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ХИМИЯ

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ФИЗИКА

АННОТАЦИИ

УДК 544.7

Русанов А. И. **Распространение законов Коновалова на поверхностные явления** // Вестн. С.-Петерб. ун-та. Сер. 4. 2013. Вып. 1. С. 9–15.

Обсуждается распространение законов Коновалова на поверхностные явления. Показывается, что известное в коллоидной химии правило поверхностной активности является аналогом первого закона Коновалова. Даётся вывод аналогов второго и третьего законов Коновалова и демонстрируется применение третьего закона к оценке толщины поверхностного слоя. Библиогр. 6 назв. Ил. 2.

Ключевые слова: законы Коновалова, поверхностные явления, толщина поверхностного слоя.

УДК 544.03

Афзал В., Праусниц Дж. **Четыре метода измерения растворимости газов и паров в жидкостях и полимерах** // Вестн. С.-Петерб. ун-та. Сер. 4. 2013. Вып. 1. С. 16–31.

Кратко описаны четыре особенно полезных метода. 1. Газо-жидкостная хроматография с насадочной или капиллярной колонкой удобна для измерения растворимости умеренно-растворимых паров в малолетучих растворителях, таких как ионные жидкости или полимеры. 2. Метод струи инертного газа подходит для измерения растворимости газов и паров в жидкостях. 3. Гравиметрический метод с применением кварцевой пружины полезен для измерения растворимости хорошо растворимых паров в полимерах или нелетучих жидкостях. 4. Синтетический волюметрический метод наиболее приспособлен для измерения растворимостей слаборастворимых газов в жидкостях. Библиогр. 49 назв. Ил. 14. Табл. 4.

Ключевые слова: методы измерения, растворимость газов, пары, жидкости.

УДК 544.03

Френкель М. **Проверка достоверности экспериментальных данных и модели прогнозирования свойств в термодинамике** // Вестн. С.-Петерб. ун-та. Сер. 4. 2013. Вып. 1. С. 32–45.

Представлены системы и программные средства, предназначенные для полной проверки достоверности экспериментальных данных в области термодинамики. Дан обзор разработанных в последнее время в исследовательском центре термодинамики Национального института стандартов и технологии США технологий предсказания термофизических свойств, в частности, рассмотрены технологии предсказания, в основе которых лежат модели QSPR, UNIFAC и моделирование методом Монте-Карло. Библиогр. 77 назв. Ил. 6. Табл. 1.

Ключевые слова: QSPR, UNIFAC модели, оценка экспериментальных данных, термодинамика.

УДК 544.726+543.432

Сташкова А. Э., Пешкова М. А., Михельсон К. Н. **Влияние натрия на pH-функцию Na/pH-селективного оптода в физиологическом диапазоне концентраций: есть ли необходимость в оптических датчиках активностей индивидуальных ионов?** // Вестн. С.-Петерб. ун-та. Сер. 4. 2013. Вып. 1. С. 46–62.

Изготовлены и охарактеризованы оптические сенсоры на основе полимерных пластифицированных мембран (оптоды), селективные к соотношению pH/активность натрия в растворе. Исследованы динамический диапазон, воспроизводимость, гистерезис и время отклика полученных сенсоров, а также перекрёстное влияние парных ионов на отклик оптодных мембран. В частности, оценена погрешность измерения pH при помощи таких оптодов на фоне флуктуаций содержания натрия в пределах физиологического диапазона. Экспериментально показано, что влияние натрия на pH-функцию можно не учитывать лишь в пределах нормы, при изменении же содержания натрия внутри более широкого диапазона кратковременных нелетальных концентраций соответствующая ошибка определения pH становится больше допустимой. Продемонстрировано, что для клинического анализа представляет значительный интерес создание оптода, отклик которого будет определяться индивидуальной активностью отдельного иона. Библиогр. 47 назв. Ил. 11. Табл. 2.

Ключевые слова: ионоселективные оптоды, полимерная мембрана, индивидуальная активность иона, физиологические диапазоны pH и натрия.

УДК 536.7+544.03

Контогеоргис Г. М. **Модели ассоциации для нефтегазовых приложений** // Вестн. С.-Петерб. ун-та. Сер. 4. 2013. Вып. 1. С. 63–79.

Нефтегазовая промышленность явилась одной из первых отраслей, где интенсивно используются термодинамические модели. Основное внимание настоящего обзора сконцентрировано на моделях

ассоциации, которые в явном виде учитывают образование водородных связей и другие сложные взаимодействия. Большой успех таких моделей демонстрировался в последние 20 лет при предсказании многих термодинамических свойств, необходимых в нефтяной и газовой промышленности. Эти модели ещё не вполне заменили кубические уравнения состояния, но получаемые результаты весьма впечатляют во многих случаях, в частности, для систем, связанных с газовыми гидратами, для смесей CO_2/H_2S, вода/углеводороды и др. Библиогр. 70 назв. Ил. 9. Табл. 1.

Ключевые слова: нефтегазовая промышленность, модели SAFT/CPA, газовые гидраты, вода/углеводороды, термодинамика.

УДК 544.7+544.3

Кумана С., Гуриков П., Белугин А., Иохансен М., Меньшутина Н., Смирнова И. **Применение аэрогелей на основе диоксида кремния в качестве стационарной фазы в сверхкритической флюидной хроматографии: экспериментальное изучение и моделирование с клеточными автоматами** // Вестн. С.-Петерб. ун-та. Сер. 4. 2013. Вып. 1. С. 80–95.

На примере разделения смеси бензола и конденсированных ароматических углеводородов в работе показана принципиальная возможность применения аэрогелей в качестве стационарных фаз. В силу нерегулярной формы частиц аэрогелей и низкой насыпной плотности эффективность колонок с аэрогелями уступает коммерческим стационарным фазам. Показано, что аэрогели устойчивы при наличии в подвижной фазе 5 % метанола в качестве модификатора. В работе определены энтальпии и энтропии переноса нафталина из сверхкритического раствора различной плотности на поверхность аэрогелей. Показано, что зависимости этих термодинамических величин от плотности испытывают экстремум, чего не наблюдалось ранее для коммерческих стационарных фаз. Обсуждаются возможные причины экстремального характера этих зависимостей. Приведены результаты имитационного моделирования процесса адсорбции нафталина клеточными автоматами. Предложенная модель качественно согласуется с экспериментальными наблюдениями. Показано, что модель позволяет количественно предсказывать температурную зависимость фактора удерживания нафталина на аэрогеле. Библиогр. 40 назв. Ил. 15. Табл. 1.

Ключевые слова: сверхкритическая флюидная хроматография, аэрогели, термодинамика адсорбции, моделирование, клеточные автоматы.

УДК 544.7+536.7

Дорн У., Шрадер Ф., Эндерс С. **Агрегация и фазовое поведение неионных поверхностно-активных веществ (C_iE_j) в водном растворе** // Вестн. С.-Петерб. ун-та. Сер. 4. 2013. Вып. 1. С. 96–112.

