CHAPTER VI

RESULTS AND DISCUSSION

6.1 Results.

6.1.1 Pure Substances.

Conditions of tests:

States: T at $0.3T_b$, T_b, $0.8T_c$, T_c, and $1.2T_c$

P at 1 atm, $0.8P_c$, P_c, and $1.2P_c$.

Nonpolar substances: methane, n-nonane, and n-decane.

6.1.1.1 SRK Equation of State.

results as shown in Table B.1-B.8.

6.1.1.2 PR Equation of State.

results as shown in Table B.9-B.16.

6.1.1.3 ALS Equation of State.

results as shown in Table B.17-B.30.

6.1.1.4 TCC Equation of State.

results as shown in Table B.31-B.47.

6.1.1.5 SBC Equation of State.

results as shown in Table B.48-B.61.

6.2 Mixtures.

Conditions of tests:

States: T at $0.3T_b$, T_b, $0.8T_c$, T_c, and $1.2T_c$

Binary mixtures:

1. 0.5nonpolar/0.5nonpolar: methane/n-heptane and methane/n-decane.
2. 0.5polar/0.5nonpolar: CO_2/n-heptane and ethanol/benzene.
3. 0.5polar/0.5polar: methanol/H_2O and methanol/ethanol.

6.1.2.1 SRK Equation of State.

results as shown in Table B.62-B.67.

6.1.1.2 PR Equation of State.

results as shown in Table B.68-B.73.

6.1.1.3 ALS Equation of State.

results as shown in Table B.74-B.79.

6.1.1.4 TCC Equation of State.

results as shown in Table B.80-B.82.

6.1.1.5 SBC Equation of State.

results as shown in Table B.83-B.85.

6.2 Discussion.

6.2.1 Pure Substance.

Thermodynamic properties studied are: Z^V, Z^L, dH^V, dH^L, dS^V, dS^L, ϕ_i^V, ϕ_i^L, and K_i.
In general, when parameters in equations of state deviate, all thermodynamic properties deviate.

Phase

The following is a summary of phases at each temperature and pressure studied.

case 1: 1 atm, $0.3T_b$. This state is liquid state.

case 2: 1 atm, T_b. This state is vapor-liquid state.

case 3: 1 atm, $0.8T_c$. This state is vapor-liquid state.

case 4: 1 atm, T_c. This state is vapor state.

case 5: 1 atm, $1.2T_c$. This state is vapor state.

case 6: $0.8P_c$, $0.3T_b$. This state is liquid state.

case 7: $0.8P_c$, T_b. This state is liquid state.

case 8: $0.8P_c$, $0.8T_c$. This state is liquid state.

case 9: $0.8P_c$, T_c. This state is vapor-liquid state.

case 10: $0.8P_c$, $1.2T_c$. This state is vapor state.

case 11: P_c, $0.3T_b$. This state is liquid state.

case 12: P_c, T_b. This state is liquid state.

case 13: P_c, $0.8T_c$. This state is liquid state.

case 14: P_c, T_c. This state is vapor state.

case 15: P_c, $1.2T_c$. This state is vapor state.

case 16: $1.2P_c$, $0.3T_b$. This state is liquid state.

case 17: $1.2P_c$, T_b. This state is liquid state.

case 18: $1.2P_c$, $0.8T_c$. This state is liquid state.

case 19: $1.2P_c$, T_c. This state is vapor state.

case 20: $1.2P_c$, $1.2T_c$. This state is vapor state.

For each substance, similar results were obtained for all equations of state studied. And the representative results of n-nonane for PR equation of state are shown graphically in Figures 6.1-6.22 as examples.

SRK and PR Equations of State.

Vapor Pressure.

At low temperature, the vapor pressure value is low and higher when the temperature is higher.The magnitude of effect on the vapor pressure in decreasing order:n-decane > n-nonane > methane (see Tables B.7, B.15, B.29, B.46, and B.60). As temperature increases, when the parameter a(T) deviates, vapor pressure deviates decreasingly.

The effect of the parameter b on vapor pressure is same as that of the parameter a (T) but effect of parameter b is slightly less than that of parameter a(T).

Effect of (a/b) ratio.

The studied substances were so chosen as to provide different (a/b) ratio in increasing order: methane > n-nonane > = n-decane. In general, as the (a/b) ratio increases, the effect of the parameter a(T) and b on thermodynamic properties also increase. However, when the (a/b) ratios increases, for each case studied, the effect of parameters a(T) and b on the following thermodynamic properties decrease.

Z^L : case 1.

ϕ_i^L and K_i : case 2.

Z^L and dH^L: case 3, 6, 8, 11, 13, 16, and 18.

dH^V: case 5, and 9.

ϕ_i^L: case 7, 12, and 17.

Z^V, dH^V, and ϕi^V: case 10, and 15.

Z^V, dH^V, dS^V and ϕi^V: case 20.

Comparison of Effect of Parameter a(T) and b.

1. vapor state: parameter a(T) has influence on dH^V much more than parameter b.
2. Liquid state: parameter b effects on Z^L and dS^L much more than parameter a(T).
3. Vapor-liquid state (at 1 atm): parameter a(T) has more effect on vapor phase thermodynamic properties including fugacity coefficient and K_i. (see Tables B.1-B.6, B.9-B.14, B.17-B.28, B.31-B.45, B.48-B.59).

Table 6.1 shows the relative magnitude of influence of parameters a(T) and b in SRK and PR EOS on thermodynamic properties.

Table 6.1 Relative Magnitude of Influence of Parameters a(T) and b in SRK and PR Equations of State on Thermodynamic Properties.

state	parameter a(T)	parameter b
1	$\phi_i^L >>> dH^L > dS^L > Z^L$	$\phi_i^L >>> Z^L > dH^L > dS^L$
2	$\phi_i^L > K_i > dH^L > dH^V > dS^V > dS^L > Z^L > Z^V > \phi_i^V$	$\phi_i^L > K_i > Z^L > dH^L > dS^L > dH^V > dS^V > Z^V > \phi_i^V$
3	$\phi_i^L > K_i > dH^L > dH^V > dS^V > Z^L > dS^L > Z^V > \phi_i^V$	$\phi_i^L > K_i > Z^L > dH^L > dS^L > dH^V > dS^V > Z^V > \phi_i^V$
4[a]	$dH^V > dS^V > Z^V > \phi_i^V$	$dH^V > dS^V > Z^V > \phi_i^V$

Table 6.1 (continued).

state	parameter a(T)	parameter b
5	$dH^V > dS^V > Z^V > \phi_i^V$	$dH^V > dS^V > Z^V > \phi_i^V$
6	$\phi_i^L >> dH^L > dS^L > Z^L$	$\phi_i^L >> Z^L > dH^L > dS^L$
7	$\phi_i^L > dH^L > dS^L > Z^L$	$\phi_i^L > Z^L > dH^L > dS^L$
8	$\phi_i^L > dH^L > dS^L > Z^L$	$\phi_i^L > Z^L > dH^L > dS^L$
9[b]	$dH^V > Z^V > dS^V > \phi_i^V$	$dH^V > Z^V > dS^V > \phi_i^V$
10	$dH^V > Z^V > \phi_i^V > dS^V$	$dH^V > Z^V > \phi_i^V > dS^V$
11	$\phi_i^L >> dH^L > dS^L > Z^L$	$\phi_i^L > Z^L > dH^L > dS^L$
12	$\phi_i^L > dH^L > dS^L > Z^L$	$\phi_i^L > Z^L > dH^L > dS^L$
13	$\phi_i^L > dH^L > dS^L > Z^L$	$\phi_i^L > Z^L > dH^L > dS^L$
14	$\phi_i^L > dH^L > dS^L > Z^L$	$\phi_i^L > Z^L > dH^L > dS^L$
15	$dH^V > Z^V > \phi_i^V > dS^V$	$dH^V > Z^V > \phi_i^V > dS^V$
16	$\phi_i^L > dH^L > dS^L > Z^L$	$\phi_i^L > Z^L > dH^L > dS^L$
17	$dH^V > Z^V > \phi_i^V > dS^V$	$\phi_i^L > Z^L > dH^L > dS^L$
18	$\phi_i^L > dH^L > dS^L > Z^L$	$\phi_i^L > Z^L > dH^L > dS^L$
19	$\phi_i^L >> dH^L > dS^L > Z^L$	$\phi_i^L > Z^L > dH^L > dS^L$
20	$dH^V > Z^V > \phi_i^V > dS^V$	$dH^V > Z^V > \phi_i^V > dS^V$

[a] In this condition, the parameter a(T) deviate upwards (at 20% deviation), the state changes into 2 phase region (vapor-liquid state) and the parameter b deviate downwards (at -20% deviation), the state changes into 2 phase region (vapor-liquid state).

