrOH (37)	2.1	113.1	0.66
cyclopentane + cyclohexanol (3)	0.6	134.7	0.74	ethanol + MEK (36)	2.2	100.4	0.65
carbon tetrachloride + methanol (50)	0.6	103.5	0.38	cyclohexane + pyrrolidine (4)	2.3	101.6	0.42
cyclohexane + cyclopentanol (3)	0.6	117.0	0.72	carbon tetrachloride + cyclohexane (17)	2.3	101.2	0.63
cyclohexane + cyclohexanol (20)	0.7	122.7	0.74	cyclohexane + piperidine (4)	2.3	112.4	0.56
2-propanol + water (25)	0.7	105.0	<i>b</i>	cyclohexane + triethylene imine (4)	2.3		0.53
cycloheptane + cyclopentanol (1)	0.7	105.6	0.67	2,6-lutidine + water (24)	2.4	111.7	0.61
cyclohexane + cycloheptane (10)	0.7	109.8	0.61	cyclohexane + hexamethylene imine (4)	2.4	116.2	0.52
ethylbenzene + pyridine (29)	0.7	102.7	0.57	ethyl formate + 2-PrOH (37)	2.5	108.6	0.65
cyclooctane + cyclopentanol (1)	0.7	105.9	0.69	benzene + cyclohexane (16)	2.5	100.2	0.66
cycloheptane + cycloheptanol (1)	0.7	116.9	0.79	cyclohexane + benzene (17)	2.6	100.2	0.80
acetophenone + 2-butanol (34)	0.7	127.6	0.66	methyl acetate + PrOH (36)	2.6	112.2	0.66
benzene + methanol (49)	0.7	104.6	0.56	ethyl acetate + chloroform (43)	2.7	104.8	0.53
hexane + decane (16)	0.8	130.8	0.66	ethyl acetate + PrOH (39)	2.7	105.7	0.68
acetonitrile + carbon tetrachloride (27)	0.8	101.5	0.71	methanol + water (25)	2.9	110.5	0.58
ethanol + toluene (19)	0.8	109.2	0.51	MEK + chloroform (43)	2.9	105.5	0.57
hexane + undecane (16)	0.9	137.2	0.65	water + 2-aminoethanol (54)	3.0		0.60
cycloheptane + cyclooctane (10)	0.9	105.0	0.51	methyl acetate + 2-PrOH (36)	3.0	107.7	0.64
acetonitrile + water (59)	0.9	105.2	0.62	methyl acetate + chloroform (43)	3.1	101.3	0.61
ethanol + toluene (23)	1.0	109.2	0.42	hexamethylphosphoramide + water (21)	3.2		0.65
acetic acid + chloroform (14)	1.0	117.0	0.65	ethyl formate + chloroform (43)	3.3	102.1	0.54
ethylenediamine + ethylene glycol (15)	1.0	120.6	0.60	hexane + 2,4-dimethylpentane (18)	3.4	103.5	0.78
hexane + dodecane (16)	1.0	143.2	0.66	cyclohexane + methylpiperidine (4)	3.5		0.53
ethanol + water (35)	1.0	106.2	0.52	ethyl acetate + 2-PrOH (39)	3.7	101.5	0.62
ethanol + water (25)	1.0	106.2	0.35	MEK + 2-PrOH (36)	3.7	100.7	0.64
ethyl formate + MeOH (37)	1.1	103.2	0.67	water + methanol (9)	3.7	110.5	0.43
chloroform + ethanol (46)	1.1	105.1	<i>b</i>	1-chlorohexane + toluene (45)	3.8	106.4	0.59
acetone + methyl iodide (28)	1.2	104.4	0.53	methanol + piperidine (40)	3.8	112.4	0.66
ethyl acetate + methyl Cellosolve (5)	1.2	113.5	0.63	diethylamine + water (7)	4.1	113.5	0.64
cycloheptane + 2,3-dimethylbutane (31)	1.2	118.3	0.67	acetonitrile + chloroform (27)	4.2	106.1	0.65
carbon tetrachloride + benzene (17)	1.3	101	0.64	benzene + <i>p</i> -xylene (44)	4.2	116.5	0.64
propylene glycol + ethylene glycol (42)	1.4	102.3	0.60	dibutyl phosphate + chloroform (2)	4.3		0.67
perfluorocyclohexane + cyclohexane (8)	1.4	108.6	0.70	water + methyl-2-aminoethanol (54)	4.3		0.59
methanol + MEK ^d (36)	1.4	104.4	0.58	hexane + 2-methylpentane (18)	4.6	102.5	0.68
nitromethane + toluene (41)	1.5	102.5	0.74	1-chlorohexane + ethylbenzene (45)	5.2	100.3	0.76
cyclohexane + ethylene imine (4)	1.5		0.60	hexane + 3-methylpentane (18)	6.2	101.6	0.62
hydrogen peroxide + water (35)	1.5	113.8	0.66	trimethylamine + hexane (12)	6.2	123.8	0.64
carbon tetrachloride + benzene (48)	1.5	101.0	0.65	water + ethylene glycol (57)	7.1	126.2	0.67
cyclohexane + pyridine (29)	1.5	109.8	0.59	octane + 3-methylpentane (26)	9.7	118.5	0.63
2-propanol + 2-bromopropane (56)	1.5	106.9	0.76	diethylamine + ethanol (7)	10.4	107.0	0.49
aniline + toluene (22)	1.6	119.2	0.68	octane + 2,4-dimethylpentane (26)	11.4	112.8	0.65
perfluoroheptane + isooctane (60)	1.6		0.71	octane + 2-methylpentane (26)	12.8	119.6	0.72
perfluorocyclohexane + 1,3,5-trimethylcyclohexane (8)	1.6	126.3	0.71	1-chlorohexane + propylbenzene (45)	16.9	105.9	0.73
perfluorohexane + hexane (60)	1.6	104.9	0.65	water + dimethyl-2-aminoethanol (54)	18.8		0.58
				2,2,4-trimethylpentane + hexadecane (55)	28.6	150.4	0.70