В работе рассмотрено применение модифицированной детальной модели мицеллообразования к водным растворам неионных поли(оксиэтилен) алкиловых эфиров — поверхностно активных веществ. Модификация состоит в предположении о температурной зависимости эффективной посадочной площади гидрофобной головы. Используя экспериментальные данные о рассеянии Бриллюэна—Мандельштама, возможно выразить посадочную площадь как функцию зависящего от температуры числа гидратации полиэтиленоксида, причем полученное выражение может быть применено при всех значениях i и j. Этот подход приводит к модели, способной описать характеристики образованных агрегатов, в частности критическую концентрацию мицеллообразования (ККМ), их размер и форму. Для моделирования расслаивания, наблюдаемого при низкой концентрации поверхностно активного вещества, необходима подгонка трех дополнительных параметров, которые описывают взаимодействия. Для нескольких поверхностно активных веществ удалось найти точку пересечения линии ККМ в зависимости от температуры и ветви точек помутнения разбавленного раствора. При температуре существенно ниже этой точки полидисперсные мицеллы присутствуют в фазе разбавленного раствора. Библиогр. 74 назв. Ил. 12. Табл. 2.

Ключевые слова: агрегация, фазовое поведение, неионные поверхностно активные соединения, водные растворы.

УДК 544.3+536.7

Емельяненко В. Н., Верёвкин С. П. **Термодинамическое исследование чистых метилбензальдегидов и их смесей с ионными жидкостями** // Вестн. С.-Петерб. ун-та. Сер. 4. 2013. Вып. 1. С. 113–125.

Коэффициенты активности при бесконечном разбавлении смесей *орто*-, *мета*- и *пара*-метилбензальдегидов с ионными жидкостями [BMIM][NTf_2] и [OMIM][BF_4] были определены при 385 K с использованием метода газовой хроматографии. Парожидкостное равновесие смесей в полном диапазоне

концентраций метилбензальдегидов с этими ионными жидкостями изучено методом переноса. Методом калориметрии сгорания найдены значения энтальпий образования трёх чистых метилбензальдегидов в конденсированном состоянии. Из температурных зависимостей давлений паров соединений, измеренных методом переноса, определены энтальпии испарения. Выполненные исследования позволили найти значения энтальпий образования изомерных метилбензальдегидов в газовой фазе. Для оценки степени надёжности полученных экспериментальных данных были выполнены квантово-химические расчёты энтальпий образования метилбензальдегидов в состоянии идеального газа. Проведённые расчёты указали на хорошее согласие теоретических и экспериментальных величин. Газофазные энтальпии образования были использованы для оценки эффектов внутримолекулярных взаимодействий заместителей в бензольном кольце. Библиогр. 23 назв. Ил. 4. Табл. 9.

Ключевые слова: ионные жидкости, коэффициенты разбавления, пар—жидкость равновесие, давление паров, энтальпия образования и испарения, квантово-химические расчёты.

УДК 536.7+544.3

Шефер Д., Кампс А. П.-С., Румп Б., Маурер Г. **Экспериментальное исследование влияния борной кислоты на растворимость диоксида углерода в водных растворах гидроксида калия** // Вестн. С.-Петерб. ун-та. Сер. 4. 2013. Вып. 1. С. 126–132.

Для исследования влияния борной кислоты на растворимость диоксида углерода в водных растворах гидроксида калия применена техника ячеек высокого давления, основанная на аналитическом методе. Исследование проведено при двух температурах, типичных для стадий абсорбции и десорбции в процессе «горячего поташа». Надлежащие добавки к водному растворителю в промышленных применениях этого процесса повышают его эффективность. При автоматизированном проектировании процесса «горячего поташа» требуются модели, позволяющие установить и количественно описать характер действия этих добавок. Новые экспериментальные результаты показывают, что влияние борной кислоты на равновесную растворимость CO_2 в водных растворах KOH очень мало. Поэтому применение борной кислоты в качестве добавки в процессе «горячего поташа» обусловлено другими явлениями. Библиогр. 15 назв. Ил. 3. Табл. 1.

Ключевые слова: процесс «горячего поташа», растворимость углекислого газа в водных растворах, гидроксид калия/карбонат калия, борная кислота.

УДК 544.3+536.7

Незбеда И. **О распространении концепции исключённого объёма** // Вестн. С.-Петерб. ун-та. Сер. 4. 2013. Вып. 1. С. 133–138.

Показано, что концепция исключённого объёма может быть распространена на флюиды со сложными взаимодействиями, в частности на ассоциированные флюиды, если модель межмолекулярных взаимодействий представить в виде модели взаимодействия участок—участок, со встроенными кулоновскими центрами. Тогда исключённый объём естественным образом учитывает отталкивание между зарядами одного знака при малых межмолекулярных расстояниях. Главное внимание уделено парциальному молярному объёму при бесконечном разбавлении, который, как известно из эксперимента, чувствителен к выбору растворителя. Распространённая концепция верно предсказывает, без привлечения каких-либо дополнительных предположений или приближений, уменьшение ПМО неполярных веществ в воде, однако суждения, основанные единственно на сопоставлении относительных размеров молекул растворителя и растворённого вещества, не подтверждаются. Библиогр. 9 назв. Ил. 2.

Ключевые слова: исключённый объём, парциальный мольный объём, простейшие модели, псевдотвёрдые тела, водно-метанольные смеси.

УДК 544.03+544.7

Субраманиан Д., Клауда Дж. Б., Лейс Ж., Анисимов М. А. **Термодинамические аномалии и флуктуации структуры водных растворов третичного бутилового спирта** // Вестн. С.-Петерб. ун-та. Сер. 4. 2013. Вып. 1. С. 139–152.

Обсуждается связь между аномалиями термодинамических свойств, наблюдаемыми экспериментально для растворов третичный бутиловый спирт (ТБС) — вода и образованием молекулярных кластеров, которые обнаружены при моделировании этих растворов методом молекулярной динамики (МД). Указанные аномалии обнаружены в относительно разбавленных растворах, содержащих примерно 0,03–0,08 молярной доли ТБС и выражаются ярче при низких температурах. МД моделирование показывает, что эти растворы демонстрируют маломасштабные (порядка 1 нм) и короткоживущие (десятки пикосекунд) мицеллоподобные флуктуации структуры в том же концентрационном интервале.

Аномалии термодинамических свойств водных растворов ТБС отнесены на счёт указанных структурных флуктуаций на молекулярном масштабе. Библиогр. 49 назв. Ил. 11.

Ключевые слова: термодинамические свойства, *трет*-бутиловый спирт, водные растворы, структурные флуктуации.

УДК 544.03

Полихрониди Н. Г., Абдулагатов И. М., Батырова Р. Г., Степанов Г. В. **Метод квазистатических термо- и барограмм для точных измерений свойств фазовой границы для сложных флюидов и флюидных смесей вблизи критической точки** // Вестн. С.-Петерб. ун-та. Сер. 4. 2013. Вып. 1. С. 153–185.