[b] When the parameter a(T) decreases, the state changes into vapor phase so that $dH^V > Z^V > dS^V > \phi_i^V$ as the parameter a(T) increases, the state changes into liquid state so that $Z^L > dH^L > dS^L > \phi_i^L > K_i$ and When the parameter b increases, the state changes into vapor phase so that $dH^V > Z^V > dS^V > \phi_i^V$ as the parameter b decreases, the state changes into liquid state so that $Z^L > dH^L > dS^L > \phi_i^L > K_i$.

Effect of Temperature.

At 1 atm, when temperature increases, deviation in Z^L, dH^V, dH^L, and dS^L increase (see Table B.1 as an example).

Comparison between SRK and PR.

In general, thermodynamic properties generated by the SRK equation is more sensitive of parameters a(T) and b, except in the following cases.
Z, dH, dS, and ϕ_l of case 6, 11, and 16.

At T >= $0.5T_c$; the effect of parameters a(T) and b on vapor pressure generated by PR equation is more than that given by SRK equation, but at T < $0.5T_c$; the opposite result is obtained.

ALS Equation of state.

Vapor Pressure.

At low temperature, the vapor pressure value is low and higher when the temperature is higher.The magnitude of effect on the vapor pressure in decreasing order: n-decane > n-nonane > methane. As temperature increases, when the parameter a(T) deviates, vapor pressure deviates decreasingly.

The effect of the parameter b_l on vapor pressure is same as that of the parameter a(T) but effect of parameter b_l is slightly less than that of parameter a(T).

Table 6.2 shows the relative magnitude of influence of parameters a(T) and b_1 on the thermodynamic properties. And Table 6.3 shows the relative magnitude of influence of parameters b_2 and b_3 on the thermodynamic properties.

Parameter b_3 on thermodynamic properties has slightly more influence than parameter b_2, except compressibility factor (that condensed in Table 6.3)(see Table B. 19-B.20 as examples). When the temperature increases, the deviation of vapor pressure decreases. And parameter b_3 also has more influence than than parameter b_2. In general, therefore, the magnitude of the effect of parameters in ALS equation in decreasing order is $a(T) > b_1 > b_3 > b_2$.

Table 6.2 Relative Magnitude of Influence of Parameters a(T) and b_1 in ALS Equation of state on Thermodynamic Properties.

state	parameter a(T)	parameter b_1
1	$\phi_i^L >> dH^L > dS^L > Z^L$	$\phi_i^L >> Z^L > dH^L > dS^L$
2	$\phi_i^L>K_i>dH^L>dH^V>dS^V>dS^L>Z^L>Z^V>\phi_i^V$.	$\phi_i^L>K_i>Z^L>dH^L>dS^L>dH^V>dS^V>Z^V>\phi_i^V$
3	$\phi_i^L>K_i>dH^L>Z^L>dH^V>dS^V>dS^L>Z^V>\phi_i^V$	$\phi_i^L>K_i>Z^L>dH^L>dS^L>dH^V>dS^V>Z^V>\phi_i^V$
4[a]	$dH^V > dS^V > Z^V > \phi_i^V$	$dH^V > dS^V > Z^V > \phi_i^V$
5	$dH^V > dS^V > Z^V > \phi_i^V$	$dH^V > dS^V > Z^V > \phi_i^V$
6	$\phi_i^L >> dH^L > dS^L > Z^L$	$\phi_i^L >> Z^L > dH^L > dS^L$
7	$\phi_i^L > dH^L > dS^L > Z^L$	$\phi_i^L > Z^L > dH^L > dS^L$
8	$\phi_i^L > dH^L > dS^L > Z^L$	$\phi_i^L > Z^L > dH^L > dS^L$
9[b]	$dH^V > Z^V > dS^V > \phi_i^V$	$dH^V > Z^V > dS^V > \phi_i^V$
10	$dH^V > Z^V > \phi_i^V > dS^V$	$dH^V > Z^V > \phi_i^V > dS^V$
11	$\phi_i^L >> dH^L > dS^L > Z^L$	$\phi_i^L > Z^L > dH^L > dS^L$
12	$\phi_i^L > dH^L > dS^L > Z^L$	$\phi_i^L > Z^L > dH^L > dS^L$

Table 6.2 (continued).

state	parameter a(T)	parameter b_1
13	$\phi_i^L > dH^L > dS^L > Z^L$	$\phi_i^L > Z^L > dH^L > dS^L$
14	$\phi_i^L >> dH^L > dS^L > Z^L$	$dH^V > Z^V > dS^V > \phi_i^V$
15	$dH^V > Z^V > \phi_i^V > dS^V$	$dH^V > Z^V > \phi_i^V > dS^V$
16[c]	$\phi_i^V >> dH^V > dS^V > Z^V$	$\phi_i^L > Z^L > dH^L > dS^L$
17	$\phi_i^L > dH^L > dS^L > Z^L$	$\phi_i^L > Z^L > dH^L > dS^L$
18	$\phi_i^L > dH^L > dS^L > Z^L$	$\phi_i^L > Z^L > dH^L > dS^L$
19	$\phi_i^L >> dH^L > dS^L > Z^L$	$Z^L > dH^L > dS^L > \phi_{i.}^L$
20	$dH^V > Z^V > \phi_i^V > dS^V$	$dH^V > Z^V > \phi_i^V > dS^V$

[a] In this condition, the parameter a(T) deviate upwards (at 20% deviation), the state changes into 2 phase region (vapor-liquid state) and the parameter b deviate downwards (at -20% deviation), the state changes into 2 phase region (vapor-liquid state).

[b] When the parameter a(T) decreases, the state changes into vapor phase so that $dH^V > Z^V > dS^V > \phi_i^V$ as the parameter a(T) increases, the state changes into liquid state so that $dH^L > dS^L > Z^L > \phi_i^L > K_i$ and When the parameter b_1 increases, the state changes into vapor phase so that $dH^V > Z^V > dS^V > \phi_i^V$ as the parameter b_1 decreases, the state changes into liquid state so that $Z^L > dH^L > dS^L > \phi_i^L > K_i$.

[c] This state is vapor state.

Table 6.3 Relative Magnitude of Influence of Parameters b_2 and b_3 in ALS Equation of state on thermodynamic properties.

State	parameter b_2	parameter b_3
1	$\phi_i^L >> dH^L > dS^L > Z^L$	$\phi_i^L >> dH^L > dS^L > Z^L$
2	$\phi_i^L \approx K_i > dH^L > dS^L > Z^L > \phi_i^V > dS^V > dH^V > Z^V$.	$\phi_i^L \approx K_i > dH^L > dS^L > Z^L > \phi_i^V > dS^V > dH^V > Z^V$.
3	$\phi_i^L \approx K_i > Z^L > dH^L > dS^L > dS^V > dH^V > Z^V > \phi_i^V$.	$\phi_i^L \approx K_i > dH^L > Z^L > dS^L > dS^V > \phi_i^V .> dH^V > Z^V$

Table 6.3 (continued).

State	parameter b_2	parameter b_3
4	$dS^V > dH^V > Z^V > \phi_i^V$	$dS^V > dH^V > Z^V > \phi_i^V$
5	$dS^V > dH^V > Z^V > \phi_i^V$	$dS^V > dH^V > Z^V > \phi_i^V$
6	$\phi_i^L >> dH^L > dS^L > Z^L$	$\phi_i^L >> dH^L > dS^L > Z^L$
7	$\phi_i^L >> dH^L > dS^L > Z^L$	$\phi_i^L >> dH^L > dS^L > Z^L$
8	$\phi_i^L >> dH^L > Z^L > dS^L$	$\phi_i^L >> dH^L > Z^L > dS^L$
9	$dH^V > Z^V > dS^V > \phi_i^V$	$dH^V > Z^V > dS^V > \phi_i^V$
10	$dH^V > Z^V > dS^V > \phi_i^V$	$dH^V > \mathbf{Z}^V > \phi_i^V > dS^V$
11	$\phi_i^V > dH^V > dS^V > Z^V$	$\phi_i^V > dH^V > dS^V > \mathbf{Z}^V$
12	$\phi_i^L >> dH^L > dS^L > Z^L$	$\phi_i^L >> dH^L > dS^L > \mathbf{Z}^L$
13	$\phi_i^L >> dH^L > Z^L > dS^L$	$\phi_i^L >> dH^L > \mathbf{Z}^L > dS^L$
14	$dH \geq Z > dS > \phi_i$	$dH \geq \mathbf{Z} > dS > \phi_i$
15	$dH^V > Z^V > dS^V > \phi_i^V$	$dH^V > Z^V > dS^V > \phi_i^V$
16	$\phi_i^V > dH^V > dS^V > Z^V$	$\phi_i^V > dH^V > dS^V > \mathbf{Z}^V$
17	$\phi_i^L > dH^L > dS^L > Z^L$	$\phi_i^L > dH^L > dS^L > Z^L$
18	$\phi_i^L >> dH^L > Z^L > dS^L$	$\phi_i^L >> dH^L > Z^L > dS^L$
19	$dH \geq Z > dS > \phi_i$	$dH \geq Z > dS > \phi_i$
20	$dH^V > Z^V > dS^V > \phi_i^V$	$dH^V > Z^V > dS^V > \phi_i^V$

TCC Equation of state.

