Non-equilibrium dynamics of the piston in the Szilard engine

Deepak Bhat\textsuperscript{1}, Abhishek Dhar\textsuperscript{2}, Anupam Kundu\textsuperscript{2} and Sanjib Sabhapandit\textsuperscript{3}

\textsuperscript{1} Santa Fe Institute - 1399 Hyde Park Rd., Santa Fe, NM 87501, USA
\textsuperscript{2} International Centre for Theoretical Sciences - Bengaluru 560089, India
\textsuperscript{3} Raman Research Institute - Bengaluru 560080, India

received 11 March 2019; accepted in final form 29 June 2019
published online 31 July 2019

PACS 05.70.Ln – Nonequilibrium and irreversible thermodynamics
PACS 05.20.-y – Classical statistical mechanics
PACS 05.40.-a – Fluctuation phenomena, random processes, noise, and Brownian motion

Abstract – We consider a Szilard engine in one dimension, consisting of a single particle of mass \(m\), moving between a piston of mass \(M\) and a heat reservoir at temperature \(T\). In addition to an external force, the piston experiences repeated elastic collisions with the particle. We find that the motion of a heavy piston (\(M \gg m\)), can be described effectively by a Langevin equation. Various numerical evidences suggest that the frictional coefficient in the Langevin equation is given by \(\gamma = (1/X)\sqrt{8\pi mk_BT}\), where \(X\) is the position of the piston measured from the thermal wall. Starting from the exact master equation for the full system and using a perturbation expansion in \(\epsilon = \sqrt{m/M}\), we integrate out the degrees of freedom of the particle to obtain the effective Fokker-Planck equation for the piston, albeit with a different frictional coefficient. Our microscopic study shows that the piston is never in equilibrium during the expansion step, contrary to the assumption made in the usual Szilard engine analysis — nevertheless the conclusions of Szilard remain valid.

Copyright © EPLA, 2019

Introduction. – The Szilard engine, a simple realization of the Maxwell demon, is a paradigmatic model designed to address the conceptual foundations of the second law of thermodynamics [1]. In apparent violation of the second law, this model envisages the following thought experiment — a system, working in a cycle, extracts work from a single heat reservoir by using the information about the initial state of the system. Recently there has been renewed interest in this problem due to important developments in the areas of stochastic thermodynamics of small systems [2] and fluctuation theorems [3–7]. Moreover, recent developments of technology has made it possible to realize this thought experiment in the laboratory [8–11].

In spite of the importance of the Szilard problem, somewhat surprisingly, there have been very few microscopic studies [12,13] of its dynamics in the original set-up. In Szilard’s analysis, the idealized piston is assumed to have infinite mass, and its motion is then described by a quasi-static deterministic process. However, a realistic piston has a large but finite mass. As a result, its motion is strongly affected by fluctuations, expected to be important in small systems. Hence, it is crucial to understand the stochastic dynamics of the piston. This is the main aim of this letter.

The basic model consists of a single hard point particle of mass \(m\), confined to move in one dimension between a piston and a heat reservoir at temperature \(T\) (see fig. 1). The piston itself is taken to be another hard point particle of mass \(M \gg m\). Let \(x\) and \(v\) (\(X\) and \(V\)) respectively be the position and velocity of the particle (piston). On collisions with the thermal wall at \(x = 0\), the particle emerges with a velocity \(v > 0\), chosen independently at each time from the Rayleigh distribution \(f(v) = \beta mve^{-\beta mv^2/2}\), where \(\beta = (k_BT)^{-1}\). The collision between the particle and the piston is taken to be elastic. Between collisions with the wall and the piston, the particle moves ballistically. The piston, apart from collisions with the particle, also experiences an external force \(-dU(X)/dX\). This dynamics takes the system, at long times, to the Gibbs’s equilibrium state \(P_{\text{eq}} = Z^{-1}\exp[-\beta(mv^2/2 + MV^2/2 + U(X))]\theta(x)\theta(X-x)\), where \(Z\) is the partition function. However the dynamics of the relaxation process is non-trivial, as can be seen even when the piston is held fixed [14].

Our set-up is similar to that of the well-known adiabatic piston problem, where one usually considers the deterministic motion of a heavy piston in the presence of a gas of a thermodynamically large number of small particles.
with [13,15–25] or without reservoirs [26–29]. Here we look at the stochastic dynamics of the piston in the presence of a single particle gas, as required in the Szilard set-up, where fluctuations play an important role.