С высокой точностью измерены плотности жидкости и насыщенного пара вблизи критической точки для однокомпонентных флюидов (метанол, этанол, пропанол, ДЭЭ) и бинраных смесей (H_2O+метанол, H_2O+этанол, H_2O+аммиак, H_2O+D_2O, CO_2+н-декан) с помощью калориметрической техники (квазистатические термо- и барограммы). Одновременно измеренные значения плотностей насыщенного пара и жидкости и изохорной теплоёмкости в околокритической области использованы для вычисления параметров асимметрии a_3 и b_2 сингулярного диаметра линии сосуществования (параметры «завершённой» теории скейлинга) вблизи критической точки. Полученные значения a_3 и b_2 использованы для расчёта параметра степени аномальности Янга—Янга. Изучались вклад члена $t^{2\beta}$ «завершённого» скейлинга в поведение диаметра кривой сосуществования и вклад вторых производных по температуре (d^2P_S/dT^2) и ($d^2\mu/dT^2$) в расходимость теплоёмкости C_{V2} двухфазной системы вблизи критической точки. Расходмость диаметра кривой сосуществования $d\rho_d/d\tau$ для метанола, этанола, пропанола и ДЭЭ обусловлена совместным вкладом членов $B_2t^{1-\alpha}$ и $t^{2\beta}$. Параметр степени аномальности Янга—Янга R_μ для ДЭЭ равен примерно 0,45, что означает практически эквивалентный вклад в аномалию от производных химического потенциала и давления пара. Для этанола величина R_μ очень мала (0,0024), что означает почти нулевой вклад производной химического потенциала ($d^2\mu/dT^2$) в расходимость C_{V2}, т. е. сингулярность C_{V2} обусловлена членом, происходящим от давления пара, (d^2P_S/dT^2). Для метанола и пропанола R_μ также мал (0,245 и 0,171 соответственно), поэтому сингулярность связана в основном с членами давления. Значения R_μ, полученные по измеренным C_{V2}, находятся в хорошем согласии со значениями этой величины, найденными по данным о сингулярном диаметре или о плотности на кривой сосуществования. Критические параметры бинарных смесей (данные о критических линиях) H_2O+метанол, H_2O+этанол, H_2O+аммиак, H_2O+D_2O, CO_2+н-декан определены по данным о плотности равновесных фаз вблизи критической точки. Найдена корреляция ацентрического фактора с асимптотическими критическими амплитудами, а также с диаметром асимметричной кривой сосуществования. Библиогр. 57 назв. Ил. 21. Табл. 11.

Ключевые слова: термо- и барограмная техника, границы фаз, критическая точка.

УДК 536.631+544.015.4

Гавричев К. С., Рюмин М. А., Хорошилов А. В., Никифорова Г. Е., Тюрин А. В., Гуревич В. М., Старых Р. В. **Термодинамические свойства и фазовые превращения тетрагональной модификации ортофосфата тербия** // Вестн. С.-Петерб. ун-та. Сер. 4. 2013. Вып. 1. С. 186–197.

Методами релаксационной, адиабатической и дифференциальной сканирующей калориметрии экспериментально определена теплоёмкость тетрагональной модификации ортофосфата тербия t-$TbPO_4$ в температурном интервале 4–1230 K. По сглаженным значениям теплоёмкости рассчитаны термодинамические функции t-$TbPO_4$. Термическое поведение t-$TbPO_4$ в области высоких температур изучено дифференциальной сканирующей калориметрией. Установлено наличие аномалий в области ниже 10 и выше 1600 K, связанных с фазовыми превращениями. Библиогр. 21 назв. Ил. 4. Табл. 8.

Ключевые слова: ортофосфат тербия, фазовые превращения, термодинамические функции, калориметрия.

УДК 544.3+544.7

Хебабча М., Милтген М., Модаресси А., Магри П., Аит-Каси А., Рогальски М. **Агрегация наночастиц в многофазных смесях — влияние на фазовые равновесия** // Вестн. С.-Петерб. ун-та. Сер. 4. 2013. Вып. 1. С. 198–206.

Рассмотрено влияние диспергированных наночастиц (НЧ) на фазовые равновесия жидкость—жидкость и жидкость — твёрдое тело. Понижение температуры замерзания за счёт присутствия НЧ серебра

($d < 100$ нм), алюминия ($d < 50$ нм) и кремния изучалось для циклогексана и диметилсульфоксида. Определено равновесие жидкость—жидкость для одной бинарной (ацетонитрил+н-деканол) и одной тройной (ацетонитрил+циклогексан+этанол) смеси в присутствии диспергированных НЧ. Полученные результаты свидетельствуют о заметном влиянии НЧ на фазовые равновесия. Это обстоятельство объясняется распределением компонентов смеси между объёмной фазой и жидкой фазой, зажатой в наноагрегатах, образуемых НЧ в жидких растворах. Библиогр. 24 назв. Ил. 5. Табл. 4.

Ключевые слова: агрегация наночастиц, равновесие жидкость—жидкость, равновесие жидкость — твёрдое тело, взаимодействие с растворителем.

УДК 539.1(05)

Bardavelidze M. S., Nishnianidze D. N. **Shape invariance of second order in one-dimensional quantum mechanics** // Vestnik St. Petersburg University. Ser. 4. 2013. Issue. 1. P. 207–214.

The article investigates shape invariance under supersymmetrical transformations of the second order in the derivatives. The equation representing the general conditions of additive shape invariance is obtained. The particular solutions of this equation provide an explicit form of potentials with the second order shape invariance. Bibliogr. 22 names.

Keywords: shape invariance, supersymmetric quantum mechanics.

УДК 539.18

Анисимова Г. П., Долматова О. А., Полищук В. А., Цыганкова Г. А. **Полуэмпирический расчёт параметров тонкой структуры, коэффициентов промежуточной связи и гиромагнитных отношений конфигураций $npn'f$ C I, Si I, Ge I и P II** // Вестн. С.-Петерб. ун-та. Сер. 4. 2013. Вып. 1. С. 215–227.

Полуэмпирическим методом определены параметры тонкой структуры ряда высоковозбуждённых конфигураций $npn'f$ C I, Si I, Ge I и P II. Рассчитаны энергии уровней тонкой структуры, совпадающие с экспериментальными, коэффициенты промежуточной связи и гиромагнитные отношения в разных приближениях: LS, LK, jK. g-Факторы сравниваются с имеющимися в литературе экспериментальными аналогами. Получено хорошее согласие. Путём сравнения экспериментальных g-факторов или достоверно рассчитанных g-факторов с аналогичными величинами в векторных типах связи сделана оценка характера связи в исследуемых системах. Рассмотрена возможность взаимодействия конфигураций $npn'f + npn'p$ в результате анализа энергетических спектров и по данным численного расчёта. Библиогр. 18 назв. Ил. 4. Табл. 5.

Ключевые слова: полуэмпирический расчёт, матрица оператора энергии, параметры тонкой структуры, гиромагнитные отношения, коэффициенты связи.

УДК 537.525.1

Павлов С. И., Карасёв В. Ю., Дзлиева Е. С. **Зондирование тлеющего разряда полидисперсными пылевыми частицами** // Вестн. С.-Петерб. ун-та. Сер. 4. 2013. Вып. 1. С. 228–232.

Работа посвящена методу исследования нестратифицированного тлеющего разряда. Представлен эксперимент по зондированию тлеющего разряда падающими полидисперсными частицами. Проведён анализ поведения зондирующих частиц по их траектории движения, оценены продольное и радиальное поле разряда. Библиогр. 10 назв. Ил. 2. Табл. 1.

Ключевые слова: газовый разряд, диагностика плазмы, комплексная плазма.

УДК 539.17

Жеребчевский В. И., Торилов С. Ю., Андроненков А. Н., Гриднев К. А., Мальцев Н. А. **Упругое рассеяние альфа-частиц на нейтроноизбыточном ядре ^{14}C** // Вестн. С.-Петерб. ун-та. Сер. 4. 2013. Вып. 1. С. 233–237.