<u>Vapor Pressure.</u>

The effect on vapor pressure by parameters a(T) is about that of b and more than c. At $T= 0.8T_c$, the magnitude of effect on vapor pressure in TCC equation of parameters in decreasing order is: a(T) > b > c , however, at $T< 0.8T_c$, the order becomes b ≥ a(T) > c. As pressure increases, deviation of all vapor phase thermodynamic properties values also increase including liquid fugacity coefficient.

Table 6.4 shows the relative magnitude of influence of parameters a(T), b, and c on thermodynamic properties (see Table B.31-B.45).

Table 6.4 Relative Magnitude of Influence of Parameters a(T), b, and c in TCC Equation of State on thermodynamic properties.

state	parameter a(T)	parameter b	parameter c
1	$\phi_i^L >> dH^L > dS^L > Z^L$	$\phi_i^L >> dH^L > dS^L > Z^L$	$\phi_i^L >> dH^L > dS^L > Z^L$
2	$\phi_i^L \approx K_i > dH^L > dH^V > dS^L > Z^L > dS^L > Z^V > \phi_i^V$.	$\phi_i^L \approx K_i > dH^L \geq Z^L > dS^L > dH^V > dS^V > Z^V > \phi_i^V$	$\phi_i^L \approx K_i > dH^L > dS^L > Z^L > dS^V > dH^V > Z^V > \phi_i^V$
3	$\phi_i^L \approx K_i > dH^L > dH^V > dS^L > Z^L > dS^L > Z^V > \phi_i^V$.	$\phi_i^L \approx K_i > dH^L \geq Z^L > dS^L > dH^V > dS^V > Z^V > \phi_i^V$	$\phi_i^L \approx K_i > dH^L > dS^L > Z^L > dS^V > dH^V > Z^V > \phi_i^V$
4	$dH^V > dS^V > Z^V > \phi_i^V$	$dH^V > dS^V > Z^V > \phi_i^V$	$dS^V > dH^V > Z^V > \phi_i^V$
5	$dH^V > dS^V > Z^V > \phi_i^V$	$dH^V > dS^V > Z^V > \phi_i^V$	$dS^V > dH^V > Z^V > \phi_i^V$
6	$\phi_i^L >> dH^L > dS^L > Z^L$	$\phi_i^L >> dH^L > dS^L \geq Z^L$	$\phi_i^L >> dH^L > dS^L \geq Z^L$
7	$\phi_i^L >> dH^L > Z^L > dS^L$	$\phi_i^L >> dH^L > Z^L > dS^L$	$\phi_i^L >> dH^L > Z^L > dS^L$
8	$\phi_i^L >> dH^L > Z^L > dS^L$	$\phi_i^L >> dH^L > Z^L > dS^L$	$\phi_i^L >> dH^L > Z^L > dS^L$
9	$dH^V > Z^V > dS^V > \phi_i^V$	$dH^V > Z^V > dS^V > \phi_i^V$	$dH^V > Z^V > dS^V > \phi_i^V$
10	$dH^V > Z^V > \phi_i^V > dS^V$	$dH^V > Z^V > \phi_i^V > dS^V$	$dH^V > Z^V > dS^V > \phi_i^V$
11	$\phi_i^L >> dH^L > dS^L > Z^L$	$\phi_i^L >> dH^L > dS^L \geq Z^L$	$\phi_i^L >> dH^L > dS^L > Z^L$
12	$\phi_i^L >> dH^L > Z^L > dS^L$	$\phi_i^L >> dH^L > Z^L > dS^L$	$\phi_i^L >> dH^L > dS^L > Z^L$
13	$\phi_i^L >> dH^L > Z^L > dS^L$	$\phi_i^L >> dH^L > Z^L > dS^L$	$\phi_i^L >> dH^L > dS^L > Z^L$
14	$Z^V > dH^V > dS^V > \phi^V_i$	$dH^V \geq Z^V > dS^V > \phi^V_i$	$dH^V \geq Z^V > dS^V > \phi^V_i$
15	$dH^V > Z^V > \phi_i^V > dS^V$	$dH^V > Z^V > \phi i^V > dS^V$	$dH^V > Z^V > dS^V > \phi^V_i$
16	$\phi_i^L > dH^L > dS^L > Z^L$	$\phi_i^L >> dH^L > dS^L > Z^L$	$\phi_i^L >> dH^L > dS^L > Z^L$
17	$\phi_i^L > dH^L > Z^L > dS^L$	$\phi_i^L >> dH^L > Z^L > dS^L$	$\phi_i^L >> dH^L > dS^L > Z^L$
18	$\phi_i^L >> dH^L > Z^L > dS^L$	$\phi_i^L >> dH^L > Z^L > dS^L$	$\phi_i^L >> dH^L > dS^L > Z^L$

Table 6.4 (continued).

state	parameter a(T)	parameter b	parameter c
19	$Z^V > dH^V > dS^V > \phi^V_i$	$Z^V \geq dH^V > dS^V > \phi^V_i$	$Z^V \geq dH^V > dS^V > \phi^V_i$
20	$dH^V > Z^V > \phi_i^V > dS^V$	$dH^V > Z^V > dS^V > \phi_i^V$	$dH^V > Z^V > dS^V > \phi_i^V$

In general, the influence of all parameters in TCC equation on thermodynamic properties is greater in liquid state than in vapor state.

Table 6.5 shows the relative magnitude of influence of parameters on thermodynamic properties (see Table B.31-B.45).

Table 6.5 Relative Magnitude of Influence of Parameters in TCC Equation of State on Thermodynamic Properties.

Thermodynamic Properties	Influence of Parameters
Z^V	a(T) > b.> c
Z^L	b > a(T) > c
dH^V	a(T) > b.> c
dS^V	a(T) > b.> c
dH^L	b > a(T) > c
dS^L	b > a(T) > c
ϕ^V_i	a(T) > b.> c
ϕ^L_i	a(T) > b > c
K_i	a(T) > b.> c

SBC Equation of State.

Vapor Pressure.

At T= $0.8T_c$, the magnitude of effect on vapor pressure by SBC equation of parameters in decreasing order is: $a(T) > \beta(T) > e > c(T)$, however, at $T < 0.8T_c$, the order becomes $\beta(T) \geq a(T) > e > c(T)$. As pressure increases, deviation in all vapor phase thermodynamic properties values also increase including liquid fugacity coefficient.

Table 6.6 shows the relative magnitude of influence of parameters a(T) and β(T) on thermodynamic properties (see Table B.48-B.49, B.52-B.53, and B.56-B.57). And Table 6.7 shows the relative magnitude of influence of parameters c(T) and e on thermodynamic properties (see Table B.50-B.51, B.54-B.55, and B.58-B.59).

Table 6.6 Relative Magnitude of Influence of Parameter a(T) and β(T) in SBC Equation of State on thermodynamic Properties .

state	parameter a(T)	parameter β(T)
1	$\phi_i^L >> dH^L > dS^L > Z^L$	$\phi_i^L >> Z^L > dH^L > dS^L$
2	$\phi_i^L \geq K_i > dH > dH^V > dS^L \geq Z^L > dS^L > Z^V > \phi_i^V$.	$\phi_i^L \geq K_i > Z^L \geq dH^L > dS^L > dH^V > Z^V > \phi_i^V > dS^V$
3	$\phi_i^L \geq K_i > dH^L > dH^V > dS^L \geq Z^L > dS^L > Z^V > \phi_i^V$.	$\phi_i^L \geq K_i > Z^L \geq dH^L > dS^L > dH^V > Z^V > \phi_i^V > dS^V$
4	$dH^V > Z^V > \phi_i^V > dS^V$	$dH^V > Z^V > \phi_i^V > dS^V$
5	$dH^V > Z^V > \phi_i^V > dS^V$	$dH^V > Z^V > \phi_i^V > dS^V$

Table 6.6 (continued).