Our main finding is that, in the limit of heavy piston mass ($M \gg m$), the effective stochastic dynamics is given by the Langevin equation

$$M \frac{dV}{dt} = -t' \langle \gamma(X) \rangle - \gamma(X) V + \sqrt{2 \gamma(X) k_B T} \eta(t),$$

where $\eta(t)$ is Gaussian white noise with $\langle \eta(t) \eta(t') \rangle = \delta(t-t')$, and the space-dependent dissipation is given by

$$\gamma(X) = \frac{1}{X} \sqrt{8 \pi m k_B T} =: \gamma_{sp}.$$  

The second term on the r.h.s. of eq. (1) is the pressure term, while the frictional and noise terms satisfy the fluctuation-dissipation relation. All of these three terms arise from the repeated collisions of the particle with the stationary distribution corresponding to the above Langevin equation is given by $\Psi_{eq} (X, V) = Z^{-1} \exp [-\beta (MV^2/2 + U_{\text{eff}}(X))]$, where $U_{\text{eff}} = U - k_B T \ln X$ is the effective potential and $Z$ is the partition function. This is consistent with the equilibrium distribution $P_{eq}(x, v, X, V)$ of the full system. If we replace our single particle gas by an equilibrium gas at finite density $\nu$, then the friction coefficient is given by [30] $\nu \sqrt{8 \pi m k_B T/\pi}$. Naively extending this result to our one-particle gas, by setting $\nu = 1/X$, would suggest $\gamma(X) = (1/X) \sqrt{8 \pi m k_B T/\pi} =: \gamma_{\text{gas}}$, which is different from eq. (2). As we show below, our numerical results show that eq. (1), with $\gamma(X)$ as in eq. (2), describes the piston dynamics very accurately. It should also be noted that, starting from the master equation of the full system, it is possible to derive eq. (1) (check details in the end), but our attempt to derive the exact expression for dissipation was not successful. The expression for dissipation presented in eq. (2) is primarily based on the numerical results.

**Numerical results.** We compute various physical quantities related to the piston, from the exact microscopic dynamics (EMD) of the particle-piston system, and compare them with the corresponding results obtained from the effective Langevin equation (LE) (1). In the EMD simulations we start with the piston at a fixed position $X_0$ and velocity $V = 0$, while the initial position $x$ and velocity $v$ of the small particle are chosen from the equilibrium distribution $\rho_{eq}(x, v) = (1/x_0) e^{-m v^2/(2 k_B T)} / \sqrt{2 \pi k_B T/m}$ with $0 < x < X_0$. Starting from this initial condition we follow the collisional dynamics. Note that there is a stochastic component to the dynamics, arising from the collisions between the particle and the heat bath. We compute various observables, related to the piston, by averaging over the initial configurations (of particle) as well as the trajectories. In our LE simulations we start from the same fixed initial conditions ($X = X_0, V = 0$) for the piston and then average over noise realizations. In all our simulations we have set $k_B T = 1$ and $m = 1$.

In fig. 2(a) and (b), we plot the average position $\langle X \rangle$ and average kinetic energy $\langle E \rangle$ of the piston as a function of time, obtained from the EMD and LE simulations, for the case of a constant force $-F$ ($t = FX, F > 0$), directed towards the bath. We see excellent agreement between the EMD and the LE with $\gamma(X)$ from eq. (2), whereas the LE with $\gamma_{\text{gas}}$ shows significant deviations. We see damped oscillations and an eventual approach to the expected equilibrium values $\langle X \rangle_{eq} = 2 k_B T/F$. Note that the mean position does not correspond to the minimum of the effective potential, $X_{\text{min}} = k_B T/F$, expected from a naive pressure balance. This is basically because of equilibrium in an asymmetric potential and can also be understood in terms of a two-particle system in a constant-pressure ensemble [13]. From fig. 2(c) we can see that the time period of oscillations scales as $\sqrt{M}$ and this is again due to the motion in the effective potential $U_{\text{eff}}$. Finally, the inset in fig. 2(c) shows that the equilibrium time scale $\sim M$, as can be inferred from the Langevin equation, eq. (1).

