Int J Thermophys (2010) 31:860–874
DOI 10.1007/s10765-010-0706-z

The Use of Database Influence Factors to Maintain Currency in an Evaluated Chemical Database

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Received: 17 June 2009 / Accepted: 16 January 2010 / Published online: 7 February 2010

Abstract Maintaining currency of thermophysical property values in a chemical database with the rapid pace of published new experimental data is particularly difficult for evaluated databases. Evaluated databases that provide recommended values for each of the properties require labor intensive evaluation of not only the newly published property values, but also all related property values stored in the database. One possible solution to this problem is the establishment of a triage system to evaluate the potential influence of new data on recommended property values. Such a priority assignment system for the DIPPR®801 Pure Chemical Database has been developed. Evaluation of the potential impact of new data on the recommended values is done through a correlation for the Influence Factor (IF) that includes weighting factors for the type of property, the experimental methodology, the quality of the data, the quantity of data upon which the current recommendation is based, and the significance of the potential change. Database IFs help prioritize review work on the DIPPR®801 database and thereby contribute to its quality and currency.

Keywords Database · DIPPR · Thermophysical properties · Weighting factor

1 Introduction

A hallmark of the DIPPR®801 Pure Chemical Database [1] is the extensive data evaluation performed to provide within the database recommended "best" property values and their uncertainties. The evaluation and recommendation steps apply to temperature-dependent properties as well as constant properties. The evaluation process is extremely labor intensive and time consuming as it includes not only automated

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quality control checks, but also evaluation of experimental methods and techniques, analysis of interproperty consistency using all known relationships, comparison of properties within chemical families, and consistent property trends with molecular structure. While this evaluation step is the foundation of the accuracy and consistency of property values in the DIPPR®801 database, its labor-intensive nature causes difficulties in keeping the recommended values current with the new experimental data being regularly published.

In this paper, we describe a system for efficiently determining to what extent re-evaluation is warranted by newly published data. The system presupposes the retrieval and entry of data from the literature in an efficient manner. This is being accomplished in different manners by various database providers. In the case of the DIPPR®801 database, raw data retrieval is done by "current journal" searching which places the retrieved data into the database with a "U" designation for unevaluated. Once the raw data are available in electronic form, evaluation of the data must be made in relation to the other values already in the database, not only for the specific property and chemical to which the newly reported values apply, but also in relation to related properties and chemicals in the entire database. This will become clearer in the examples given later in this paper. While the DIPPR®801 database has some 45 automated quality control checks to test these relationships [2] and the NIST database [3,4] has an automated ThermoData Engine [5] that performs dynamic data evaluation, the level of critical evaluation discussed here must be performed by database staff and requires a larger time commitment than is possible to keep the recommended values current with the most recent literature. A potential solution, recently implemented in the DIPPR®801 database procedures, is a triage system that uses the unevaluated raw data extracted from the current literature searches to calculate an Influence Factor (IF). The IF value is based on weighted factors derived from the type of property, the experimental methodology, the quality of the data, the quantity of data upon which the current recommendation is based, and the significance of the potential update. The IF serves not only to prioritize updates, but also as a map of the most efficient way to make the update.

2 Interproperty and Interchemical Evaluations

The DIPPR®801 database is a "complete" database, meaning that all 47 properties are included for each chemical. Where no experimental data are available, the recommended value is predicted using one or more of over 120 critically evaluated techniques. Many prediction methods involve not only the structure of the molecule, but also the values of other properties of the chemical. For example, properties predicted using the principle of corresponding states are dependent upon the values of the critical constants (critical temperature, critical pressure, and critical volume). Similarly, other property prediction methods require various input properties such as density, heat capacity, normal boiling point, dipole moment, acentric factor, etc. This interconnectivity of properties is illustrated in Fig. 1. The acronyms used for the properties are defined in Table 1. The blue connections represent direct consistency relationships that must be resolved because of rigorous thermodynamic relationships; the red

