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Discussions
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Interactive comment on "Henry's law constants of diacids and hydroxypolyacids: recommended values" *by* S. Compernolle and J.-F. Müller

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Reply to Rolf Sander

We thank Dr. Sander for his positive review and helpful comments. We answer them sequentially below.

General comments

There are two fundamental types of Henry's law constants: They can either be defined as a solubility (i.e., aqueous phase divided by gas phase) or as a volatility (gas phase

/ aqueous phase). A statement like "the HLC appears to be higher than. . . " in the abstract is meaningless unless it is specified which type of HLC it refers to.

This was indeed not made clear by us. We therefore modify the last sentence of the abstract "The HLC -defined as gas-to-water partition coefficients- of diacids...". We repeat this also in the introduction, p. 25126, line 22. We do not use here the expression "defined as a solubility" to avoid confusion with the concept of solubility of a solid, taken at the solubility limit rather than at the infinite dilution limit, already employed in this work.

Regarding experimental data, it could be mentioned that Mentel et al. measured a value of 1.9E9 M/atm for glutaric acid: Mentel, T. F., Folkers, M., Tillmann, R., Henk, H., Wahner, A., Otjes, R., Blom, M., and ten Brink, H. M.: Determination of the Henry coefficients for organic aerosol components, Geophys. Res. Abstr., 6, 1525, 2004

We thank the reviewer for pointing out this measurement. We add on p. 25126, line 21: "We note that Mentel et al. (2004) did measure the HLC of glutaric acid." We add this value to Table 3.

Normally, the supplement is used for data sets, movies, animations, etc. Here, the supplement contains text describing how the activity coefficient ratios were obtained. I don't see the reason for separating this from the main paper. I suggest to merge the supplement into the main text.

As suggested by Dr. Zuend, we moved the supplement to an appendix.

Specific comments

The title promises recommended values. However, Table 3 only lists several options depending on the choice of partial pressure. If the authors have a sug- gestion which of them are the best values those should be indicated in the table. Otherwise I suggest to remove the phrase "recommended values" from the title.

For linear diacids, we recommend now the HLC, derived from the sublimation data of Cappa (2007, 2008) as being the most reliable. We did not do this before, because of an outlier in HLC for azelaic acid (see Fig. 6a). However, we noticed now, by recalculating the sublimation pressure from the sublimation enthalpies and entropies in the same Table, that the sublimation pressure for azelaic acid in Table 1 of Cappa (2007) contained a typo. The HLC variation of Cappa is now more reasonable. As it contains no even-odd alternation with carbon number (as opposed to HLC derived from data of Bilde, and the enthalpies of gas-phase dissolution derived from data of Bilde, Booth), no strong decrease with carbon number (as opposed to HLC derived from data Salo, Chattopadhyay), and the sublimation data is obtained at a temperature closer to room temperature as compared to the data of Ribeiro (1999, 2001). In addition, we recommend the HLC from the Soonsin data. They are relatively close to the HLC derived from the Cappa data. Moreover, Soonsin (2010) gives some good arguments in favor for their data, e.g. that it is essential to perform the experiment over a long time to arrive at the low sublimation pressures.

For the hydroxypolyacids, we derived new HLC values based on data of Huisman, as suggested by reviewer Zuend. These are recommended as well.

In the abstract it is mentioned that "the HLC of diacids appear to be higher than estimated by the often cited review work of Saxena and Hildemann (1996)." This, however, is not true for malic acid and tartaric acid, which are also diacids.

We changed the sentence into "the HLC of linear α, ω-diacids appear..."

What is the meaning of the citation "Meylan and Howard (2000)" for Henry's law constants in Table 1? As far as I know, Meylan and Howard (2000) refers to the EPI Suite software, not to a paper. Are these values calculated by that software?

The EPI Suite software, besides providing estimates for physicochemical properties, also contains a compilation of experimental values. To clarify, we change the sentence p. 25130, 24. "from the data compilation available in the EPI Suite Software (Meylan

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and Howard 2000)."

Reply to Andreas Zuend

We are grateful for Dr. Andreas Zuend's detailed comments and recommendations. Our answers to his questions are given below.