The prediction $\gamma(X) = \gamma_{\text{gas}}$ is made for a heavy particle interacting with a many-particle gas in equilibrium. A question naturally arises, as to whether $\gamma(X) = \gamma_{\text{gas}}$ is better than eq. (2), in describing correlations when the heavy particle is in equilibrium with the single particle gas. This leads us to investigate the velocity auto-correlation $\langle V(0)V(t) \rangle_{eq}$ for the piston, as shown in fig. 2(d). We plot this correlation quantity as a function of time, as obtained by simulating the EMD and from the LE with both $\gamma_{sp}$ and $\gamma_{\text{gas}}$. Once again we observe that $\gamma_{sp}$ works much better than $\gamma_{\text{gas}}$. As in the non-stationary case (fig. 2(a) and (b)), here too the oscillation period scales as $\sqrt{M}$ while the relaxation time scales as $M$.

So far we have looked at averages of time-instantaneous quantities and found that the Langevin description (with $\gamma_{sp}$) agrees very well with the EMD. It is natural to ask if this agreement will continue to hold for time-integrated quantities, e.g., physical observables such as heat and work. These are quantities that are of direct relevance in the original context of the Szilard engine. We consider a protocol where the piston is released from an initial position $X_i$ and velocity $V_i$, and allowed to evolve till
it reaches a specified final position $X_f$ for the first time. Note that the time $\tau$ required for this process is a random variable. For a given realization of the trajectory $\{X(t), V(t), 0 \leq t \leq \tau\}$, the work done by the piston and the change in the kinetic energy are, respectively,
\[ W = \int_{X_i}^{X_f} F dX \quad \text{and} \quad \Delta E = \frac{1}{2} M V_f^2 - \frac{1}{2} M V_i^2, \quad (3) \]
where $V_f$ is the final velocity (which is random) of the piston. From the first law of thermodynamics, the amount of heat absorbed in the process is given by
\[ Q = \Delta E + W. \quad (4) \]

Because of the definition in eq. (3), the work extracted depends only on the end points $X_i$ and $X_f$ and therefore it is not a stochastic variable. The repeated cyclic extraction of work does not alter the conclusion drawn from the further analysis. We numerically compute $Q$ and $\Delta E$ from trajectories, with $X_i = L/2$, $V_i = 0$ and $X_f = L$, generated by both the EMD and the LE (1). In fig. 3, we plot the averages of these quantities as a function of the scaled variable. For a given realization of the trajectory $\{X(t), V(t)\}$, the change in kinetic energy of the piston $(\Delta E)$ decreases with increasing $F$, as expected.

In the $M \to \infty$ limit, $\Delta E = Q - W = k_B T \log(2) - F L / 2$, as seen in fig. 3(b), for the largest mass case. It then follows that at a critical value of $F = 2 k_B T \ln 2 / L$, the change in energy vanishes and all the heat absorbed gets converted to work, as in the ideal Szilard engine. Note that in the original single molecule Szilard engine, the work and heat computations are carried out under the assumption that the system is always in equilibrium and described by the equation of state $\langle X \rangle = k_B T / F$. However, as pointed out recently by Hondou [13], in the single particle case the equation of state is in fact $\langle X \rangle = 2 k_B T / F$ and this seems to contradict the basic premise of the Szilard calculation. This equation of state in fact follows on noting that $\langle 1 / X \rangle = 2 / \langle X \rangle$ with the average taken over $F_{eq}$. One of the finding of our microscopic study is that in the large piston mass limit, there is a critical force $F_{eq}$, when one can convert $k_B T \ln 2$ amount of heat completely into work and this happens while the system is never in equilibrium —hence Szilard’s conclusions remain valid.

Figure 3(c) shows that the time required to reach $X_f = L$ grows rapidly beyond $F_{eq}$, and this growth is faster for larger $M$. We note that, for $M \to \infty$, the (scaled) time required for the piston to reach $X_f = L$, given by $T / \sqrt{M} = \sqrt{1/2} \int_{L/2}^{L} [U_{\text{eff}}(L/2) - U_{\text{eff}}(X)]^{-1/2} dX$, diverges at $F = F_{eq}$. For large but finite $M$, the piston finally reaches $X_f = L$ after a large time because of the noise and dissipation terms. It is easy to see that the piston gains energy $O(M^{-1/2})$ from the noise term during the time period $O(M^{1/2})$ required to reach $L$ (as seen in fig. 3(c)). Interestingly, we see that $\Delta E$ for finite masses has a minimum at $F = F_{eq}$ and beyond $F_{eq}$, the $\Delta E$ increases.