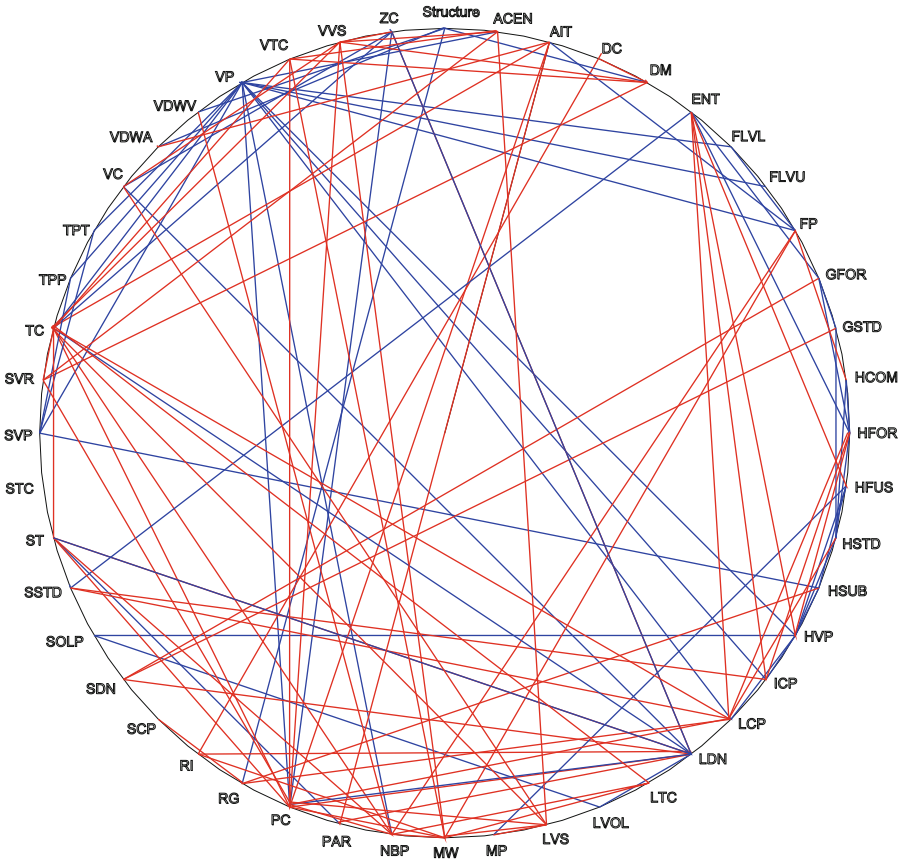

Fig. 1 Interconnectivity of the properties in the DIPPR® 801 database showing thermodynamic or rigorous relations (*blue lines*) and predictive equation relations (*red lines*). (Color figure online)

connections represent relationships between properties that occur in the prediction methods commonly used by DIPPR® 801. Thus, updates to a property require re-assessment of all the properties connected to it with the blue lines. Updates may also require re-evaluation of any properties that were predicted using that property, as indicated by the red connections. There is also a cascade effect: primary connection points that are in turn connected to additional points may represent additional required re-evaluation of those properties, and so on.

In addition to performing the interproperty consistency evaluation illustrated in Fig. 1, interchemical consistency is also evaluated in conjunction with updates suggested by the IF analysis. The objective of this additional constraint is to improve the quality of the recommendations by employing a broad range of experimental data and requiring smooth property trends for structurally related chemicals, particularly those within a homomorphic family.

IF values suggest not only when the properties of the chemical should be re-evaluated, but they also indicate the extent (which properties are affected) of the evaluation that should be performed. They provide a map for the evaluation process.

Table 1 DIPPR®801 database properties and their abbreviations

Constants			
Abbreviations	Property	Abbreviations	Property
ACEN	Acentric factor	MP	Melting point at 1 bar
AIT	Autoignition temperature	MW	Molecular weight
DC	Dielectric constant at 298 K	NBP	Normal boiling point
DM	Dipole moment	PAR	Parachor
ENT	Entropy of ideal gas at 298 K and 1 bar	PC	Critical pressure
FLVL	Lower flammability limit in volume percent	RG	Radius of gyration
FLVU	Upper flammability limit in volume percent	RI	Refractive index
FP	Flash point	SOLP	Solubility parameter at reference T and P
GFOR	Gibbs energy of formation at 298 K and 1 bar	TC	Critical temperature
GSTD	Standard state Gibbs energy of formation at 298 K and 1 bar	TPP	Triple point pressure
HCOM	Net standard state enthalpy of combustion at 298 K	TPT	Triple point temperature
HFOR	Enthalpy of formation for ideal gas at 298 K	VC	Critical volume
HFUS	Enthalpy of fusion at melting point	VDWA	Van der Waals area
HSTD	Standard enthalpy of formation at 298 K and 1 bar	VDWV	Van der Waals reduced volume
HSUB	Heat of sublimation at the triple point	ZC	Critical compressibility factor
LVOL	Liquid molar volume at a reference T and P		
Temperature-dependent			
HVP	Heat of vaporization	ST	Surface tension
ICP	Ideal gas heat capacity	STC	Solid thermal conductivity
LCP	Liquid heat capacity	SVP	Solid vapor pressure
LDN	Liquid density	SVR	Second virial coefficient
LTC	Liquid thermal conductivity	VP	Liquid vapor pressure
LVS	Liquid viscosity	VTC	Vapor thermal conductivity
SCP	Solid heat capacity	VVS	Vapor viscosity
SDN	Solid density		