Рассмотрено упругое рассеяние альфа-частиц с энергией 27 МэВ на ядре ^{14}C в угловом диапазоне $\Theta_{c.m.}$ от 30 до 80,5°. Для получения экспериментальной информации были использованы новые прецизионные методы. Экспериментальное угловое распределение проанализировано в рамках SPP модели. Библиогр. 9 назв. Ил. 2.

Ключевые слова: ядерные реакции, нейтронный избыток, экспериментальные методы, глобальный потенциал.

УДК 539.192

П у ч к о в А. М. **Суммирование рядов теории возмущений для многозарядных ионов с помощью метода гипервириальных соотношений** // Вестн. С.-Петерб. ун-та. Сер. 4. 2013. Вып. 1. С. 238–245.

Систематически исследован вопрос о применении метода гипервириальных соотношений для суммирования рядов теории возмущений в случае многозарядных водородоподобных ионов. Получены рекуррентные формулы, которые позволяют находить в явном виде выражения для сумм содержащих матричные элементы с произвольными степенями. Показано, что в некоторых частных случаях общий подход приводит к известным выражениям. Обсуждаются возможные применения полученных результатов. Библиогр. 9 назв.

Ключевые слова: гипервириальные соотношения, вычисление поправок высоких порядков к сверхтонкой структуре и g-фактору.

УДК 535.4

T o l m a c h e v Yu. A. **Operation over an optical signal using generalized diffraction grating** // Vestnik St. Petersburg University. Ser. 4. 2013. Issue. 1. P. 246–252.

The general type of a scalar wave signal transformation in time by a flat 1D diffraction grating is described. The analysis is based on the concept of impulse response of the linear optical system that permits for the study of transformation of an arbitrary signal. To demonstrate the effectiveness of the method, the article examines traditional problem of the plane wave scattering by a transparent grating and shows the coincidence of final relation for monochrome wave with that for the classical diffraction grating. Afterwards, the generalized form of grating structure which grooves can be non-equidistant but positioned accordingly to some special law is studied. The effective velocity of observation of the moment of wave scattering by the grating is introduced, its value may vary from $c/2$ up to infinity. As a result, the conditions are derived for the realization of the incoming signal convolution and/or correlation with the function describing the spatial density of the grating grooves. Bibliogr. 10 names. Fig. 1.

Keywords: diffraction grating, signal transformation, delta-wave approach, cross-correlation, convolution.

УДК 537(533.9.082.5)

Б е л ь с к и й Д. Б., Г у ц е в С. А., К о с ы х Н. Б. **Некоторые особенности зондовых измерений в распадающейся плазме гелия** // Вестн. С.-Петерб. ун-та. Сер. 4. 2013. Вып. 1. С. 253–261.

Работа посвящена экспериментальным исследованиям распадающейся плазмы гелия с помощью зондов Ленгмюра. Давление газа, сила тока разряда и момент послесвечения выбирались для получения зондовых характеристик в бесстолкновительном, промежуточном и дрейфовом режимах движения заряженных частиц. Показано, как изменяется форма вольт-амперной характеристики при переходе от бесстолкновительного движения к диффузионному. Подробно разбирается источник ошибок при применении формул орбитального движения (OLM) и метода логарифмирования к обработке зондовых кривых. Показано, что пренебрежение учётом столкновений заряженных частиц в слое зонда приводит к завышению плотности ионов более чем в три раза, а температуры электронов — в два раза. Для коррекции методики определения температуры предложена модель взаимодействия заряженных частиц в слое зонда. Такой подход позволяет также определить слой объёмного заряда зонда и значение самосогласованного поля. Наблюдается хорошее соответствие между эксперементальными и теоретическими результатами. Библиогр. 18 назв. Ил. 4. Табл. 2.

Ключевые слова: плазма низкого давления, послесвечение гелия, зонды Ленгмюра, орбитальное движение, вольт-амперная характеристика, функция распределения электронов по энергиям, температура электронов, плотность частиц, слой объёмного заряда.

ABSTRACTS

УДК 544.7

R u s a n o v A. I. **Extension of Konovalov's laws to surface phenomena** // Vestnik St. Petersburg University. Ser. 4. 2013. Issue. 1. P. 9–15.

Anatoliy I. Rusanov — Dr. Sci. in chem., Professor, academician of RAS, Saint Petersburg State University; e-mail: rusanov@ar1047.spb.edu

The article discusses Konovalov's laws and how they can be used to study interfacial phenomena. It shows that the rule known in colloid chemistry as a rule of surface activity corresponds to the first Konovalov's law. It reveals the analogues of the second and third Konovalov's laws, and shows how the third law can be used to estimate the thickness of a surface layer. To that end, it is assumed that the surface layer of finite thickness is in stable condition, which is regarded as a similar change of the compositions of the surface layer and the bulk phase. It cannot be applied to the surface layers of low thickness values, and by choosing suitable values a minimal possible thickness of the surface layer can be determined. By using this method, we made a thermodynamic prediction of the surface layer thickness in the solution/gas interface near the critical solution point being increased dramatically. This relation between the minimal possible thickness of the surface layer and solution composition correspond to direct measurements of the surface layer thickness by using the method of ellipsometry.

Keywords: Konovalov's laws, superficial phenomena, surface layer thickness.

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УДК 544.03

A f z a l W., P r a u s n i t z J. **Four methods to measure the solubility of gases and vapors in liquids and polymers** // Vestnik St. Petersburg University. Ser. 4. 2013. Issue. 1. P. 16–31.

Waheed Afzal — post-doc, university of California, Berkeley, USA; e-mail: waheed.afzal@gmail.com
John Prausnitz — professor, university of California, Berkeley, USA; e-mail: prausnit@cchem.berkeley.edu

Solubility of gases and vapors at low or moderate pressures are frequently required in chemical technology. While numerous methods have been proposed for measuring such solubility, four particularly useful methods are briefly reviewed here.

1. Packed-bed or capillary-column gas-liquid chromatography is convenient to measure the solubility of moderately-soluble vapors in low-volatile solvents such as ionic liquids or polymers.

2. The inert gas-stripping method is appropriate to measure the solubility of gases or vapors in liquids.

3. The gravimetric quartz-spring method is useful to measure solubility of readily-soluble vapors in polymers or non-volatile liquids.

4. The synthetic-volumetric method is best suited to measure solubility of sparingly-soluble gases in liquids.

Keywords: method of measuring gas solubility, gases and vapors in liquids.

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F r e n k e l M. **Experimental data validation and property prediction models in thermodynamics** // Vestnik St. Petersburg University. Ser. 4. 2013. Issue. 1. P. 32–45.

Michael Frenkel — PhD, professor, director of the Thermodynamics Research Center at the U.S. National Institute of Standards and Technology, Boulder, Colorado, USA; e-mail: michael.frenkel@nist.gov

The article provides an overview of the systems and software tools designed for global validation of experimental data in the field of thermodynamics, and experimental data-driven technologies for thermophysical property prediction developed recently at the Thermodynamics Research Center (TRC) of the U. S. National Institute of Standards and Technology (NIST), including those based on QSPR, UNIFAC, and Monte Carlo simulation methods. QSPR-based and UNIFAC-based prediction methods developed at NIST TRC are discussed with the emphasis on the importance of the use of the combined expanded uncertainties of the experimental data selected and performance of the phenomenological data quality tests to obtain high fidelity predictive models. A formal procedure for generation of transferrable force fields for Monte Carlo molecular simulations with simultaneous use of well-defined experimental data for a number of properties (liquid density, vapor pressure, enthalpy of vaporization) is described for the chemical class of fluorohydrocarbons.