General comments

In the introduction (p. 25126) it is stated that: "The Henry's law constant is a fundamental molecular property regulating the partitioning between the gas and aqueous phase. In the atmosphere, this aqueous phase can be a cloud droplet or an aqueous aerosol." Further down on the same page it is also stated: "Of course, due to the presence of organic and inorganic molecules, an aqueous aerosol can hardly be regarded as a pure water phase, as is required for HLC.". I agree with the latter statement and think that there is a contradiction between the two sentences in the introduction. I suggest rephrasing the first sentence, because the HLC is not a "fundamental molecular property"; rather it is a property based on a limiting law that describes the partitioning of a compound between the gas phase and a specified highly dilute liquid phase (aqueous or any other solvent).

We rephrased the sentence as follows:

"The Henry's law constant describes the partitioning of a compound between the gas phase and a liquid, highly dilute solution. In the atmosphere, such dilute solutions, with water as solvent, can be reached in cloud droplets. Aqueous aerosols represent another example of an aqueous phase in the atmosphere. Although in the latter case clearly this phase is not a highly dilute aqueous phase due to the large concentration of other organic and inorganic molecules, Henry's law constants for aqueous phase are

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still relevant as a reference point."

In aqueous aerosol phase, unless very close to 100 % relative humidity, does not meet that criterion (as recognized by the authors) and the partitioning of an organic compound can be substantially influenced by other solutes. This is why gas-particle partitioning schemes should use activity coefficient models that depend on solution composition, rather than using HLC. I would therefore focus on cloud droplets when describing atmospheric applications of HLC.

While we recognize that HLC as defined here do not strictly apply to partitioning between gas phase and aqueous aerosol, we still think it is a useful first guide, especially if one has no detailed information on the mixture composition. To emphasize the approximate nature of such an assessment, we rephrase the sentence starting from line 5, p 25141 as follows:

"To the extent that the Henry's law constants reported here are applicable, one can conclude that significant partitioning to the aqueous phase or the gas-phase are both possible, depending on the species and the LWC. However, an aqueous aerosol is not a dilute aqueous solution, but on the contrary a concentrated solution containing both organics and inorganics. Therefore, in a more rigorous treatment, an activity coefficient model (e.g. AIOMFAC) should be used, provided the mixture composition is known."

Effective and intrinsic HLC. The authors mention the distinction between effective and intrinsic HLC (Eq. 8), which is of importance for strong acids. However, it is not mentioned which definition they use in their tables, for Eq. (3), etc. I assume their data evaluation approach and tabulated values should reflect intrinsic values. However, the experimental activity coefficient ratios obtained from water activities will yield effective HLC values unless corrected, which could present a source of uncertainty for the relatively strong diacids that tend to partially dissociate in highly dilute aqueous solutions. In that context, the availability and treatment of experimental data at very high dilution of the solute, including consideration of certain points as outliers, as done in the

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cases of malic and tartaric acid (in the Supplement), may influence considerably the final value taken and its interpretation as effective or intrinsic HLC (see also my Specific Comments to the Supplement below). I suggest to discuss this more clearly in the paper and to state what definition is used in Eq. (3) and where appropriate.

With the exception of oxalic acid, acid dissociation will be a minor phenomenon at the concentrations considered here. Therefore, the HLC reflect essentially intrinsic HLC. We mention this now in the appendix (which replaces the supplement):

"The dissociation of the acids could in principle affect the water activity data. To derive the intrinsic k_h, one needs $\gamma_s^\infty/\gamma_s^{\text{sat}}$ of the undissociated acid. However, for most acid-water mixtures considered here, even the most dilute ones, acid dissociation is a minor phenomenon. This was confirmed with the activity calculator at the E-AIM site, where the acid dissociation can be taken explicitly into account; the effect on $\gamma_s^\infty/\gamma_s^{\text{sat}}$ is very small. An exception is oxalic acid, for which we followed the analysis of Clegg and Seinfeld (2006a). In all other cases, we neglected acid dissociation, but still the derived k_h should reflect reasonably intrinsic Henry's law constants."