state	parameter a(T)	parameter β(T)
6	$\phi_i^L >> dH^L > dS^L > Z^L$	$\phi_i^L >> Z^L > dH^L > dS^L$
7	$\phi_i^L >> dH^L > Z^L > dS^L$	$\phi_i^L >> Z^L > dH^L > dS^L$
8	$\phi_i^L >> dH^L > Z^L > dS^L$	$\phi_i^L >> Z^L > dH^L > dS^L$
9	$dH^V > Z^V > dS^V > \phi_i^V$	$dH^V > Z^V > dS^V > \phi_i^V$
10	$dH^V > dS^V > Z^V > \phi_i^V$	$dH^V > Z^V > \phi_i^V > dS^V$
11	$\phi_i^L >> dH^L > dS^L > Z^L$	$\phi_i^L >> Z^L > dH^L > dS^L$
12	$\phi_i^L >> dH^L > Z^L \geq dS^L$	$\phi_i^L >> Z^L > dH^L > dS^L$
13	$\phi_i^L >> dH^L > Z^L \geq dS^L$	$\phi_i^L >> Z^L > dH^L > dS^L$
14	$Z^V > dH^V > dS^V > \phi^V_i$	$Z^V > dH^V > dS^V > \phi^V_i$
15	$dH^V > Z^V > dS^V > \phi_i^V$	$dH^V > Z^V > \phi i^V > dS^V$
16	$\phi_i^L >> dH^L > dS^L > Z^L$	$\phi_i^L >> Z^L > dH^L > dS^L$
17	$\phi_i^L >> dH^L > Z^L \geq dS^L$	$\phi_i^L >> Z^L > dH^L > dS^L$
18	$\phi_i^L >> dH^L > Z^L \geq dS^L$	$\phi_i^L >> Z^L > dH^L > dS^L$
19	$Z^V > dH^V > dS^V > \phi^V_i$	$Z^V > dH^V > dS^V > \phi^V_i$
20	$dH^V > Z^V > dS^V > \phi_i^V$	$dH^V > Z^V > \phi_i^V > dS^V$

Table 6.7 Relative Magnitude of Influence of Parameter c(T) and e in SBC Equation of State onThermodynamic Properties .

state	parameter c(T)	parameter e
1	$\phi_i^L >> dS^L > dH^L > Z^L$	$\phi_i^L >> dH^L > dS^L > Z^L$
2	$\phi_i^L \approx K_i > dH^L > dS^L > Z^L > dH^V > Z^V > \phi_i^V > dS^V$	$\phi_i^L \approx K_i > dH^L > dS^L > Z^L > dH^V > Z^V > \phi_i^V > dS^V$

Table 6.7 (continued).

state	parameter c(T)	parameter e
3	$\phi_i^L \approx K_i > dH^L > Z^L > dS^L > dH^V > Z^V > \phi_i^V > dS^V$	$\phi_i^L \approx K_i > dH^L > dS^L > Z^L > dH^V > Z^V > \phi_i^V > dS^V$
4	$dH^V > Z^V > \phi_i^V > dS^V$	$dH^V > Z^V > \phi_i^V > dS^V$
5	$dH^V > Z^V > dS^V > \phi_i^V$	$dH^V > Z^V > \phi_i^V > dS^V$
6	$\phi_i^L >> dH^L > dS^L > Z^L$	$\phi_i^L >> dH^L > Z^L > dS^L$
7	$\phi_i^L >> dH^L > dS^L > Z^L$	$\phi_i^L >> dH^L > Z^L > dS^L$
8	$\phi_i^L >> dH^L > Z^L > dS^L$	$\phi_i^L >> dH^L > Z^L > dS^L$
9	$dH^V > Z^V > dS^V > \phi_i^V$	$dH^V > dS^V > Z^V > \phi_i^V$
10	$dH^V > dS^V > Z^V > \phi_i^V$	$dH^V > dS^V > Z^V > \phi_i^V$
11	$\phi_i^L >> dH^L > dS^L > Z^L$	$\phi_i^L >> dH^L > dS^L > Z^L$
12	$\phi_i^L >> dH^L > dS^L > Z^L$	$\phi_i^L >> dH^L > dS^L > Z^L$
13	$\phi_i^L >> dH^L > Z^L \geq dS^L$	$\phi_i^L >> dH^L > dS^L > Z^L$
14	$Z^V > dH^V > dS^V > \phi^V_i$	$dH^V > dS^V > Z^V > \phi^V_i$
15	$dH^V > Z^V > dS^V > \phi_i^V$	$dH^V > dS^V > Z^V > \phi^V_i$
16	$\phi_i^L >> dH^L > dS^L > Z^L$	$\phi_i^L >> dH^L > dS^L > Z^L$
17	$\phi_i^L >> dH^L > dS^L > Z^L$	$\phi_i^L >> dH^L > dS^L > Z^L$
18	$\phi_i^L >> dH^L > dS^L > Z^L$	$\phi_i^L >> dH^L > dS^L > Z^L$
19	$Z^V > dH^V > dS^V > \phi^V_i$	$dH^V > Z^V > dS^V > \phi_i^V$
20	$dH^V > Z^V > dS^V > \phi_i^V$	$dH^V > Z^V > dS^V > \phi_i^V$

In general, the influence of all parameters in SBC equation of state on thermodynamic properties is greater in liquid state than in vapor state.

Table 6.8 shows conparison between parameters in SBC equation of state on thermodynamic properties (see Table B.48-B.59).

Table 6.8 Comparison between Parameters in SBC Equation of State on Thermodynamic Properties.

Thermodynamic Properties	Parameters
Z^V	a(T) > β(T).> e > c(T)
Z^L	β(T) > a(T).> e > c(T)
dH^V	a(T) > β(T).> e > c(T)
dS^V	a(T) > β(T).> e > c(T)
dH^L	a(T) > e > β(T) > c(T)
dS^L	a(T) > e > β(T) > c(T)
ϕ^V_i	a(T) > β(T).> e > c(T)
ϕ^L_i	a(T) > e > β(T) > c(T)
K_i	a(T) > e > β(T) > c(T)

Table 6.9 shows the relative influence of parameter a(T) in various equations of state on thermodynamic properties(see all Table).

Table 6.9 Relative Influence of Parameter a(T) in Various Equations of State on Thermodynamic Properties.

Thermodynamic Properties	Equations of State in decreasing Influence
Z^V	SBC > TCC ≥ ALS ≥ PR > SRK
Z^L	SBC > SRK > PR > ALS > TCC
dH^V	SRK > PR ≥ ALS > TCC > SBC
dS^V	TCC ≥ SBC
dH^L	SBC > TCC
dS^L	SBC > TCC
ϕ_i^V	SBC > TCC ≥ ALS > PR > SRK
ϕ_i^L	SBC > TCC ≥ PR ≥ ALS > SRK
K_i	SBC > TCC ≥ PR ≥ ALS > SRK

Though the order of magnitude of effect on thermodyanmic properties by parameter a(T) in each equation of state tends to be the same. The magnitude of sensitivity of this effect is summarized in Table 6.9. The effect of parameter a(T) on vapor pressure, at $T \leq 0.3T_c$, in decrasing order is SBC > SRK > PR > TCC > ALS, while at $T \geq 0.5T_c$, the order is SBC > TCC > ALS > PR > SRK.

6.2.2 Mixtures.

In general, the magnitude of influence of fundamental properties and binary interaction on the thermodynamic properties is as follows:

for SRK, PR, and ALS equations: T_c, > P_c > ω > k_{ij};

for TCC equation: T_c, > P_c > Z_c > k_{ij} for negative deviation in either T_c,, P_c, Z_c, or k_{ij} and $Z_c > T_c > P_c > k_{ij}$ for positive deviation in these properties.

for SBC equation: $V_c > T_c > \omega$. And the results are as shown in Figures 6.23-6.32.

In detail, it can be concluded for SRK and PR equations that

1. the magnitude of influence of T_c on parameter a(T) is about twice of that on parameter b.
2. the magnitude of influence of P_c on parameters a(T) and b are about the same.

<u>Effect of Temperature.</u>

1. As temperature increases, the influence of T_c on parameter a(T) increases.
2. As temeprature increases, the influence of ω on parameter a(T) increases.
3. As temperature increases, the magnitude of k_{ij} on parameter a(T) decreases.

(see Table B.62-B.75).

Table 6.10 Relative the Effect of Fundamental Properties on Parameters in ALS and TCC Equations of State.

Fundamental Properties	Parameters in ALS	Parameters in TCC
low T_c	$b_1 > b_2 > b_3$	c > b
high T_c	$b_3 > b_2 > b_1$	b > c
low P_c	$b_3 > b_2 > b_1$	b > c
high P_c	$b_1 > b_2 > b_3$	c > b
ω	$b_3 > b_1 > b_2$	-

In general, the magnitude of effect of acentric factor on parameters in equations of state is ordered as follows: SRK > PR > ALS.