Keywords: QSPR, UNIFAC, and Monte Carlo simulation methods, validation of experimental data, thermodynamics.

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S t a s h k o v a A. E., P e s h k o v a M. A., M i k h e l s o n K. N. **Sodium interference with the pH-response of Na/pH-selective optode in the physiological concentration range: optical sensors of the individual ion activities?** // Vestnik St. Petersburg University. Ser. 4. 2013. Issue. 1. P. 46–62.

Anastasiya E. Stashkova — student, Saint Petersburg State University; e-mail: stashkova_69@mail.ru
Maria A. Peshkova — PhD in chem., lecturer, Saint Petersburg State University;
e-mail: maria.a.peshkova@gmail.com
Konstantin N. Mikhelson — Dr. Sci. in chem., Professor, Saint Petersburg State University;
e-mail: konst@km3241.spb.edu

Plasticized polymer-based optical sensors (optodes) with selectivity towards a(Na)/a(H) ratio in the solution were composed and characterized. The article carries out a quantitative analysis of dynamic range, reproducibility, hysteresis and response time of the sensors, as well as cross-interference of complementary ions on the sensor response. In particular, it spots the error of pH measurements in case of sodium content in the sample fluctuating within the physiological range. The experiments show that sodium influence on the pH-response can be neglected only within a narrow range of normal sodium concentration while neglecting it within wider short-term non-lethal range leads to unacceptable errors in pH determination. Thus, it was demonstrated that it is crucial for the clynical analysis to develop optode, which would response with regard to single ion activity.

Keywords: ion-selective optodes, polymer membranes, single ion activity, pH and sodium physiological ranges.

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Kontogeorgis G. M. **Association models for petroleum applications** // Vestnik St. Petersburg University. Ser. 4. 2013. Issue. 1. P. 63–79.

Georgios M. Kontogeorgis — professor, Center for Energy Resources Engineering (CERE), Department of Chemical and Biochemical Engineering. Technical University of Denmark.

Thermodynamics plays an important role in many applications in the petroleum industry, both upstream and downstream, ranging from flow assurance, (enhanced) oil recovery and control of chemicals to meet production and environmental regulations. There are many different applications in the oil & gas industry, thus thermodynamic data (phase behavior, densities, speed of sound, etc) are needed to study a very diverse range of compounds in addition to the petroleum ones (CO_2, H_2S, water, alcohols, glycols, mercaptanes, mercury, asphaltenes, waxes, polymers, electrolytes, biofuels, etc) within a very extensive range of conditions, up to very high pressures. Actually, the petroleum industry was one of the first industrial sectors which used extensively thermodynamic models and even contributed to the development of several of the most popular and still widely used approaches. While traditional thermodynamic models like cubic equations of state have been the dominating tools in the petroleum industry, the focus of this review is on the association models. Association models are defined as models of the SAFT/CPA family (and others) which incorporate hydrogen bonding and other complex interactions. Such association models have been, especially over the last 20 years, proved to be very successful in predicting many thermodynamic properties in the oil & gas industry. They have not so far replaced cubic equations of state but the results which have been obtained by using these models are very impressive in many cases, e. g. for gas hydrate related systems, CO_2/H_2S mixtures, water/hydrocarbons and others. This review highlights both the major advantages of these association models and some of their limitations which we believe should be discussed in the future.

Keywords: petroleum industry, SAFT/CPA association models, gas hydrate, water/hydrocarbons, thermodynamics.

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Cumana S., Gurikov P., Belugin A., Johannsen M., Menshutina N., Smirnova I. **Application of silica aerogels as stationary phase in Supercritical fluid chromatography: experimental study and modelling with cellular automata** // Vestnik St. Petersburg University. Ser. 4. 2013. Issue. 1. P. 80–95.

Sucre Cumana — PhD student, M. Sc., Institute of Thermal Separation Processes, Hamburg University of Technology, Germany.
Pavel Gurikov — Dr., postdoctoral fellow, Institute of Thermal Separation Processes, Hamburg University of Technology, Germany; e-mail: pavel.gurikov@tu-harburg.de
Alexander Belugin — PhD student, M. Sc., Computer Aided Process Engineering, Mendeleev University of Chemical Technology of Russia.
Monika Johannsen — Dr. habil., Associate lecturer, Institute of Bioprocess and Biosystems Engineering, Hamburg University of Technology, Germany.
Natalia Menshutina — Professor, Dean, Computer Aided Process Engineering, Mendeleev University of Chemical Technology of Russia.
Irina Smirnova — Professor Dr.-Ing., head of the Institute of Thermal Separation Processes, Hamburg University of Technology, Germany; e-mail: irina.smirnova@tu-harburg.de

This paper discusses the possibility of using silica aerogels as a stationary phase for supercritical fluid chromatography (SFC) separations. Two types of silica aerogel particles were prepared by the well-established two-step sol-gel method and subsequent drying with supercritical carbon dioxide. The first kind was obtained by crushing and sieving monolithic aerogels and the second one — by spraying the sol in an autoclave, where aging and drying occurred. The results show that it is possible to separate alkyl-benzenes with good resolution using both types of aerogels. The efficiency of aerogel columns was low comparing to a commercial stationary phase mainly due to the irregular morphology of aerogels particles and low loose weight density. The experiments showed that there was no visible damage of the aerogel packing after dissolving modifier in the mobile phase. Thus it was firstly demonstrated that aerogels can indeed be successfully used as stationary phases for SFC. Further it proves an ability of SFC to study the interactions between selected solutes and the surface of the silica aerogels under supercritical conditions. Thermodynamic parameters for adsorption of naphthalene on silica aerogels were determined and compared with the ones obtained with commercial silica-gel. Finally the empirical data were compared with modeling by cellular automata. This approach was found to be able to reflect major observations in SFC. Quantitative

correspondence between experimental and calculated retention factors was demonstrated for several operating conditions.

Keywords: supercritical fluid chromatography, aerogels, thermodynamics of adsorption, coarse-grained modeling, cellular automata.

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Dorn U., Schrader P., Enders S. **Aggregation and phase behavior of nonionic surfactants (C_iE_j) in aqueous solution** // Vestnik St. Petersburg University. Ser. 4. 2013. Issue. 1. P. 96–112.

Udo Dorn — graduate student of Technical University Berlin, Germany.

Philipp Schrader — graduate student of Technical University Berlin, Germany.
Sabine Enders — Chair of Thermodynamics and Thermal Separation Science, Technical University Berlin, Germany; e-mail: sabine.enders@tu-berlin.de

The paper deals with the application of a modified detailed micelle formation model to aqueous solutions of nonionic poly(oxyethylene) alkyl ethers (C_iE_j) surfactants. The modification implies an assumption of effective cross-section area of the hydrophilic head being dependant on temperature. By using independently experimental data from Brillouin—Mandelstam-scattering experiments it is possible to express the cross-section area as a function of temperature-dependent hydration number of poly(ethylene oxide), and this expression can be applied for all i and j values. This approach leads to a model to describe the properties of the formed aggregates like critical micelle concentration (cmc), size and shape. For the calculation of the demixing behavior which occurs at low surfactant concentration the ajustment of three additional parameters describing the interactions is required. For several surfactants an intersection point between the cmc as a function of temperature and diluted branch of cloud point curve could be found. At temperatures below this intersection point the micelles with a large polydispersity are present in the dilute phase.