Qualitatively similar thermodynamic features can also be seen for other choices of the external force, for instance harmonic force like $F = -\kappa (X - L/2)$ or $F = -k_B T \log(2) / L^2$ or $\mu = \mu_0 = k_B T$ we can get $(\Delta E) = 0$, $\langle Q \rangle = k_B T \ln(2)$ and work extracted is $k_B T \ln(2)$ in the limit $\epsilon = \sqrt{m / M} \to 0$. 
So far, we have presented various numerical evidence which suggests that (1) is the correct effective Langevin description of the piston motion. We now present a possible theoretical derivation based on van Kampen’s \( \Omega \)-expansion method \cite{31}, where \( \epsilon = \sqrt{m/\mathcal{M}} \) is the expansion parameter. We start with the master equation for the joint probability distribution function \( P(x, X, v, V, t) \) as follows \cite{13}:

\[
\frac{\partial P}{\partial t} = \mathcal{L}P; \quad \mathcal{L} = \mathcal{L}_d + \mathcal{L}_r + \mathcal{L}_c.
\]

Here,

\[
\mathcal{L}_dP = -v \frac{\partial P}{\partial x} - V \frac{\partial P}{\partial X} + \frac{F}{M} \frac{\partial P}{\partial V}
\]

corresponds to the deterministic evolution of the particle and piston, in between collisions. The collision of the small particle with the thermal reservoir is represented by the term

\[
\mathcal{L}_rP = \int \mathrm{d}v' \mathcal{R}_c(v|v')P(x, X, v', V) - \mathcal{R}_c(v'|v)P(x, X, v, V),
\]

with \( \mathcal{R}_c(v|v') = \delta(x - v') \theta(v - v')f(v) \). The first term in (7) corresponds to gain in probability from events in which a particle with a negative velocity hits the reservoir and emerges with a velocity \( v \) with probability \( f(v) \). The second term corresponds to loss of probability when a particle with velocity \( v \) hits the reservoir. Finally the elastic collisions between the particle and piston are represented by the term

\[
\mathcal{L}_cP = \int \mathrm{d}v' \mathrm{d}V' \mathcal{R}_c(v, V|v', V')P(x, X, v', V') - \mathcal{R}_c(v'|v, V)V'P(x, X, v, V),
\]

where \( \mathcal{R}_c(v, V|v', V') = \delta(X - x)\theta(v' - V')\theta(v - V')\delta[v' - \frac{\epsilon^2 - 1}{\epsilon^2 + 2\epsilon'}V']\delta[V' - \frac{2\epsilon x + (1 - \epsilon^2)V}{1 + \epsilon^2}] \). The \( \delta \)-function constraints on the velocities arise from the momentum and energy conservation during the elastic collisions. Our aim now is to integrate out the particle-degrees of freedom, to get an effective Fokker-Planck equation for the piston.

We first rescale the velocity of the piston and the particle as \( U = V\sqrt{\mathcal{M}}, \ u = v\sqrt{\mathcal{M}} \) and time as \( \tau = t/\sqrt{\mathcal{M}} \). We write the joint distribution of the rescaled variables \( Q(x, X, u, U, \tau) \) as

\[
Q(x, X, u, U, \tau) = \Phi(x, u, \tau|X, U)\Psi(X, U, \tau),
\]

where the expansion parameter \( \epsilon \) is explicit (see supplementary material Supplementarymaterial.pdf (SM)). To proceed further we expand the operator \( \mathcal{L} \) and the distributions \( \Phi, \Psi \) in powers of \( \epsilon \) as follows (see SM):

\[
\mathcal{L} = \mathcal{L}_0 + \epsilon \mathcal{L}_1 + \epsilon^2 \mathcal{L}_2 + \mathcal{O}(\epsilon^3), \quad \Phi = \Phi_0 + \epsilon \Phi_1 + \epsilon^2 \Phi_2 + \mathcal{O}(\epsilon^3), \quad \Psi = \Psi_0 + \epsilon \Psi_1 + \epsilon^2 \Psi_2 + \mathcal{O}(\epsilon^3).
\]