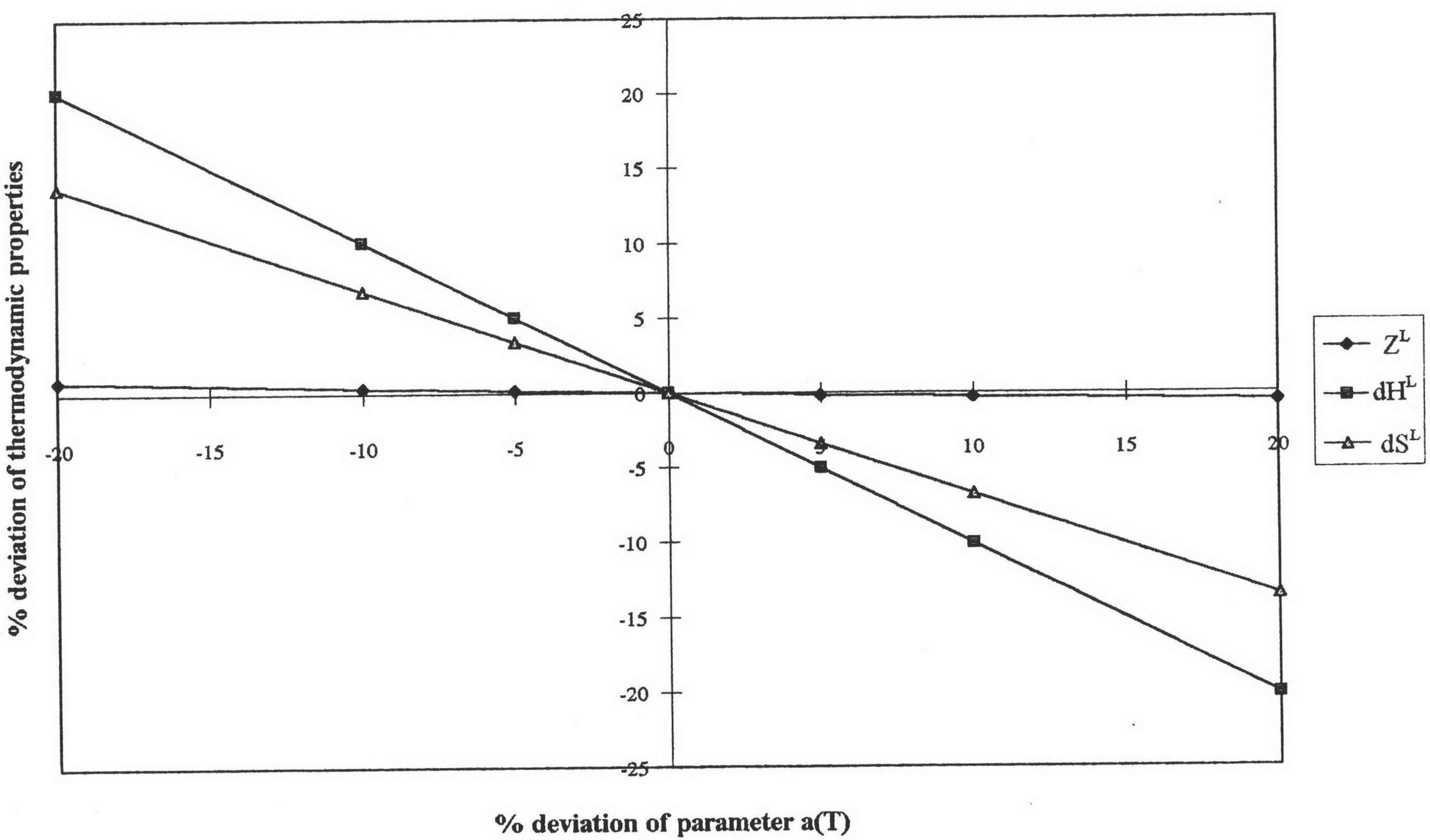

Figure 6.1a PR EOS; n-nonane; at $0.3T_b$, 1 atm; % deviation of thermodynamic properties as parameter a(T) is varied.

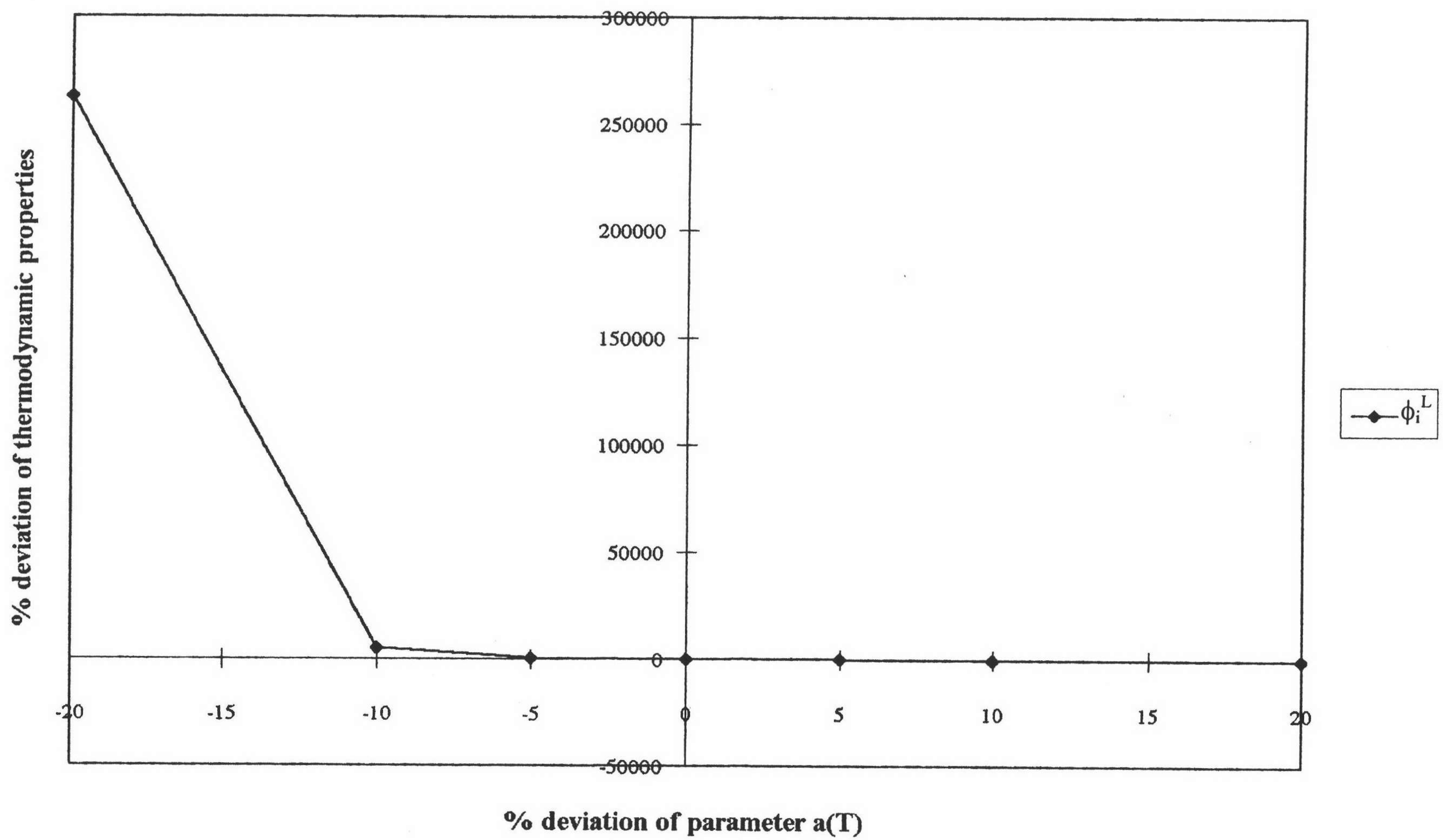

Figure 6.1b PR EOS; n-nonane; at $0.3T_b$, 1 atm; % deviation of fugacity coefficient as parameter a(T) is varied.