The necessity of such a triage procedure for the DIPPR®801 database is illustrated by the statistics given in Table 2 that show the substantial person hours involved in evaluating, predicting, and ensuring both the interproperty and interchemical consistency described above. These projected hours include data retrieval, data entry, and review by DIPPR project sponsors in addition to the important evaluation step. It is immediately evident that the rate of regular complete reviews cannot keep pace with

Table 2 Statistics on the DIPPR® 801 database

Database inception date	1980
Number of chemicals in database	2,100
Number of constant properties	32
Number of temperature-dependent properties	15
Additions to database	
New chemicals added annually	~45
Person hours to add new chemical	~200
Data points added annually from current journal searches	~4,000
Reviews without the IF system	
Extant chemicals completely reviewed annually	~30
Person hours to perform complete review	~220
Annual entire-database property reviews	1

the growth rate of the database let alone maintain currency of the chemicals already present.

3 Influence Factors

3.1 Constant Properties

An algorithm has been developed and implemented to provide a numerical IF, the magnitude of which is used to identify those compounds most in need of being updated based on newly published data. The algorithm for the constant properties is

$$\mathrm{IF} = \frac{K}{5}\left[2\Delta M + 0.4DK + 3A + P + 2Q\right] \quad \text{(constant properties)}, \tag{1}$$

where ΔM, D, K, A, P, and Q are parameters related to the expected influence; they are determined from the database as developed below. An IF is calculated for each property and for the chemical itself. The total IF for the compound is a sum of the IFs for the various properties in which any negative IF values are set to zero to avoid concealing the positive IF values.

3.1.1 K

The parameter K is a weight for the importance of the property. In Fig. 1, highly connected properties are those of most significance to users of the database and the accuracy of their values are of most significance to the integrity of the database itself. Values of K assigned to each property are shown in Table 3.

3.1.2 M

The parameter M refers to the method used to obtain the value. The DIPPR® 801 database stores metadata for the method as experimental, smoothed, or predicted. Values of M, as given in Table 4, are designed to give significant weight to experimental data.

Table 3 Values of K for the DIPPR® 801 database constant properties

Prop.	K	Prop.	K	Prop.	K
TC	10	HFOR	3	FP	5
PC	10	GFOR	3	LFL	3
VC	8	HSTD	3	UFL	3
ZC	2	GSTD	3	AIT	3
MP	5	HCOM	3	HSUB	3
TPT	5	ACEN	1	PAR	1
NBP	10	DM	2	DC	2
VOL	3	RI	1		

Table 4 Values of M for the DIPPR® 801 database constant properties

Method	M	Method	M
Experimental	10	Predicted	2
smoothed	5	No value	0

For example, the value of ΔM, defined as M for the new data minus M for the extant data, which appears in Equation 1 would be positive if the new data were experimental and the extant data were predicted.

3.1.3 D

The parameter D indicates the magnitude of the potential change to the recommended value if the new value replaced the extant value. The value of D is calculated from

$$D = \left| \frac{\text{New} - \text{Accepted}}{\text{Accepted}} \right| \times 100\,\%. \tag{2}$$

3.1.4 A

The parameter A in the IF correlation gives weight to new raw data extracted from the literature when few data were previously available. The value of A is determined from the number of raw data points, using the values in Table 5, that had been previously analyzed in establishing the currently recommended value of the property. Thus, a new value for a property that has been measured many times before will not carry much weight unless it is quite different from the current value (large D).