Table 1 (Continued)

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Chem.* 1952, 74, 3729-3733. ^b ΔH changes sign with concentration. ^c TKEBS, tetrakis(2-ethylbutoxy)silane. ^d MEK, methyl ethyl ketone.

Replacing the expressions for I and Σ in eq 6, we get

$$\frac{100|J|}{\Sigma} < 50 \left| \frac{\Delta H_m}{\Delta G_m^E} \right| \left| \frac{T_1^\circ - T_2^\circ}{T_i} \right| \quad (10)$$

The next step taken by Herington was to derive a maximum probable value for the ratio $\Delta H_a/\Delta G_m^E$. She did so by examining 15 actual systems for which these parameters had been measured. Herington reported that the average and maximum values of the parameter are 1.5 and 2.9, respectively, and since the systems examined comprise mixtures of all types and contain polar and nonpolar liquids, she concluded that the value of 3.0 for the function $\Delta H_a/\Delta G_m^E$ will rarely be exceeded. Inserting $\Delta H_a/\Delta G_m^E = 3$ in eq 10 yields eq 11, which represents the Herington inequality

$$D = \frac{100|J|}{\Sigma} < 150 \left| \frac{T_{\max} - T_{\min}}{T_{\min}} \right| = J \quad (11)$$

$$|D| < J \quad (12)$$

According to Herington, some deviations from the expected behavior will result from small experimental errors, and in the light of experience gained in the application of the test to isothermal data, an uncertainty of 10 units in D may be arbitrarily assigned to this source. Allowance may be made for the effect of these small deviations in the test by postulating that $|D - J|$ must exceed 10 units before the data be considered inconsistent. The Herington criteria then becomes $|D - J| < 10$ for consistent data and $|D - J| > 10$ for inconsistent data.

The Herington test is very simple to apply, and since its publication more than 40 years ago, it has been widely used to test the thermodynamic consistency of isobaric

vapor-liquid equilibrium data. It is one of the two consistency tests utilized by the Dortmund data bank (Gmehling and Onken, 1977) in their evaluation of thermodynamic data. Because of the practical importance of the Herington test and the fact that more than 200 publications are available today that simultaneously report data on ΔH and ΔG^E (Wisniak and Tamir, 1978, 1982, 1986), it was decided to reevaluate the test by taking a very large sample of the available data and calculating the necessary parameters. These are presented in Table 1 together with some additional information.

Inspection of Table 1 indicates the following shortcomings of the Herington test:

1. In the deviation of eq 6 the average heat of mixing ΔH_a is replaced by its maximum value ΔH_m . The last column in the Table indicates that the ratio $\Delta H_a/\Delta H_m$ varies between 0.38 and 0.79.

2. In the derivation of eq 6 the value of $|T_1^\circ - T_2^\circ|/(T_1^\circ T_2^\circ)$ is replaced by $(T_{\max}^\circ - T_{\min}^\circ)/T_{\min}^2$, where T_2° and T_1° become the maximum and minimum boiling temperatures, respectively. From Table 1 we see that if no azeotrope is present then eq 6 will overestimate the error by 15% on the average. If an azeotrope is present, there will be a sizable increase in the allowable error.