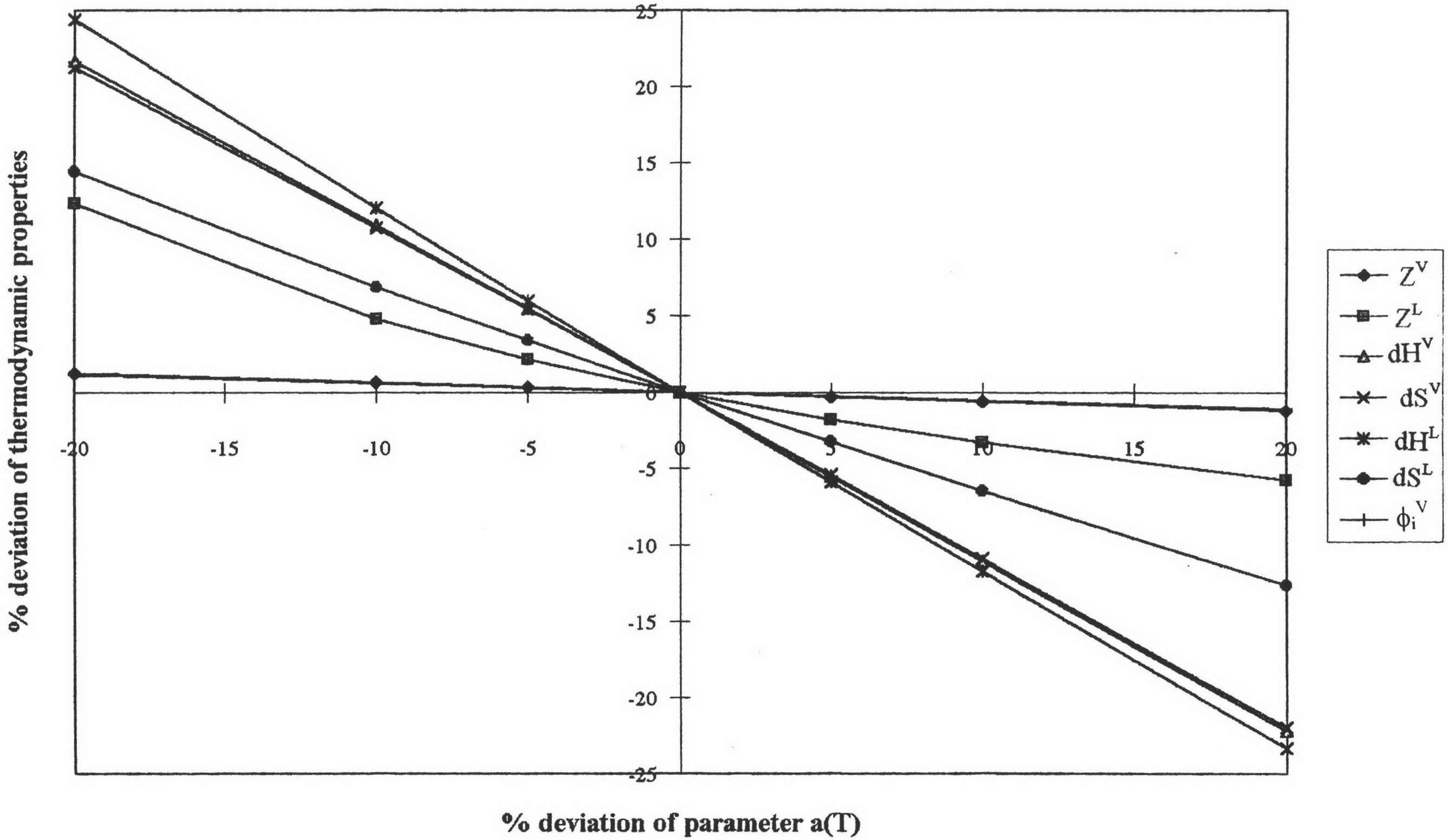

Figure 6.2a PR EOS; n-nonane; at T_b, 1 atm; % deviation of thermodynamic properties as parameter a(T) is varied.

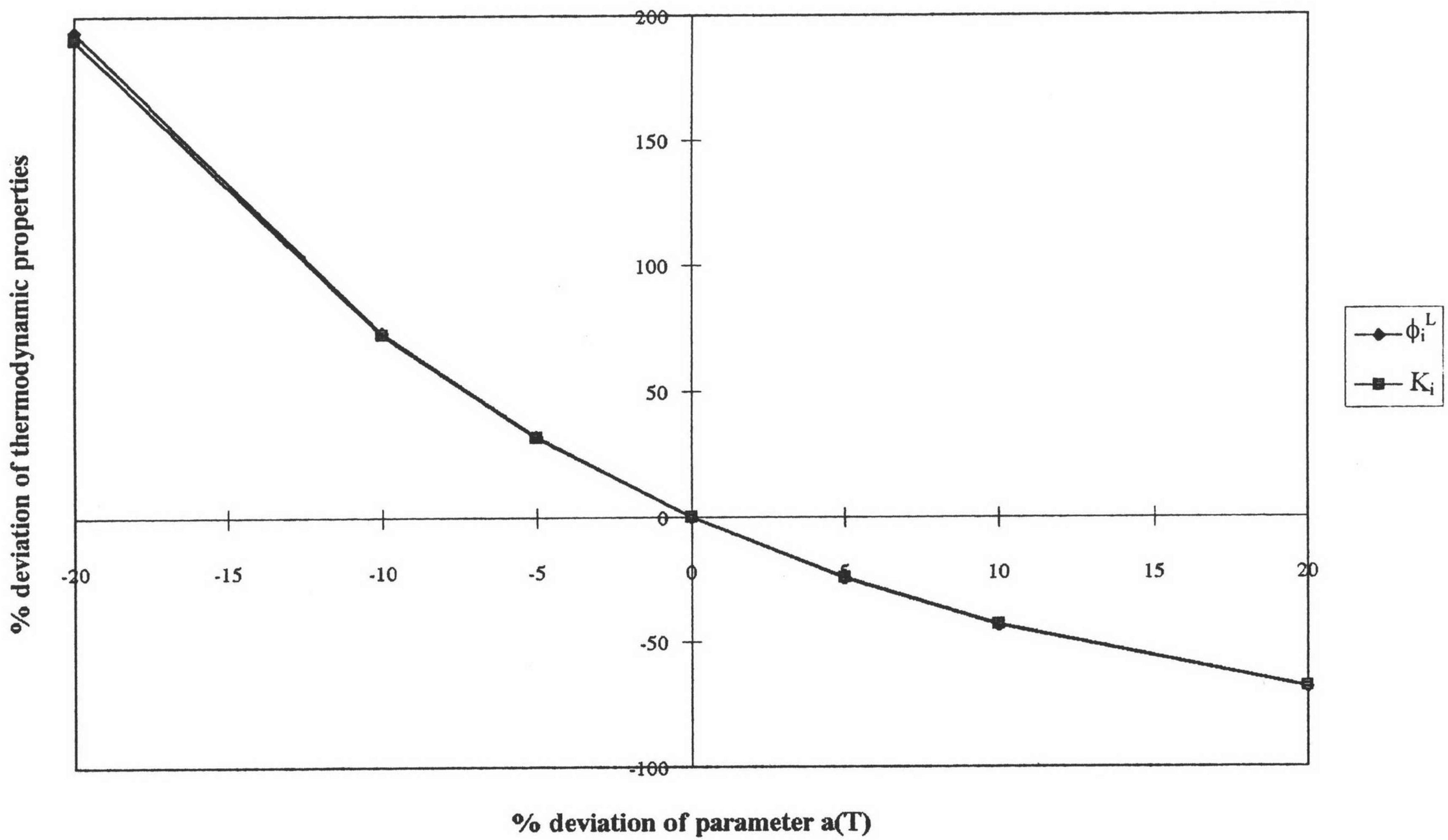

Figure 6.2b PR EOS; n-nonane; at T_b, 1 atm; % deviation of fugacity coefficient and equilibrium ratio as parameter a(T) is varied.