Regarding the suspected data outliers for malic and tartaric acid, these were not due to acid dissociation, but rather to a suboptimal numerical integration of the Gibbs-Duhem equation (see answer to Specific Comment below). We completely revised the supplement, included more experimental data and activity coefficient expressions fitted directly to the γ_w data. These outliers are therefore no longer an issue.

Use of activity coefficient models for obtaining HLC. In Section 3 (p. 25131) the use of group-contribution activity coefficient models (UNIFAC-Peng, UNIFAC-Raatikainen, AIOMFAC) is discussed. In addition, for the actual data evaluation, fitted expressions for binary mixture's activity coefficients (Margules, Van Laar, Wilson) are used. For the readers less familiar with these models and their advantages and drawbacks, it may seem unclear why the group-contribution models are discussed at all. This should be pointed out more clearly. One could argue that a mixture-specific model that fulfills the

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Gibbs-Duhem relation, when fitted to a selection of experimental data, will always perform as good or better than a predictive group-contribution model. Zuend et al. (2008) (in their section 3.4) discuss some of the differences between group-contribution and system-specific activity coefficient models. Clegg and Seinfeld (2006) and Zuend et al. (2011) (in their section 4.1) also show the usefulness of specifically fitted models (Gibbs-Duhem-Margules parameterization) for binary mixtures, being superior to predictive group-contribution models for a specific system, but limited to that system and by the available experimental data. A key advantage of group-contribution models is their versatility for predicting properties of various complex systems, including for systems containing organic compounds for which no experimental data is available. Hence, for systems where a Margules type model could not be fitted to experimental data for the purpose of retrieving activity coefficients.

To better explain the differences between mixture-specific and group-contribution methods, we have included the following paragraphs near the start of this section:

"Activity coefficients can be estimated by fitting an activity coefficient expression (e.g. Margules, Van Laar and Wilson, see Prausnitz et al., 1999; Carlson and Colburn, 1942) to activity coefficient data of a particular binary system. The parameters of this mixture-specific model allow then to obtain the IDAC γ_s^∞.

Another way to obtain activity coefficient is through the use of group-contribution methods. UNIFAC (Fredenslund et al., 1975; Hansen et al., 1991) is arguably the most popular activity coefficient estimation method based on this group-contribution concept. While a mixture-specific model will generally perform better than a group-contribution model for that specific mixture, its use is limited to that binary mixture. A group-contribution method like UNIFAC, on the other hand, can be used to predict the activity coefficients of more complex mixtures, including molecules for which no experimental data is available."

The UNIFAC-Peng model and models that inherited some of its interaction parame-

ters, such as the AIOMFAC model, as well as the UNIFAC version by Raatikainen and Laaksonen, have been fitted to some experimental water activity data for dicarboxylic acids and hydroxypolycarboxylic acids by Peng et al. (2001) as stated by the authors. Therefore, in this case the models could be considered somewhat biased to represent the Peng et al. (2001) data well, which is probably why the authors use these models in a comparison in this study. Moreover, the AIOMFAC model is aimed at describing organic-inorganic interaction in solutions that also include dissolved electrolytes. Hence, AIOMFAC could be useful in estimating HLC of diacids in dilute aqueous systems containing salts, for which experimental data is very limited.

We have included the sentence

"It should be mentioned that the AIOMFAC model can also describe organic-inorganic and water-inorganic interactions, and is therefore useful for aqueous systems containing salts."

Also, regarding the final values of the HLC listed in this study, given the uncertainty from the vapor pressure data, it would be of interest how much of a difference it would make when using UNIFAC-Peng or AIOMFAC instead of the Margules model for the activity coefficient ratios. I suggest to consider some of these aspects in the revised version of the paper.

We have extended Table 2 with the activity coefficient ratios, such that it includes also values estimated by UNIFAC-Peng, AIOMFAC, UNIFAC-Raatikainen. Also estimations by the activity calculator for dicarboxylic acids (available at the E-AIM website, (Clegg and Seinfeld, 2006a,b)) are included. The latter estimations are based on per-system fitted models, and the obtained values are very similar to ours. Linear dicarboxylic acids C6-C9 are now also included in the Table. Concerning the group-contribution methods: overall, UNIFAC-Peng is closest to the per-system fitted models. UNIFAC-Raatikainen deviates the most and gives an exceptionally low $\gamma_s^\infty/\gamma_s^{\text{sat}}$ value for tartaric acid.