Inserting these in the master equation (10), we look at the resulting equation at different orders of \( \epsilon \). At each order we integrate the particle position \( x \) and velocity \( u \) to get following time evolution equations for \( \Psi_0, \Psi_1 \) and \( \Psi_2 \):

\[
\frac{\partial \Psi_0}{\partial \tau} = 0, \quad \frac{\partial \Psi_1}{\partial \tau} + \frac{\partial \Psi_0}{\partial X} - \beta_1 \frac{\partial \Psi_0}{\partial U} = -1 \frac{\partial \Psi_0}{X \partial U}, \quad \frac{\partial \Psi_2}{\partial \tau} + \frac{\partial \Psi_1}{\partial X} + \left[ -\beta_1 + \frac{1}{X} \right] \frac{\partial \Psi_1}{\partial U} = \gamma(X) \frac{\partial}{\partial U} \left[ U \Psi_0 + \frac{\partial \Psi_0}{\partial U} \right],
\]

which provide the equation for \( \Psi = \Psi_0 + \epsilon \Psi_1 + \epsilon^2 \Psi_2 + \mathcal{O}(\epsilon^3) \). In the original variables, we find

\[
\frac{\partial \Psi}{\partial \tau} = -V \frac{\partial \Psi}{\partial X} - \frac{M}{F} \left( -F \frac{\partial \Psi}{X} + \frac{k_B T}{X} \frac{\partial^2 \Psi}{\partial V^2} \right) + \frac{\gamma(X, t) k_B T}{M} \frac{\partial^2 \Psi}{\partial V^2}.
\]

where the expression for \( \gamma(X, t) \) is given in terms of an inverse Laplace transform in (SM). The small and large time asymptotic forms of \( \gamma(X, t) \) are

\[
\gamma(X, t) \sim \begin{cases} \frac{1}{X} \sqrt{\frac{3mk_B T}{\pi}} \log(t), & t \to 0 \\ \frac{\sqrt{mk_B T}}{X} \log(t), & t \to \infty \end{cases}
\]

Note that the Fokker-Planck equation (15) corresponds precisely to the Langevin equation (1). However, our previously presented numerical evidences suggest that the friction coefficient is given by eq. (2) which is different from the prediction in eq. (16).

At short times the predicted \( \gamma(X) \) is same as \( \gamma_{\text{gas}} \) while at large times it diverges logarithmically. This divergence indicates the breakdown of the perturbation theory, which however provides the correct form of equation of motion. The possible reasons for this breakdown are the following: i) the perturbation theory here implicitly assumes a separation of time scales. As pointed out in a recent paper, for the case of a fixed piston the small particle shows a slow power-law relaxation to equilibrium \cite{14}. This suggests that there may be no time scale separation between the particle and the piston; ii) secondly, we have not taken the multiple collisions into account. These two possible reasons for breakdown of the perturbation theory arise
because, in our expansions in eqs. (11)–(13), we have implicitly assumed that the velocity $v$ of the small particle is always of order $\sqrt{k_B T}$. This is not always true since it is possible that the small particle can emerge from the bath with a very small value ($\sim \epsilon$), and then the above perturbation expansion fails. Hence the derivation of exact expression for $\gamma$ is non-trivial. More details about the derivation of eq. (15) are given in the SM.

**Conclusion.** — In this letter, we looked at the non-equilibrium dynamics of the Szilard engine. We find that, in the limit of large mass of the piston, its effective stochastic dynamics is given by a Langevin equation (eq. (1)) with a space-dependent friction coefficient $\gamma(X)$ (eq. (2)). To arrive at this equation, we integrated out the particle degrees of freedom in the full master equation, following the $\Omega$-expansion method. While this perturbation method correctly provides the form of the Langevin equation, it does not give the right form for the friction term, and we argue that this arises due to rare events in the small particle’s dynamics. However, our extensive numerical studies suggest that the form of the friction coefficient $\gamma(X)$ given in eq. (2) is in fact accurate. To verify this form further, we have also considered the situation where the piston interacts with one thermal particle on each side. In this case also we find excellent numerical agreement (see SM).