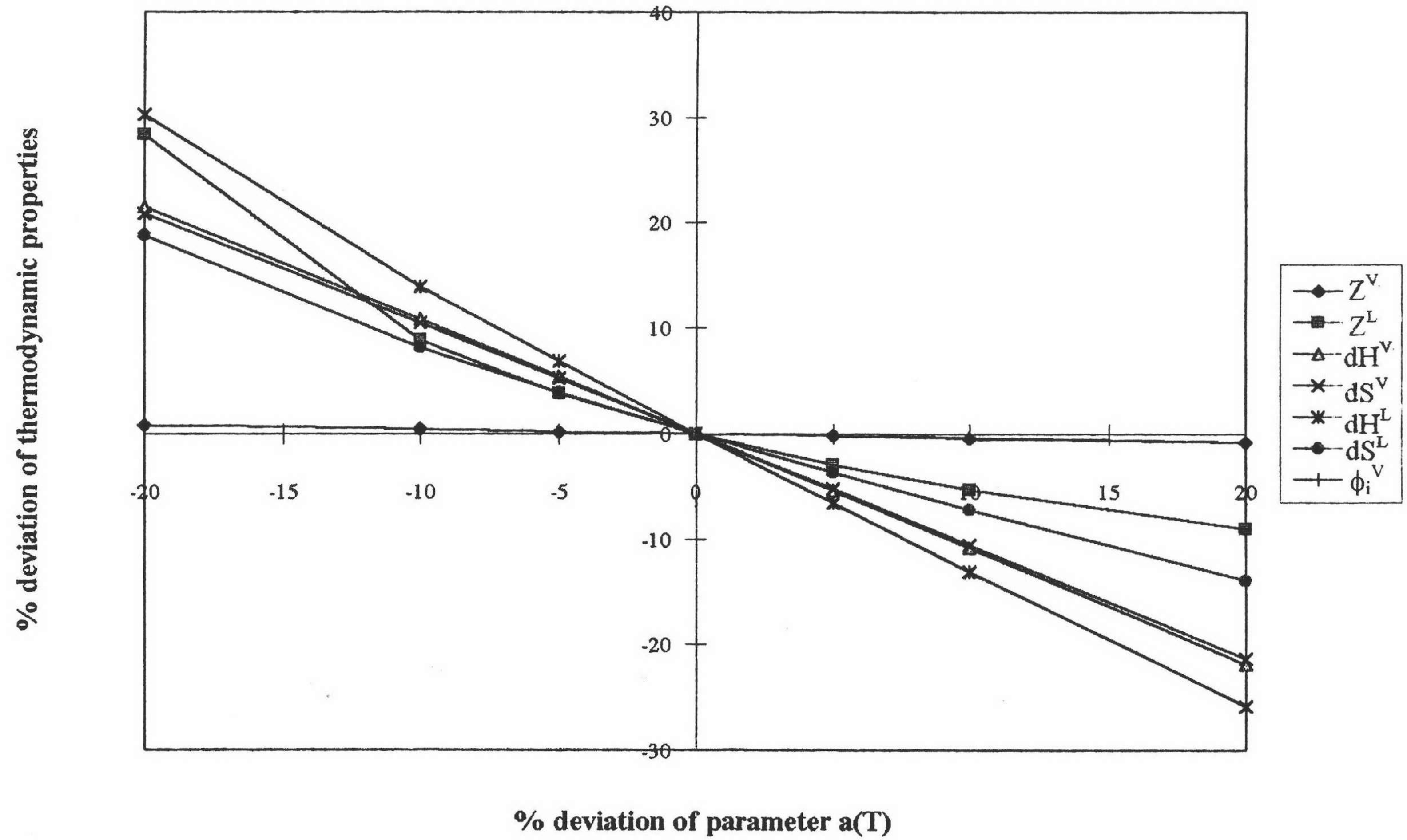

Figure 6.3a PR EOS; n-nonane; at $0.8T_c$, 1 atm; % deviation of thermodynamic properties as parameter a(T) is varied.

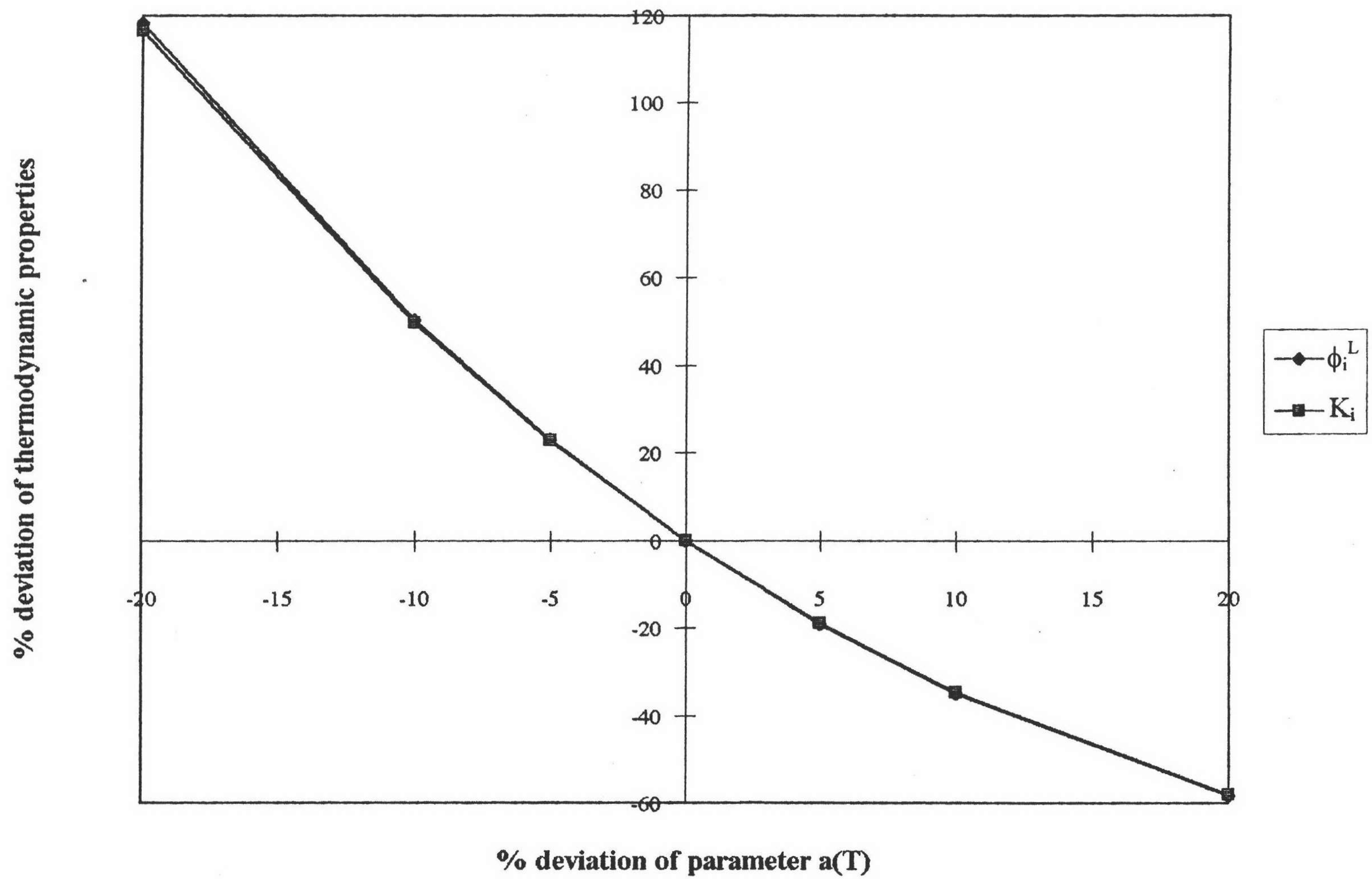

Figure 6.3b PR EOS; n-nonane; at $0.8T_c$, 1 atm; % deviation of fugacity coefficient and equilibrium ratio as parameter a(T) is varied.

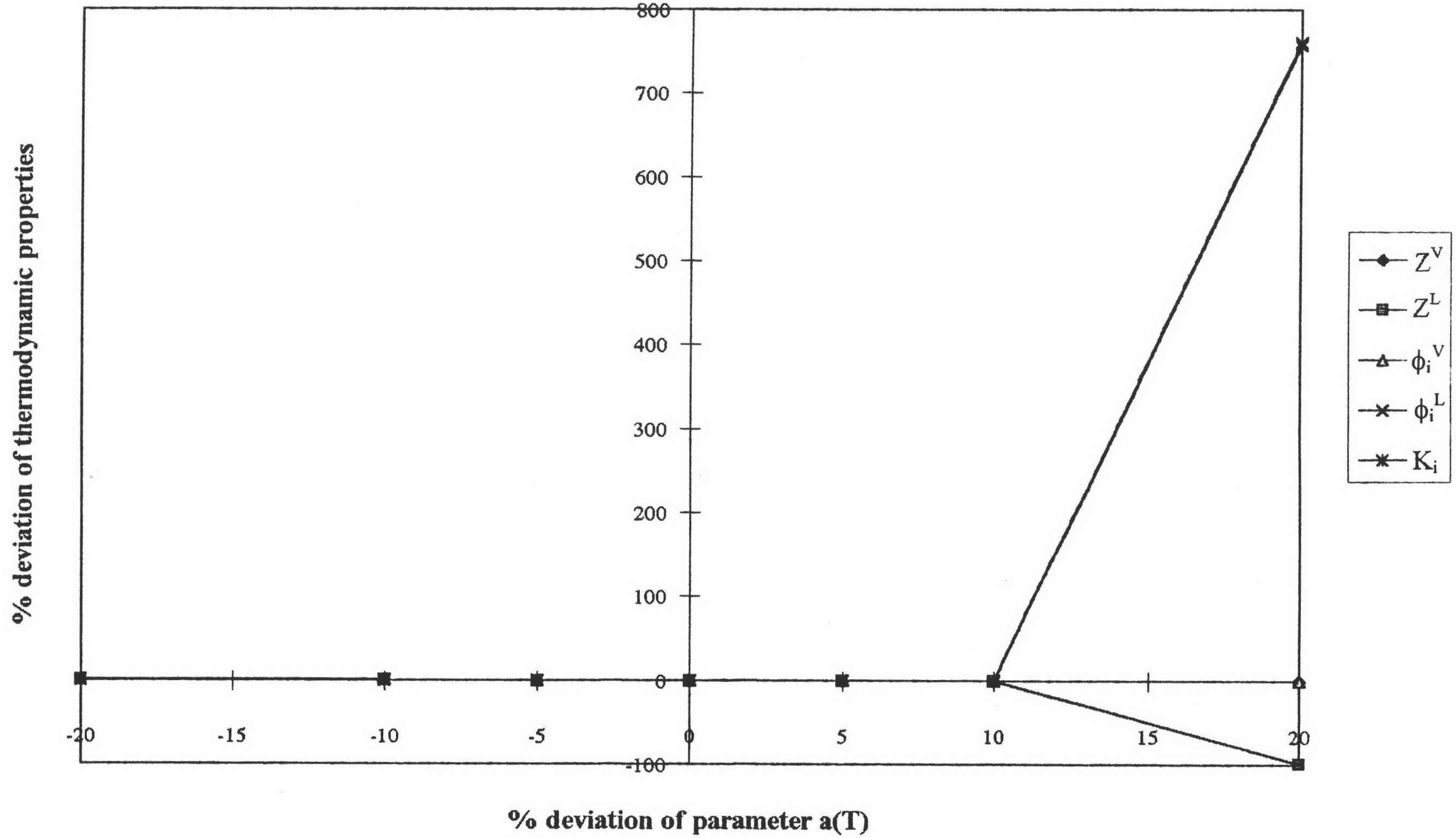

Figure 6.4a PR EOS; n-nonane; at T_c, 1 atm; % deviation of thermodynamic properties as parameter a(T) is varied.