Keywords: agregation, phase behavior, nonionic surfactants, aqueous solution.

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E m e l ' y a n e n k o V. N., V e r e v k i n S. P. **Thermodynamic study of pure methylbenzaldehydes and their mixtures with ionic liquids** // Vestnik St. Petersburg University. Ser. 4. 2013. Issue. 1. P. 113–125.

V. N. Emel'yanenko — Department of Physical Chemistry, University of Rostock, Rostock, Germany.
Sergey P. Verevkin — PhD, docent, Faculty of Interdisciplinary Research, Department "Life, Light and Matter", University of Rostock; e-mail: sergey.verevkin@uni-rostock.de

Activity coefficients at infinite dilution of the systems containing ortho-, meta, and para-methylbenzaldehyde in the 1-methyl-3-butyl-imidazolium bis(trifluoromethylsulfonyl)imide [BMIM][NTf_2] and 1-methyl-3-octyl-imidazolium tetrafluoroborate [OMIM][BF_4] at 385 K using ionic liquids as a stationary phase were determined by gas chromatography. Vapour—liquid equilibrium of binary mixtures methyl-benzaldehydes with these ILs was studied in the full concentration range by using transpiration method. The molar enthalpies of vaporization of three pure methyl-benzaldehydes were obtained from the data on temperature dependence of the vapour pressure measured by the transpiration method. The standard molar enthalpies of formation of the liquid methyl-benzaldehydes were measured using the combustion calorimetry. These experimental data have provided the molar enthalpies of formation in the gaseous phase for the pure methyl-benzaldehydes. For validation of the experimental results the high level ab initio calculations of methyl-benzaldehydes have been performed using the G4 and G3(MP2) basis sets, and the results from the "atomization" and "bond separation" methods correspond to the results of the experiment. The gaseous enthalpies of formation were used for quantification of substituents interaction on the benzene ring in methylbenzaldehydes.

Keywords: ionic liquids, activity coefficients at infinite dilution, vapor—liquid equilibria, vapor pressure, enthalpy of formation, enthalpy of vaporization, quantum chemical calculations.

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Schäfer D., Kamps Á. P.-S., Rumpf B., Maurer G. **Experimental investigation of the influence of boric acid on the solubility of carbon dioxide in aqueous solutions of potassium hydroxide** // Vestnik St. Petersburg University. Ser. 4. 2013. Issue. 1. P. 126–132.

Dirk Schäfer — University of Kaiserslautern, Germany.

Álvaro Pérez-Salado Kamps — University of Kaiserslautern, Germany.

Bernd Rumpf — University of Kaiserslautern, Germany.

Gerd Maurer — prof. dr.-ing., professor, University of Kaiserslautern, Germany; e-mail: maurer@mv.uni-kl.de

Based on the analytical method, a high-pressure cell technique was used to investigate the influence of boric acid on the solubility of carbon dioxide in aqueous solutions of potassium hydroxide at two temperatures that are typical for absorption and desorption step in the "hot-potash" process. In industrial applications of these processes appropriate additives to the aqueous solvent improve the process performance. The mode of action of these additives has to be studied and quantified in models for the computer-assisted design of the "hot-potash" process. The new experimental results show that the influence of boric acid on the equilibrium solubility of CO_2 in aqueous solutions of

KOH is very small. Therefore, another factors account for applying boric acid as an additive in the "hot-potash" process.

Keywords: "hot-potash" process, gas solubility of carbon dioxide in aqueous solutions of potassium hydroxide/potassium carbonate, boric acid.

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N e z b e d a I. **On the excluded volume concept** // Vestnik St. Petersburg University. Ser. 4. 2013. Issue. 1. P. 133–138.

Ivo Nezbeda — DrSc., professor, J. E. Purkinje University, Usti nad Labem, Czech Republic;
e-mail: zrzekin@seznam.cz

The paper shows that the excluded volume concept can be applied to the fluids with complex interactions, particularly associating ones, if the intermolecular interaction model is considered as a site—site model with embedded Coulombic sites. Thus, the excluded volume, as a matter of fact, incorporates the effect of the repulsive interactions between the like charges at short intermolecular distances. We have focused on the partial molar volume at infinite dilution which is known

from experiment to discriminate between different solvents. Without resorting to any additional assumptions or approximations the extended volume concept can predict a decrease of the PMV of non-polar solutes in water, whereas claims based solely on the relative size of the solute and solvent molecules are not justified.

Keywords: excluded volume, partial molar volume, primitive models, pseudo-hard bodies, water-methanol mixtures.

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S u b r a m a n i a n D., K l a u d a J. B., L e y s J., A n i s i m o v M. A. **Thermodynamic anomalies and structural fluctuations in aqueous solutions of tertiary butyl alcohol** // Vestnik St. Petersburg University. Ser. 4. 2013. Issue. 1. P. 139–152.

Deepa Subramanian — Department of Chemical and Biomolecular Engineering, University of Maryland, College Park, USA.
Jeffery B. Klauda — Department of Chemical and Biomolecular Engineering, University of Maryland, College Park, USA.
Jan Leys — Laboratorium voor Akoestiek en Thermische Fysica, Departement Natuurkunde en Sterrenkunde, KU Leuven, Belgium.
Mikhail A. Anisimov — Institute for Physical Science and Technology, University of Maryland, College Park, USA; e-mail: anisimov@umd.edu

In this work, we discuss the connection between the anomalies of the thermodynamic properties, experimentally observed in tertiary butyl alcohol (TBA) — water solutions, and the molecular clustering in these solutions, as revealed by molecular dynamics (MD) simulations. These anomalies are observed in relatively dilute solutions of about 0.03–0.08 mole fraction of TBA and become more pronounced at low temperatures. MD simulations show that these solutions exhibit short-ranged (order of 1 nm), short-lived (tens of picoseconds) "micelle-like" structural fluctuations in the same concentration range. We attribute the anomalies in the thermodynamic properties of aqueous TBA solutions to these structural fluctuations on the molecular scale.

Keywords: thermodynamic properties, *tert*-butyl alcohol, aqueous solutions, structural fluctuations.

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Polikhronidi N. G., Abdulagatov I. M., Batyrova R. G., Stepanov G. V.
Quasistatic thermo- and barograms techniques for accurate measurements of the phase boundary properties of complex fluids and fluid mixtures near the Critical Point // Vestnik St. Petersburg University. Ser. 4. 2013. Issue. 1. P. 153–185.