3.1.5 P

The chemical identification number (Chem ID) used in the DIPPR® 801 database originally related to a priority list for the chemicals as they were recommended by the sponsors and to the type of functional groups in the chemical. More recently, the Chem ID has become more of an indicator of how long the chemical has been in

Table 5 Values of A for the DIPPR® 801 database constant properties

Number of points in database	A
0–1	5
2–3	4
4–8	3
8–10	2
>10	1

Table 6 Values of P for the DIPPR® 801 database constant properties

Chem ID	P
<100	4
<500	3
<1000	2
>1000	1

the database—smaller numbers indicate earlier inclusion in the database. More recent additions to the database are weighted less heavily through the parameter P than those entered into the database earlier as shown in Table 6.

3.1.6 Q

The parameter Q is designed to emphasize high-accuracy values over those with larger uncertainties. Property values are stored along with an uncertainty in the DIPPR® 801 database. The uncertainty can be that assigned by the original author or by the database staff. The value of Q, calculated using the following equation, is positive if the uncertainty of the new value is larger than that of the extant value:

$$Q = \frac{\text{Uncertainty of accepted value (\%)}}{\text{Uncertainty of new value (\%)}} - 1. \tag{3}$$

3.2 Influence Factors for Temperature-Dependent Properties

The algorithm constructed for temperature-dependent properties is

$$\text{IF} = \frac{K}{5}\left[2\Delta M + 2D + 3(AN - AD) + P + Q\right] \quad (T\text{-dependent properties}). \tag{4}$$

As in the constant property case, the total IF is calculated as a sum of the individual property IF values while replacing any negative values with zero to avoid compensation of positive IF values for one property with negative values for another in the total.

Table 7 Values of K for the DIPPR® 801 database temperature-dependent properties

Prop.	K	Prop.	K	Prop.	K
SDN	5	SCP	4	VVS	3
LDN	8	LCP	6	VTC	4
SVP	10	ICP	4	STC	5
VP	10	SVP	5	LTC	5
HVP	10	LVS	5	ST	3

Table 8 Values of M for the DIPPR® 801 database temperature-dependent properties

Method	M	Method	M
Experimental	10	Predicted	2
Smoothed	8	Unkown	0
Experimental/Predicted	5		

3.2.1 K

The parameter K has the same meaning for the temperature-dependent properties as for the constant properties. Values for use in Eq. 4 are given in Table 7.

3.2.2 M

The parameter M has the same meaning for the temperature-dependent properties as for the constant properties. Values for use in Eq. 4 are given in Table 8. One of the methods available in the DIPPR® 801 database is "Experimental/Predicted," which means that some predicted values were used in addition to experimental data in the regression of the temperature-dependent correlation.

3.2.3 D

As with the constant properties, the parameter D is designed to provide an indication of how large the potential change could be if the new literature values are used to develop the temperature-dependent correlation for the property. In this case, D is evaluated by comparing the new experimental values to the values obtained from the extant correlation at the same temperature using

$$D = \frac{1}{N}\sum_{i=1}^{N}\left|\frac{\text{New}_i - \text{Correlation}_i}{\text{Correlation}_i}\right| \times 100\,\%, \tag{5}$$

where N is the number of new data points for the property.

Table 9 Values of *AN* and *AD* for the DIPPR® 801 database temperature-dependent properties

Number of points	*AN*	*AD*
0–2	2	2
3–5	4	3
6–10	6	4
11–20	8	5
>20	10	6

3.2.4 AN and AD

For temperature-dependent properties, $AN - AD$ represents the amount of new data available (*AN*) compared to the extant data (*AD*) upon which the current T-dependent correlation was based. Table 9 shows the point values assigned to *AD* and *AN* for use in Eq. 5. The overall contribution of this term in Eq. 4 is positive if *AN* is greater than *AD*. While the temperature range of the data obviously is an important factor when actually evaluating and revising the recommended temperature correlation, the current capability in generating the weighting factor is based only on the relative number of data points. A possible future refinement of the weighting factors could involve a comparison of the temperature range of the new data relative to the extant data.

3.2.5 P and Q

The parameters P and Q in the temperature-dependent correlation are identical to those for constant properties.

4 Examples

4.1 1,2-Propylene Glycol

1,2-Propylene glycol was first entered into the DIPPR® 801 database in 1983. It was again reviewed in 1989, but it had not been reviewed since that date. Calculation of the IF values for all the chemicals in the database in 2009 produced the information shown in Table 10 for this compound. Again, these numbers are based upon the new data that had entered into the database from current journal searches since the last time the chemical was rigorously reviewed and evaluated.