I agree with the comment of Rolf Sander regarding the Supplement. I would prefer the information from the Supplement to be presented in the main article, perhaps as an appendix.

We have put the content of the (thoroughly revised) supplement in the appendix.

Specific comments

p. 25127, Eq. (2), line 19: Here activity coefficients on mole fraction basis are introduced. The basis should be mentioned since there are other scales for activity coefficients (molality, mass fraction, molarity, etc.). And "compared to a solvent of pure s itself" would be the pure component reference state at the same tem-perature and pressure.

We reworded the sentence.

"γ_s is the mole fraction based activity coefficient. It expresses the preference of the solute to the mixture, compared to the pure component reference state at the same temperature and pressure."

Eq. (2) also implies ideal gas behavior of the organic compound (the "solute"), which should be stated, because certain organic acids tend to form dimers in the gas phase (this is probably not an issue at the low partial pressures the HLC refer to).

We added "Note that in Eq. (2) it is assumed that the gas-phase of the solute behaves ideally, a reasonable assumption given that the partial pressure of the solute will be small."

p. 25127, Eq.(3): Define the symbol p 0 L,s .

It was already defined on p. 25127, line 14 as the liquid saturation vapour pressure. For clarity, we repeat the definition after Eq. (3).

p. 25128, line 3: Revise the sentence "Now if the solute is added to water above its saturation point, a solid phase will form in the water phase." ("water above its saturation point" = beyond its solubility limit in water?, "water phase" = aqueous phase?

Sentence revised to "Now if the solute is added to water beyond its solubility limit, a solid phase will form in the aqueous phase."

p. 25128, line 9: Correct the statement:"In principle, liquid and solid can only co-exist at the fusion point,"; there is not just a fusion "point" in the (p, T) phase diagram, unless restricted to a single temperature or pressure (there is a melting curve). For correctness also state: "In principle, a compound's pure liquid and solid state can only...".

Sentence revised to "In principle, a compound's pure liquid and solid state can only co-exist at the melting curve, where $p_{Cr}^0 = p_L^0$."

p. 25128, line 15 (and at other occurrences): Replace "fluidization" by "melting" or "dissolution"; fluidization is a different process unrelated to what the authors mean here.

We replaced "fluidization" by melting at all occurrences.

p. 25134, line 10: It is stated: "As UNIFAC-Peng matches aw well for citric acid over the entire concentration range, and already overestimates aw in the supersaturation range for malic and tartaric acid, it follows that the IDAC of UNIFAC- Peng should be more reliable than those of AIOMFAC.". As a developer of AIOM-FAC, I may be a bit biased on this point, but I would suggest some changes regarding a few statements about AIOMFAC and UNIFAC-Peng. First, UNIFAC- Peng matches the experimental water activity data of citric acid better over the concentration range where data is available. Second, "and already overestimates aw in the supersaturation range for malic and tartaric acid": if it overestimates, how can you be sure that it is more reliable than AIOMFAC? It seems to me from Fig. 2 that AIOMFAC actually matches the aw data of

tartaric acid better than UNIFAC-Peng. I also assume that the infinite dilution activity coefficients from these models were actually directly calculated for a finite, tiny solute concen- tration, it therefore would be of interest to see a model-experiment comparison figure for the dilute range, to see which model better matches the data at the very dilute conditions (not implying to say that AIOMFAC would do better there).

In Fig. 2, only subsaturation data of Maffia and Meirelles (2001) were included; for tartaric acid these were indeed closer to AIOMFAC than UNIFAC-Peng. In our statement, we referred actually to the figures of Peng et al. (2001), where also supersaturation data was included. We admit this was confusing. In Fig. 2, we have now included data from different sources in the sub- and supersaturated region. For all three hydroxypolyacids, the overall STD in $\ln \gamma_w$ is lower for UNIFAC-Peng than for AIOMFAC. In the Appendix, we have now also included a_w comparison figures in the subsaturation range. For malic and citric acid, UNIFAC-Peng matches the subsaturation data better than AIOMFAC, but for tartaric acid, AIOMFAC is the better match. This is now reflected in the text.