N. G. Polikhronidi — Senior researcher, Institute of Physics of the Dagestan Scientific Center of the Russian Academy of Sciences, Makhachkala, Russia; e-mail: polikhronidi@rambler.ru
Ilmutdin Magomedovich Abdulagatov — professor, present address: National Institute of Standards and Technology, Colorado, USA; e-mail: ilmutdin@boulder.nist.gov
R. G. Batyrova — Senior researcher, Institute of Physics of the Dagestan Scientific Center of the Russian Academy of Sciences, Makhachkala, Russia; e-mail: polikhronidi@rambler.ru
G. V. Stepanov — Division chief, Institute of Physics of the Dagestan Scientific Center of the Russian Academy of Sciences, Makhachkala, Russia; e-mail: polikhronidi@rambler.ru

By using calorimetric (quasi-static thermo- and barograms) technique the saturated liquid and vapor densities of pure fluids (methanol, ethanol, propanol, DEE) and binary mixtures (H_2O+methanol, H_2O+ethanol, H_2O+ammonia, H_2O+D_2O, and CO_2+n-decane) have been accurately measured near the critical point. Simultaneously measured values of saturated liquid and vapor density and isochoric heat capacity near the critical point have been used to calculate asymmetric parameters a_3 and b_2 of singular diameter in the coexistence curve (parameters of "complete" scaling theory) near the critical point. The derived values of a_3 and b_2 were used to calculate the strength of the Yang—Yang anomaly. The paper examines contributions of a "complete" scaling term $t^{2\beta}$ in diameter behavior in the coexistence curve and contribution of second temperature derivatives

(d^2P_S/dT^2) and $(d^2\mu/dT^2)$ in the divergence of two-phase heat capacity C_{V2} near the critical point. The divergence of the coexistence curve diameter, $d\rho_d/d\tau$, for methanol, ethanol, n-propanol, and DEE is shared between the terms $B_2t^{1-\alpha}$ and $t^{2\beta}$. The Yang—Yang anomaly strength parameter R_μ for DEE is about 0.45, which means that C_{V2} anomaly almost equivalently shared between the vapor pressure and chemical potential terms. For ethanol the value of R_μ is very small (0.024), which means that the contribution of the chemical potential $(d^2\mu/dT^2)$ to C_{V2} divergence is almost zero i. e. singularity of C_{V2} being caused by vapor pressure term (d^2P_S/dT^2). For methanol and n-propanol R_μ is relative small (0.245 and 0.171, respectively), therefore the singularity of the C_{V2} basically being caused by vapor pressure term. The values of R_μ derived from C_{V2} measurements correspond to the values derived from the coexistence curve density or singular diameter data. The critical parameters for binary mixtures (critical curve data) (H_2O+methanol, H_2O+ethanol, H_2O+ammonia, H_2O+D_2O, CO_2+n-decane) were determined near the critical points by using the saturated density data. The correlations between the asymptotic critical amplitudes, asymmetric coexistence curve diameter and acentric factor were revealed.

Keywords: quasistatic thermo- and barograms technique, phase boundary properties, fluid mixtures, critical point.

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Gavrichev K. S., Ruimin M. A., Khoroshilov A. V., Nikiforova G. E., Tuirin A. V., Gurevich V. M., Starykh R. V. **Thermodynamic properties and phase transformations of tetragonal reorganization of terbium orthophosphate** // Vestnik St. Petersburg University. Ser. 4. 2013. Issue. 1. P. 186–197.

Konstantin S. Gavrichev — Dr. Sci. in chem., Professor, Institute of General and Inorganic Chemistry named N. S. Kurnakov of RAS, Moscow; e-mail: gavrich@igic.ras.ru

Mikhail A. Ruimin — PhD in chem., researcher, Institute of General and Inorganic Chemistry named N. S. Kurnakov of RAS, Moscow.

Andrey V. Khoroshilov — PhD in chem., senior researcher, Institute of General and Inorganic Chemistry named N. S. Kurnakov of RAS, Moscow.

Galina E. Nikiforova — researcher, Institute of General and Inorganic Chemistry named N. S. Kurnakov of RAS, Moscow.

Alexandr V. Tuirin — researcher, Institute of General and Inorganic Chemistry named N. S. Kurnakov of RAS, Moscow.

Vyacheslav M. Gurevich — Institute of Geochemistry and Analytical Chemistry named V. I. Vernadski of RAS, Moscow.

Roman V. Starykh — PhD in engin., Associated Professor, Saint Petersburg State Polytechnic University.

By using relaxation, adiabatic and differential scanning calorimetry methods we have determined a thermal capacity of tetragonal reorganization of terbium orthophosphate t-$TbPO_4$ in a temperature interval 4–1230 K. Thermodynamic functions of t-$TbPO_4$ are calculated by the smoothed values of a thermal capacity. The thermal behavior of t-$TbPO_4$ at the high temperature was studied by the differential scanning calorimetry by using the continuous heating method. Anomalies in the area below 10 K and above 1600 K connected with the phase transformations were revealed. In the field of 0.51–22 K the temperature dependence of a thermal capacity is characterized by the anomaly connected with transition t-$TbPO_4$ in an antiferromagnetic phase. The field of 1620–1720 K is characterized by endothermal effect with enthalpy of the transformations, which equals 4.8 kJ/mol and corresponds to structural reorganization. At 298.15 K thermodynamic functions have following

values: $C_p^0(298.15\ \mathrm{K}) = 105.11 \pm 0.06$ J/(K·mol), $S^0(298.15\ \mathrm{K}) = 125.92 \pm 0.13$ J/(K·mol), $H^0(298.15\ \mathrm{K}) - H^0(0\ \mathrm{K}) = 17.803 \pm 0.013$ kJ/mol, $\Phi^0(298.15\ \mathrm{K}) = 66.205 \pm 0.29$ J/(K·mol).

Keywords: terbium orthophosphate, phase transformations, thermodynamic functions, calorimetry.

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Hebabcha M., Miltgen M., Modaressi A., Magri P., Ait-Kaci A., Rogalski M. **Aggregation of Nanoparticles in Polyphase Mixtures — Impact on Phase Equilibria** // Vestnik St. Petersburg University. Ser. 4. 2013. Issue. 1. P. 198–206.

Mustapha Hebabcha — assistant, LTMM, Université Houari Boumédiène des Sciences et Technologie, Algeria.
Morgane Miltgen — student, LCP-A2MC, Université de Lorraine, France.
Ali Modaressi — Dr., associate professor, LCP-A2MC, Université de Lorraine, France.
Pierre Magri — Dr., researcher, LCP-A2MC, Université de Lorraine, France.
Ahmed Ait-Kaci — Dr., professor, LTMM, Université Houari Boumédiène des Sciences et Technologie, Algeria.

Marek Rogalski — Dr., professor, LCP-A2MC, Université de Lorraine, France; e-mail: rogalski@univ.metz.fr

In this work we were concerned with the influence of dispersed nanoarticles (Nps) on liquid—liquid and solid—liquid phase equilibria. The cryoscopic depression due to the presence of Nps of silver ($d < 100$ nm), alumina ($d < 50$ nm) and silica (10 nm $< d <$ 20nm) was studied in cyclohexane and dimethysulfoxide. Next, the liquid—liquid equilibria of one binary (acetonitrile+n-decanol) and one ternary (acetonitrile+cyclohexane+ethanol) mixtures were determined in presence of Nps dispersion. The results have shown a significant influence of Nps on phase equilibria. This finding was explained by partition of the mixture components between the bulk phase and the liquid phase confined in nanoagreggates formed by Nps in liquid solutions.

Keywords: nanoparticle aggregation, liquid—liquid equilibria, liquid—solid equilibria, solvent mediated interaction.

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Bardavelidze M. S., Nishnianidze D. N. **Shape invariance of second order in one-dimensional quantum mechanics** // Vestnik St. Petersburg University. Ser. 4. 2013. Issue. 1. P. 207–214.

Malkhaz Simon Bardavelidze — teacher, Akaki Tsereteli State University, Kutaisi, Georgia;
e-mail: m.bardaveli@gmail.com
David Nodar Nishnianidze — Professor, Akaki Tsereteli State University, Kutaisi, Georgia;
e-mail: cutaisi@yahoo.com

The article investigates shape invariance under supersymmetrical transformations of the second order in the derivatives. The equation representing the general conditions of additive shape invariance is obtained. The particular solutions of this equation provide an explicit form of potentials with the second order shape invariance.