The IF values coupled with the interconnectivity chart (Fig. 1) provide a road map for efficient updating of the 47 properties in the database. The large IF value for the constant properties is primarily due to new data on the critical properties. The large value of M (together with the large value of A) indicates that the new value is measured while the old is predicted. The large value of D suggests that there is significant difference in the currently recommended value and the new measured value. In this case, Q is zero because the relative uncertainties of the new values were unknown. Negative IF values for HVP, VP, LDN, and LVS suggest that new data

Table 10 Influence factors for 1,2-propylene glycol in 2009

Constant properties						
IF	*M*		*D*	*A*	*P*	*Q*
406	101		118	148	40	0
	Values by property					
	Property	IF	Property	IF	Property	IF
	TC	134	PC	91	VC	47
	HFOR	12	ACEN	8	FLVL	11
	FLVU	12	DC	13		
Temperature-dependent properties						
IF	*M*		*D*	*A*	*P*	*Q*
153	−557		525	−2299	855	0
	Values by property					
	Property	IF	Property	IF	Property	IF
	HVP	−654	VP	−388	LDN	−253
	ICP	9	LVS	−190	FLVL	11
	FLVU	12	DC	13		

are available for these properties, but they are likely predicted (negative *M* value) while the current correlations are based on experimental data. The amount of new data also appears to be small relative to the quantity of extant data for these properties (negative *A*).

The high IF value for the constant properties and the moderate value for the temperature-dependent properties prompted a review of this compound in 2009. The review required a small fraction of the time listed in Table 2 because the information in Table 10 directed attention to only those properties to be updated based on new information, and Fig. 1 provided the connection to other dependent properties that also required updating. A summary of the independent (because of the IF data) and the dependent (because of property interconnectivity) changes made is shown in Table 11. In this case, very little re-evaluation was required for the remaining 36 properties.

The changes in the vapor–pressure correlation and the heat-of-vaporization correlation are shown in Figs. 2 and 3.

4.2 2-Methyl-1,3-Propanediol

2-Methyl-1,3-propanediol has not undergone a review since it was originally entered into the DIPPR®801 database in 1994. In 2008, the IF calculations generated the

Table 11 Summary of 2009 updates for 1,2-propylene glycol

Property	Change in recommended value(s)[a]	Type of change	Reason for change
TC	+8.1	Independent	New experimental data to replace predicted value [6,7]
PC	−2.6	Independent	New experimental data to replace predicted value [6,7]
VC	+1.3	Dependent	Interaction with LDN
ZC	−8.6	Dependent	Interaction with TC, PC and VC
ACEN	−45.1	Dependent	Interaction with VP which interacts with TC & PC
SOLP	+0.5	Dependent	Interaction with HVP which interacts with VP which interacts with TC & PC
VP	22.5	Independent	Change in TC & PC as well as some new VP data [8–11]
HVP	9.9	Dependent	Interaction with VP and some new data [11]
LVOL	−0.03	Dependent	Interaction with LDN which interacts with TC and PC
LDN	8.5	Independent	New data [12–19] and interaction with TC
ST	16.3	Dependent	Changed value of TC

[a] Average absolute deviation for all points for T-dependent properties

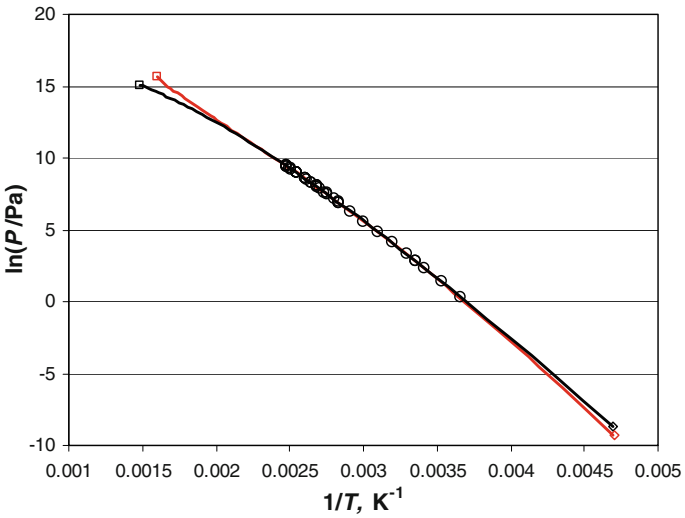

Fig. 2 Previous (*red*) and new (*black*) correlation for 1,2-propylene glycol VP updated with new TC, PC, and VP (*circles*) data. The corresponding critical (*square*) and triple (*diamond*) points are also marked. (Color figure online)

information shown in Table 12 for this compound based upon the new unevaluated data that had accumulated in the database since 1994.