3. Taking both of the above arguments together indicates that eq 10 should read, approximately,

$$\frac{100|J|}{\Sigma} < 34 \left| \frac{\Delta H_a}{\Delta G_m^E} \right| \left| \frac{T_1^\circ - T_2^\circ}{T_i} \right| \quad (13)$$

In other words, the present form of Herington's criterion is too liberal; it allows for a thermal effect much larger than the real and will declare the data consistent when they are not. Equation 13 will test for thermodynamic information if data on heat of mixing (or its average value) are available.

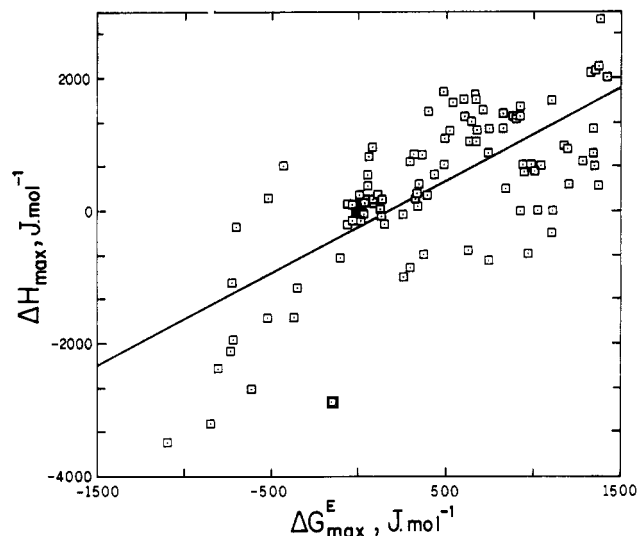


Figure 2. Plot of ΔH_{\max} against ΔG_{\max}^E .

4. The most serious flaw of Herington's reasoning is in passing from eq 10 to eq 11. According to Herington the value of $\Delta H_a/\Delta G_m^E$ will seldom exceed 3. This is contrary to the data reported in Table 1, where it is seen that the ratio $\Delta H_a/\Delta G_m^E$ varies between 0 and 28.6, and that the value 3.0 is exceeded in more than 20% of the cases examined. In addition, no polarity pattern is clear; for example, for nonpolar mixtures the ratio $\Delta H_a/\Delta G_m^E$ varies between 0.1 for cyclohexane + 2,3-dimethylbutane and 28.6 for 2,2,4-trimethylpentane + hexadecane.

We have plotted the values of ΔH_{\max} against those of ΔG_m^E (Figure 2) and found that they are significantly correlated as follows:

$$\Delta H_{\max}(\text{J mol}^{-1}) = -237.02 + 1.3863\Delta G_m^E(\text{J mol}^{-1}) \quad (14)$$

with a coefficient of determination $R^2 = 0.520$.

If the data can be represented by Wilson's equation (Wilson, 1964)

$$\frac{\Delta G^E}{RT} = -x_1 \ln(x_1 + A_{12}x_2) - x_2 \ln(x_2 + A_{21}x_1) \quad (15)$$

then we can use the relation

$$\frac{\partial(\Delta G^E/RT)}{\partial T} = -\frac{\Delta H}{RT^2} \quad (16)$$

to obtain

$$\Delta H = x_1 x_2 \left[\frac{A_{12}(\lambda_{12} - \lambda_{11})}{x_1 + x_2 \lambda_{12}} + \frac{A_{21}(\lambda_{12} - \lambda_{22})}{x_2 + x_1 \lambda_{21}} \right] \quad (17)$$

Equation 17 can be then used to calculate the value of ΔH_a (instead of ΔH_m) to be replaced in eq 6.

It is clear then that the so-called Herington's criterion for thermodynamic consistency is wrong and should not be used for consistency testing, unless some information is available on heat of mixing, in which case the test should be performed using eq 15. In the absence of these kind of data, eq 14 or Figure 2 can be used to calculate the ratio $\Delta H_a/\Delta G_m^E$ to be replaced in eq 13.

Nomenclature

A_{12}, A_{21} = Wilson parameters, eq 15
 D = dimensionless parameter defined by eq 11
 ΔG^E = excess Gibbs energy
 ΔH = heat of mixing
 I = parameter defined by eq 4
 J = dimensionless parameter defined by eq 11
 R = universal gas constant
 T = absolute temperature, K
 T_1° = boiling point of pure component 1, K
 T_2° = boiling point of pure component 2, K
 T_i = minimum boiling point, K
 ΔV = molar volume of mixing
 x_i = molar composition of liquid phase
 γ_i = activity coefficient
 λ_{ij} = interaction energies, eq 17
 Σ = total area
 ω = concentration at which $\gamma_1 = \gamma_2$ (see Figure 1)

Subscripts

a = average
 m = maximum or minimum value
 max = maximum

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