Keywords: shape invariance, supersymmetric quantum mechanics.

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УДК 539.18

Anisimova G. P., Dolmatova O. A., Polischuk V. A., Tsygankova G. A. **Semi-empirical calculation of the fine-structure parameters, coupling coefficients and gyromagnetic ratios for $npn'f$ configurations of C I, Si I, Ge I and P II** // Vestnik St. Petersburg University. Ser. 4. 2013. Issue. 1. P. 215–227.

Galina Pavlovna Anisimova — PhD in physics and mathematics, Associate Professor, St. Petersburg State University; e-mail: olgadolmatova@gmail.com

Olga Aleksandrovna Dolmatova — PhD in physics and mathematics, Associate Professor, St. Petersburg State University; e-mail: olgadolmatova@gmail.com

Vladimir Anatoljevitch Polischuk — Dr. Sci. in physics and mathematics, St. Petersburg State University; e-mail: vpvova@rambler.ru

Galina Aleksandrovna Tsygankova — PhD in physics and mathematics, St. Petersburg State University; e-mail: galusinka@mail.ru

The fine-structure parameters are calculated semiempirically for a number of high-excited configurations of C I, Si I, Ge I and P II. Using different coupling schemes: LS, LK, jK, the article calculates the fine-structure energy values, which coincide with the experimental data, coupling coefficients and gyromagnetic ratios. The results of the gyromagnetic ratios are compared with data available in the literature. The probability of the interaction for the $npn'f + npn'p$ configurations is considered on the base of energetic spectra analysis and calculated data.

Keywords: semi-empirical computation, matrix of the energy operator, fine-structure parameters, gyromagnetic values, coupling coefficients.

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P a v l o v S. I., K a r a s e v V. Yu., D z l i e v a E. S. **Sounding of glow discharge by polydisperse dust particles** // Vestnik St. Petersburg University. Ser. 4. 2013. Issue. 1. P. 228–232.

S. I. Pavlov — student, Department of General Physics 1, St. Petersburg State University;
e-mail: sergey_pavlov86@mail.ru
Viktor Yu. Karasev — Dr. Sci., Professor, Department of Physics, St. Petersburg State University;
e-mail: viktor.karasev@pobox.spbu.ru
E. S. Dzlieva — PhD, Assistant Professor, Department of Physics, St. Petersburg State University;
e-mail: viktor.karasev@pobox.spbu.ru

The paper is devoted to the method of analysis of unstratified glow discharge. It presents an experiment on sensing glow by falling polydisperse particles. It analyses behavior of probe particles in their trajectories, evaluates the longitudinal and radial field of the discharge.

Keywords: gas discharge, diagnostics of plasma, complex plasma.

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Zherebchevsky V. I., Torilov S. Yu., Andronenkov A. N., Gridnev K. A., Maltsev N. A. **Elastic scattering of alpha-particles by neutron excess nucleus ^{14}C** // Vestnik St. Petersburg University. Ser. 4. 2013. Issue. 1. P. 233–237.

Vladimir Iosifovich Zherebchevsky — PhD, senior teacher, Saint-Petersburg State University; e-mail: vozhereb@mail.ru

Sergey Yurievich Torilov — PhD, Associate Professor, Saint-Petersburg State University; e-mail: torilov@hotmail.com

Alekxey Nikolaevich Andronenkov — PhD, Assistant, Saint-Petersburg State University; e-mail: andr_alexey@mail.ru

Konstantin Aleksandrovich Gridnev — Dr. Sci., Head of nuclear department, Saint-Petersburg State University; e-mail: kgridnev@yahoo.com

Nikolay Aleksandrovich Maltsev — researcher, Saint-Petersburg State University; e-mail: namaltsev@gmail.com

The elastic scattering of alpha-particles by ^{14}C has been observed for alpha with energy 27 MeV and in angular range $\Theta_{c.m.}$ from 30° to 80.5°. New precision methods for obtaining experimental data were used. Experimental angular distribution was analyzed in terms of the SPP model.

Keywords: nuclear reactions, neutron excess, experimental methods, global potential well.

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P u c h k o v A. M. **Summation of perturbation series for multi-charged ions by hyper-virial relations method** // Vestnik St. Petersburg University. Ser. 4. 2013. Issue. 1. P. 238–245.

Andrei Mikhailovich Puchkov — Saint Petersburg State University; e-mail: putchkov@mail.ru

The paper presents a systematic study of hyper-virial relation method in summation of perturbation series for multi-charged hydrogen-like ions. It reveals recurrent relations which allow to find explicit expressions for sums with matrix elements of arbitrary powers. It shows that, in some cases, the general approach leads to previously obtained results. In addition, it discusses some possible applications of research results.

Keywords: hyper-virial relations, calculations of higher-order corrections to the hyperfine spliting and g-factor.

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T o l m a c h e v Yu. A. **Operation over an optical signal using generalized diffraction grating** // Vestnik St. Petersburg University. Ser. 4. 2013. Issue. 1. P. 246–252.

Yurii A. Tolmachev — professor, faculty of physics, Saint-Petersburg state university;
e-mail: yurii.tolmach@rambler.ru

The general type of a scalar wave signal transformation in time by a flat 1D diffraction grating is described. The analysis is based on the concept of impulse response of the linear optical system that permits for the study of transformation of an arbitrary signal. To demonstrate the effectiveness of the method, the article examines traditional problem of the plane wave scattering by a transparent grating and shows the coincidence of final relation for monochrome wave with that for the classical diffraction grating. Afterwards, the generalized form of grating structure which grooves can be non-equidistant but positioned accordingly to some special law is studied. The effective velocity of observation of the moment of wave scattering by the grating is introduced, its value may vary from $c/2$ up to infinity. As a result, the conditions are derived for the realization of the incoming signal convolution and/or correlation with the function describing the spatial density of the grating grooves.

Keywords: diffraction grating, signal transformation, delta-wave approach, cross-correlation, convolution.

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B e l s k i y D. B, G u t s e v S. F., K o s y k h N. B. **On the probe measurements in Helium plasma afterglow** // Vestnik St. Petersburg University. Ser. 4. 2013. Issue. 1. P. 253–261.

Denis Borisovich Belskiy — Engineer-researcher, Department of Optics, Saint-Petersburg state university; e-mail: den_piter87@mail.ru
Sergey Anatolievich Gutsev — Engineer-researcher, Department of Optics, Saint-Petersburg state university; e-mail: gsa_ges@mail.ru
Nikolay Borisovich Kosykh — Engineer-researcher, Department of Optics, Saint-Petersburg state university; e-mail: ipnk5419@mail.ru

The paper presents experimental Langmuir probe measurements in Helium plasma afterglow. The research was carried out in three different dimensions: under classical Langmuir condition, moderate pressure and diffusion drift of charged particles to the probe. With pictures and estimate calculations, it was shown that formula of orbital motion correctly describes only the collisionless case in the electric field of the probe. Sources of concentration and errors in electron temperature measurements are given in detail. It presents logarithmic method to determine electron temperature, with calculation of sheath of spatial charge near the probe being done and changing of shape of volt-ampere characteristic from classical to diffusion condition being shown.

Keywords: Helium plasma afterglow, electron temperature, probe sheath.

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