A review of this chemical was initiated because of the IF value for the temperature-dependent properties. The property IF values show that this is because of new

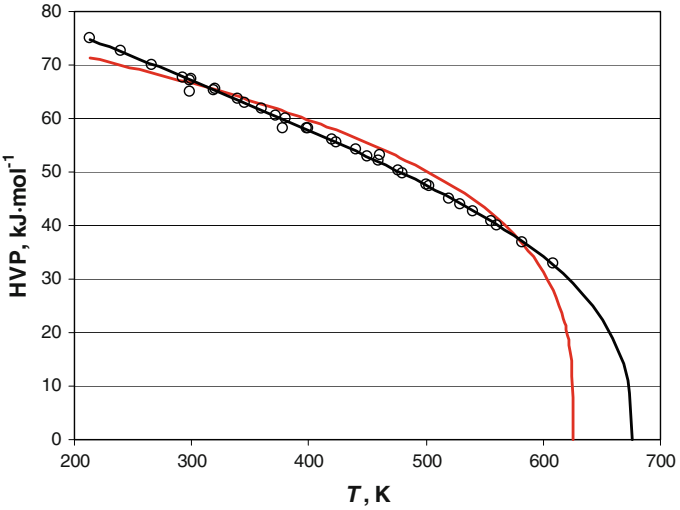

Fig. 3 Previous (*red*) and new (*black*) correlation for 1,2-propylene glycol HVP updated through relationships to new TC, PC, and VP data. Points represent data from experiment and derived from vapor pressure data. (Color figure online)

Table 12 Influence factors for 2-methyl-1,3-propanediol in 2008

Constant properties					
IF	*M*	*D*	*A*	*P*	*Q*
141	64	13	60	4	0
	Values by property				
	Property	IF	Property	IF	
	TC	77	PC	64	
Temperature-dependent properties					
IF	*M*	*D*	*A*	*P*	*Q*
2240	1624	533	−336	128	289
	Values by property				
	Property	IF	Property	IF	
	HVP	1245	VP	993	

vapor pressure and heat-of-vaporization data. The large value of *M* indicates that new data are experimental while at least some of the old data are likely to be predicted values. The moderately large value of *D* suggests the new values have the potential of making a significant change in the accepted correlation. A negative *A* value indicates that there are considerable data already in the database, but the large *Q* value indicates that the new data are of improved accuracy over that currently in the database. Table 11 also suggests that there is some new TC and PC measured data, but the small value

Table 13 Summary of 2008 updates for 2-methyl-1,3-propanediol

Property	Change in recommended value(s)[a]	Type of change	Reason for change
TC	+1.6	Independent	New experimental data to replace predicted value [20]
PC	0.0	Independent	New experimental data to replace predicted value [20]
ZC	−1.9	Dependent	Interaction with TC and PC
TPP	−85.6	Dependent	Interaction with VP
ACEN	−13.8	Dependent	Interaction with VP and TC
SOLP	+2.9	Dependent	Interaction with HVP which interacts with VP and TC
VP	25.5	Independent	New data [20,21] and change in TC
HVP	14.8	Dependent	Interaction with VP and some new data [21]
ICP	0.3	Dependent	Interaction with LDN which interacts with TC and PC
SVR	NA[b]	Dependent	Interaction with TC
ST	13.6	Dependent	Changed value of TC

[a] Average absolute deviation for all points for T-dependent properties
[b] Because SVR goes through zero, percent change is not a good measure of the significance of the update

of *D* indicates that they may not change the recommended value very much, but the value of *M* suggests that there is an improvement in the method used to obtain the data.

An update of this chemical was efficiently made based on the guidance provided by the information in the IF table. The results of that update are shown in Table 13.

The previously recommended value for TC was 697 K, but that value had been predicted by the Ambrose method [22]. The new TC value [20] was measured in a flow apparatus with short residence time to minimize decomposition, and this value of 708 K is now the recommended value. Interestingly, the PC value reported in the experimental study was identical to the recommended value in the database, although that value had also been predicted by the Ambrose method. The newly recommended value is the same, but now referenced to the experimental work.