Finally, we used the Langevin equation description to study the thermodynamics of work extraction process in the Szilard engine. We found that, in the limit $M \to \infty$, and at a crucial value of the force $F_c$, the work extracted from the engine becomes equal to the heat absorbed, $k_B T \ln(2)$ — even though the piston remains out of equilibrium during the entire process. The analytical derivation of the result $\gamma(X) = \gamma_{sp} = (1/X)\sqrt{8\pi mk_B T}$ for the dissipation constant remains an interesting open problem.

***

DB acknowledges Arghya Dutta, Udo Seifert, Onuttom Narayan, Tridibh Sadhu and Satya Majumdar for discussions. AD, AK and SS acknowledge support of the Indo-French Centre for the promotion of advanced research (IFCPAR) under Project No. 5604-2. AK acknowledges support from DST grant under project No. ECR/2017/000634.

REFERENCES

[1] Szilard L., Z. Phys., 53 (1929) 840.
[2] Bustamante C., Lipphardt J. and Ritort F., Phys. Today, 58, issue No. 7 (2015) 43.
[3] Jarzynski C., Phys. Rev. Lett., 78 (1997) 2690.
[4] Jarzynski C., Annu. Rev. Condens. Matter Phys., 2 (2011) 329.
[5] Evans D. J. and Searles D. J., Adv. Phys., 51 (2002) 1529.
[6] Seifert U., Rep. Prog. Phys., 75 (2012) 126001.
[7] Kurchan J., J. Phys. A: Math. Gen., 31 (1998) 3719.
[8] Toyabe S., Sagawa T., Ueda M., Muneyuki E. and Sano M., Nat. Phys. Lett., 6 (2010) 988.
[9] Koski J. V., Maisi V. F., Pekola J. P. and Averin D. V., Proc. Natl. Acad. Sci. U.S.A., 111 (2014) 13786.
[10] Berut A., Arakelyan A., Petrosyan A., Ciliberto S., Dillenschneider R. and Lutz E., Nature, 483 (2012) 187.
[11] Ribezzi-Crivellari M. and Ritort F., Nat. Phys., 15 (2019) 660.
[12] Hatano N. and Sasa S., Prog. Theor. Phys., 100 (1998) 695.
[13] Hondou T., EPL, 80 (2007) 50001.
[14] Bhat D., Sabhapandit S., Kundu A. and Dhar A., J. Stat. Mech.: Theory Exp., 2017 (2017) 113210.
[15] Cerino L., Puglisi A. and Vulpiani A., Phys. Rev. E, 91 (2015) 032128.
[16] Neishtadt A. I. and Sinai Y. G., J. Stat. Phys., 116 (2004) 815.
[17] Gruber C., Pache S. and Lesne A., J. Stat. Phys., 108 (2002) 669.
[18] Mansour M. M., Garcia A. L. and Baras F., Phys. Rev. E, 73 (2006) 016121.
[19] Cerino L., Gradenigo G., Sarracino A., Villamaina D. and Vulpiani A., Phys. Rev. E, 89 (2014) 042105.
[20] Proesmans K., Driesen C., Cleuren B. and Van den Broeck C., Phys. Rev. E, 92 (2015) 032105.
[21] Baule A., Evans R. M. L. and Olmsted P. D., Phys. Rev. E, 74 (2006) 061117.
[22] Hoppenau J., Niemann M. and Engel A., Phys. Rev. E, 87 (2013) 062127.
[23] Chernov N. I., Lefebvre J. L. and Sinai Y. G., Russ. Math. Surv., 57 (2002) 1045.
[24] Chernov N. and Lefebvre J. L., J. Stat. Phys., 109 (2002) 507.
[25] Lefebvre J. L., Piasecki J. and Sinai Y., Scaling Dynamics of a Massive Piston in an Ideal Gas, in Hard Ball Systems and the Lorentz Gas, edited by Szász D., Encycl. Math. Sci., Vol. 101 (Springer, Berlin) 2000.
[26] Sinai Y. G., Theor. Math. Phys., 121 (1999) 1351.
[27] Wright P., Nonlinearity, 19 (2006) 2365.
[28] Hurtado P. I. and Redner S., Phys. Rev. E, 73 (2006) 016136.
[29] Hurtado P. I. and Redner S., Phys. Rev. E, 73 (2006) 016137.
[30] van Kampen N. G., Can. J. Phys., 39 (1961) 551.
[31] van Kampen N. G., Stochastic Processes in Physics and Chemistry (North-Holland, Amsterdam) 2007.