In principle, a model that fulfills Gibbs-Duhem relation may match the true infinite dilution activity coefficient value perfectly while deviating from experimental data at higher concentrations. As long as Eq. (3) would be used for HLC values and not Eq. (14), that would not be a problem.

If the model matches the water activity data well between $x_s = x_s^{\mathsf{sat}}$ and $x_s = 0$, but not for $x_s > x_s^{\mathsf{sat}}$, than Eq. (14) is more appropriate than Eq. (3), as $\gamma_s^\infty / \gamma_s^{\mathsf{sat}}$ will be close to the true value, while γ_s^∞ can be very different.

p. 25134, line 17: Sentence needs rewording. "This combination was done to widen the scope method, but clearly this comes at a prize." I suggest to delete the "but clearly this comes at a prize" part, because (1) the combination of UNIFAC parameters within AIOMFAC does also lead to reasonable descriptions for other systems (see tartaric acid), perhaps as good or better then UNIFAC-Peng; (2) all of these UNIFAC versions

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are actually hybrid methods because they in- clude parameters from several sources (UNIFAC-Peng contributes just a small subset of refitted parameters (as stated on page 25132); (3) to judge whether the approach taken in AIOMFAC comes at a prize or not, given the predictive and broad scope of all UNIFAC-based models, this would need to be evaluated on a much wider data basis.

The section on hydroxy polyacids has been rewritten. This specific sentence has been removed.

p. 25136, line 15: Statement: "Therefore we conclude that they cannot be used as a tool to estimate their IDAC, or finally the HLC." is somewhat misleading, as in fact, UNIFAC models could be used for exactly that, an estimation based on its predictive capability. Of course, it is less reliable than using a specifically fitted model based on actual activity coefficient data.

Agreed. We replaced the statement by:

"These longer chain molecules were not in the data set used to develop UNIFAC-Peng or UNIFAC-Raatikainen, and this can explain the lower performance of both methods for these compounds. "

p. 25140, line 7-11: To my knowledge, it should be possible to estimate a HLC value from vapor pressures measured by Huisman et al. (2013) using Eq. (3) and the IDAC from the fitted Margules or Van Laar model. I suggest to include the data from such a derivation in Table 3.

We have followed the referee suggestion. As the IDACs derived here will not be very precise, we also tested an alternative: using fusion data to convert the liquid vapour pressure to solid state vapour pressure, and (as before) combine these with the activity coefficient ratio $\gamma_s^\infty / \gamma_s^{\mathsf{sat}}$ to obtain the HLC. The resulting HLC are several orders of magnitude higher than those derived from the Booth data. Partly because Huisman's vapour pressures are very low, and partly because the IDAC derived here are very low.

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Supplement, page 1: A comment: the water activity data from the measurements of Peng et al. (2001) is available in tabulated form online.

We thank Dr. Zuend for pointing this out to us. We use now these tabulated values.

Same page: It is unclear to me how the experimental data points shown in the figures (Supplement) were obtained from Eq. (1). What functional form for ln gw(t) was used in the integral term?

Supplement, Figures 1-4: The experimental data points at very high dilution (xs → 0) seem to indicate a relative increase or "upward curvature" in the activity coefficient ratio (gs/g sat s) and two experimental points at the lowest xs were considered outliers by the authors. Could it be that the data points are actually showing the correct behavior due to acid dissociation at very high dilution, which is not considered in the model fit curves? Such dissociation effects on activity coefficients are known for inorganic salts and acid at high dilution in water (see, e.g., Fig. 3 - 5 of Zuend et al., 2008). Especially for tartaric acid (Fig. 3), the trend seems not to be captured by any of the fitted models. This raises the question of effective vs. intrinsic HLC extracted from such data and model fits. I suggest that the authors briefly comment on this.