The most significant updates arise from the new vapor–pressure [20,21] and heat-of-vaporization data [21]. The extant VP data were over a fairly narrow temperature range from 356 K to 489 K. High-temperature data are difficult to obtain because of decomposition. The new data sets added 61 additional VP points over the temperature range 297 K to 708 K. The results of this update are shown in Fig. 4. This change in the vapor–pressure curve subsequently significantly changed TPP, which is obtained from the vapor–pressure curve at the triple-point temperature (TPT). The new heat-of-vaporization data were used in conjunction with the relationship to the vapor–pressure equation to obtain the newly recommended HVP correlation in the database and the results are shown in Fig. 5. Importantly, the IF table indicates that changes in the other 36 properties are not required at this time.

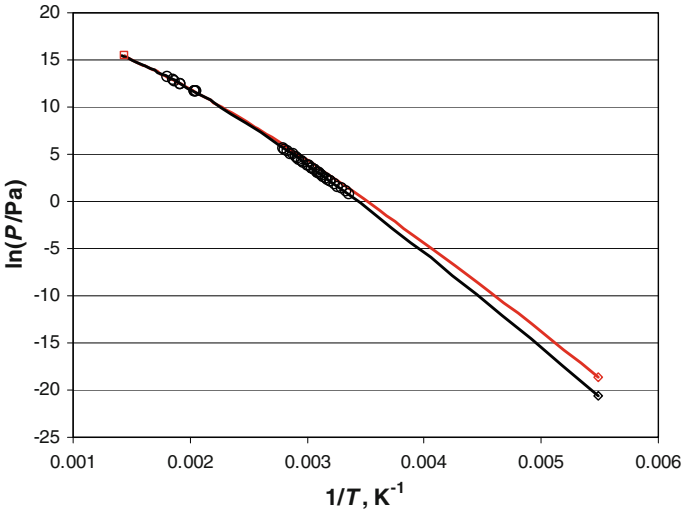

Fig. 4 Previous (*red*) and new (*black*) correlation for 2-methyl-1,3-propanediol VP updated with new TC, PC, and VP (*circles*) data. The corresponding critical (*square*) and triple (*diamond*) points are also marked. (Color Figure online)

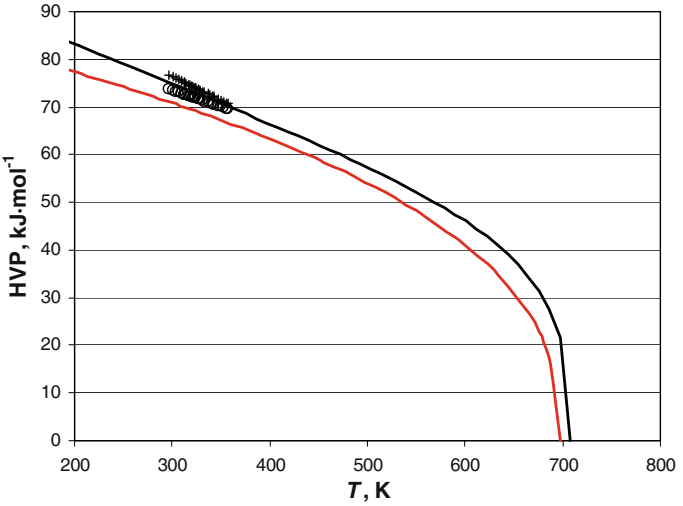

Fig. 5 Previous (*red*) and new (*black*) correlation for 2-methyl-1,3-propanediol HVP updated using new experimental data (*circles*) and the relationship of HVP to the new VP correlation (+). (Color Figure online)

5 Conclusion

A triage system has been established to address the problem confronted by providers of evaluated-property chemical databases that require substantial time and man-power to perform re-evaluation of all interconnected data and properties whenever updates are made to the database. Unevaluated data, collected and stored in the database as

they are extracted from the most recent literature, are used to calculate IFs for the chemical and the individual properties. The overall IF value is used to decide which chemicals have priority for the time-consuming data evaluation step leading to updates of the recommended values and temperature-dependent correlations in the database. The individual IF values for each of the properties provide a mapping of the independent changes which are propitious at the time, and the specific contributions to the IF provide guidance as to the impact the changes are likely to make on the database. The IF system therefore improves efficiency in management of evaluated chemical databases where keeping current with the publication of new property data has been overwhelming, if not impossible, in the past.

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