As explained in the Supplement, the integral in Eq. (1) was integrated with the Simpson's rule integration technique from the python package scipy, to obtain $\gamma_s/\gamma_s^{\text{sat}}$ data points from the γ_w data. We see now that this is an unnecessary complicated procedure. The outliers were probably a consequence of this procedure and the coarseness of the γ_w data, and not of the acid dissociation. We now directly fitted the activity coefficient expressions (Margules, Van Laar, Wilson) to the γ_w data from dilute up to the solubility limit. The derived parameters were then used to derive $\gamma_s^{\infty}/\gamma_s^{\text{sat}}$. Moreover, the experimental data is considerably extended, among else by using the collection of Clegg and Seinfeld (2006a). While the final $\gamma_s^{\infty}/\gamma_s^{\text{sat}}$ values do not deviate much from the values given in the ACPD version, they are more reliable.

Technical corrections

p. 25128, line 2 (and at other occurrences): I suggest to replace the expression "sublimation pressure" by "solid state vapor pressure" because sublimation is a phase transition process not a physical state.

Replaced all occurrences of "sublimation pressure".

p. 25137, line 19: delete "only".

Deleted "Only".

Other changes

The HLC values in Table 3 and Fig. 6a have changed. This is because the $\gamma_s^{\infty}/\gamma_s^{\text{sat}}$ values are updated, but also because some p_{Cr}^0 values have been corrected. Most importantly, the p_{Cr}^0 value at 298.15 K for azelaic acid in Table 1 of Cappa et al. (2007) contained a typo, changing the value by one order of magnitude. This is clear if one compares with the $\Delta H_{\text{sub}}, \Delta S_{\text{sub}}$ values in that same table. I overlooked that the tabulated p_{Cr}^0 values of Bilde et al. (2003) were at 296 K instead of 298.15 K. This has been corrected by evaluating Bilde's p_{Cr}^0 correlations at 298.15 K.

References

Bilde, M., Svenningsson, B., Mønster, J., and Rosenørn, T.: Even-odd alternation of evaporation rates and vapor pressures of C3-C9 dicarboxylic acid aerosols, Environ. Sci. Technol., 37, 1371–1378, 2003.

Cappa, C. D., Lovejoy, E. R., and Ravishankara, A. R.: Determination of evaporation rates

and vapor pressures of very low volatility compounds: A study of the C-4-C-10 and C-12 dicarboxylic acids, J. Phys. Chem. A, 111, 3099–3109, doi:10.1021/jp068686q, 2007.

Carlson, H. C. and Colburn, A. P.: Vapor-Liquid Equilibria of Nonideal Solutions, Ind. Eng. Chem., 34, 581–589, doi:10.1021/ie50389a013, 1942.

Clegg, S. L. and Seinfeld, J. H.: Thermodynamic models of aqueous solutions containing inorganic electrolytes and dicarboxylic acids at 298.15 K. 1. The acids as nondissociating components., J Phys Chem A, 110, 5692–5717, doi:10.1021/jp056149k, 2006a.

Clegg, S. L. and Seinfeld, J. H.: Thermodynamic models of aqueous solutions containing inorganic electrolytes and dicarboxylic acids at 298.15 K. 2. Systems including dissociation equilibria., J Phys Chem A, 110, 5718–5734, doi:10.1021/jp056150j, 2006b.

Fredenslund, A., Jones, R. L., and Prausnitz, J. M.: Group-Contribution Estimation Of Activity-Coefficients In Nonideal Liquid-Mixtures, AIChE J., 21, 1086–1099, 1975.

Hansen, H. K., Rasmussen, P., Fredenslund, A., Schiller, M., and Gmehling, J.: Vapor-Liquid Equilibria By UNIFAC Group Contribution .5. Revision And Extension, Ind. Eng. Chem. Res., 30, 2352–2355, 1991.

Maffia, M. C. and Meirelles, A. J. A.: Water Activity and pH in Aqueous Polycarboxylic Acid Systems, J. Chem. Eng. Data, 46, 582–587, doi:10.1021/je0002890, 2001.

Peng, C., Chan, M. N., and Chan, C. K.: The hygroscopic properties of dicarboxylic and multi-functional acids: Measurements and UNIFAC predictions, Environ. Sci. Technol., 35, 4495–4501, 2001.

Prausnitz, J. M., Lichtenthaler, R. N., and de Azevedo, E. G.: Molecular thermodynamics of fluid-phase equilibria, Prentice-Hall PTR, Upper Saddle River, New Jersey 07458, third edn., 1999.

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