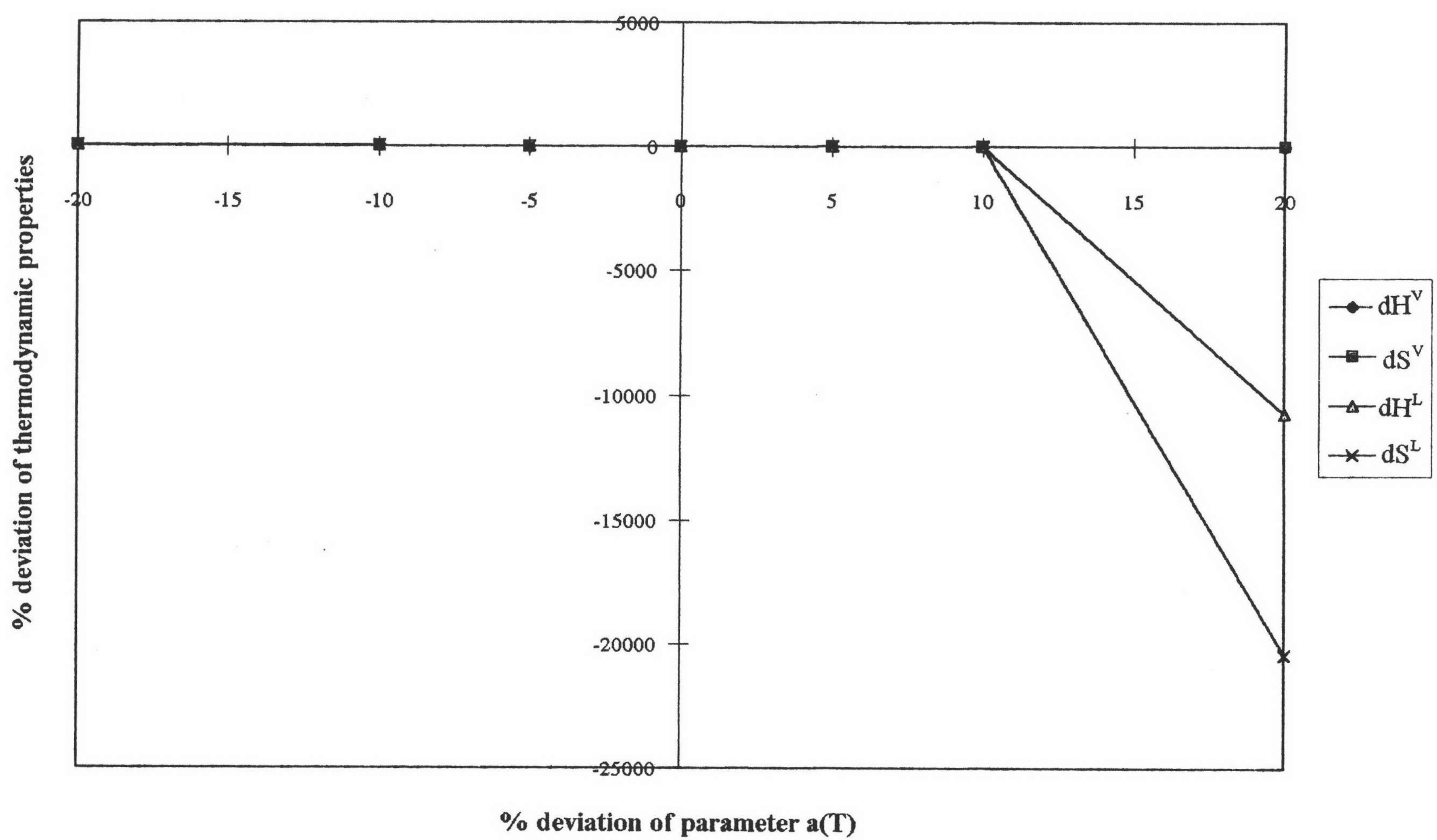

Figure 6.4b PR EOS; n-nonane; at T_c, 1 atm; % deviation of enthalpy and entropy departures as parameter a(T) is varied.

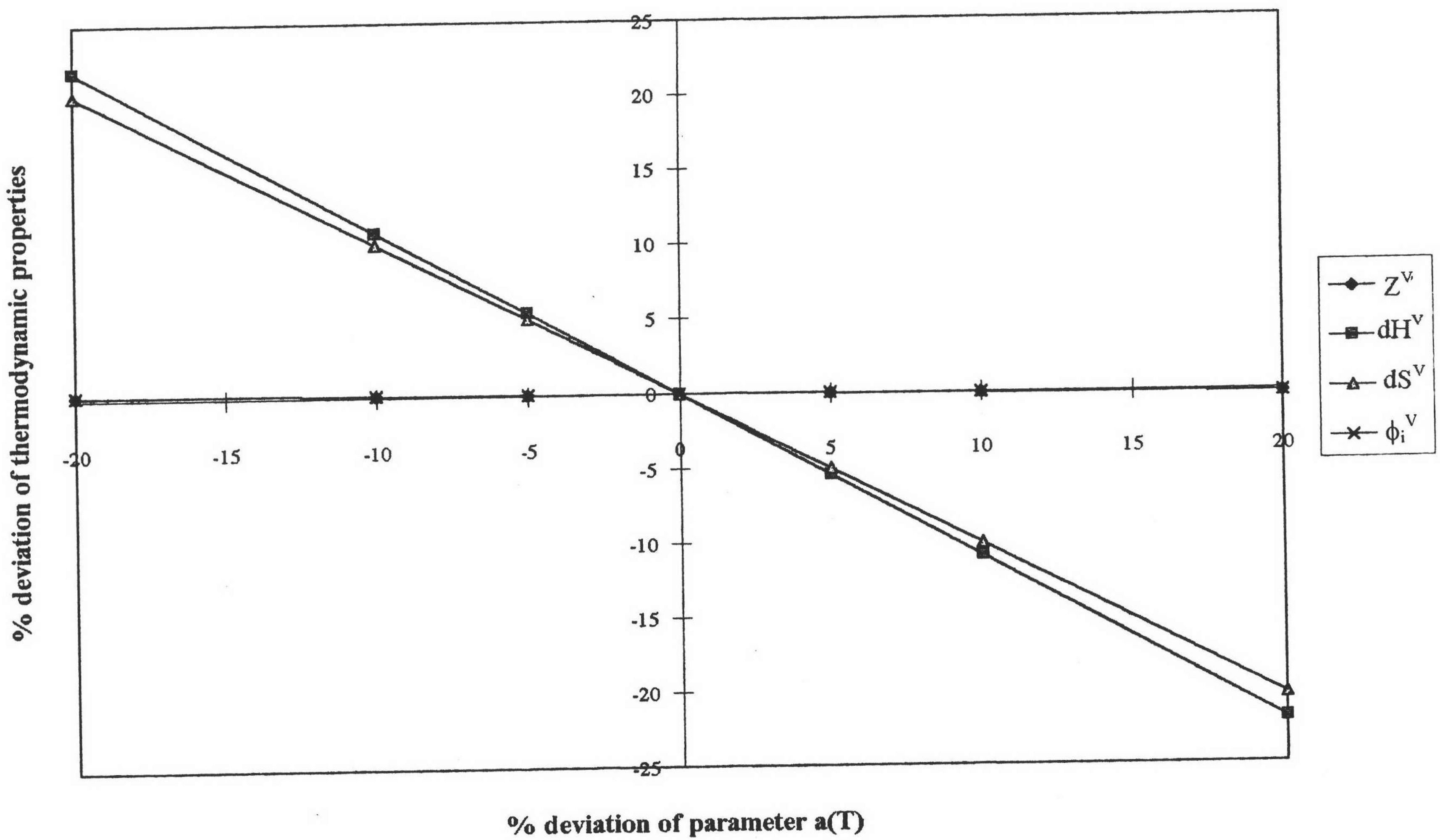

Figure 6.5 PR EOS; n-nonane; at 1.2T_c, 1 atm; % deviation of thermodynamic properties as parameter a(T) is varied.

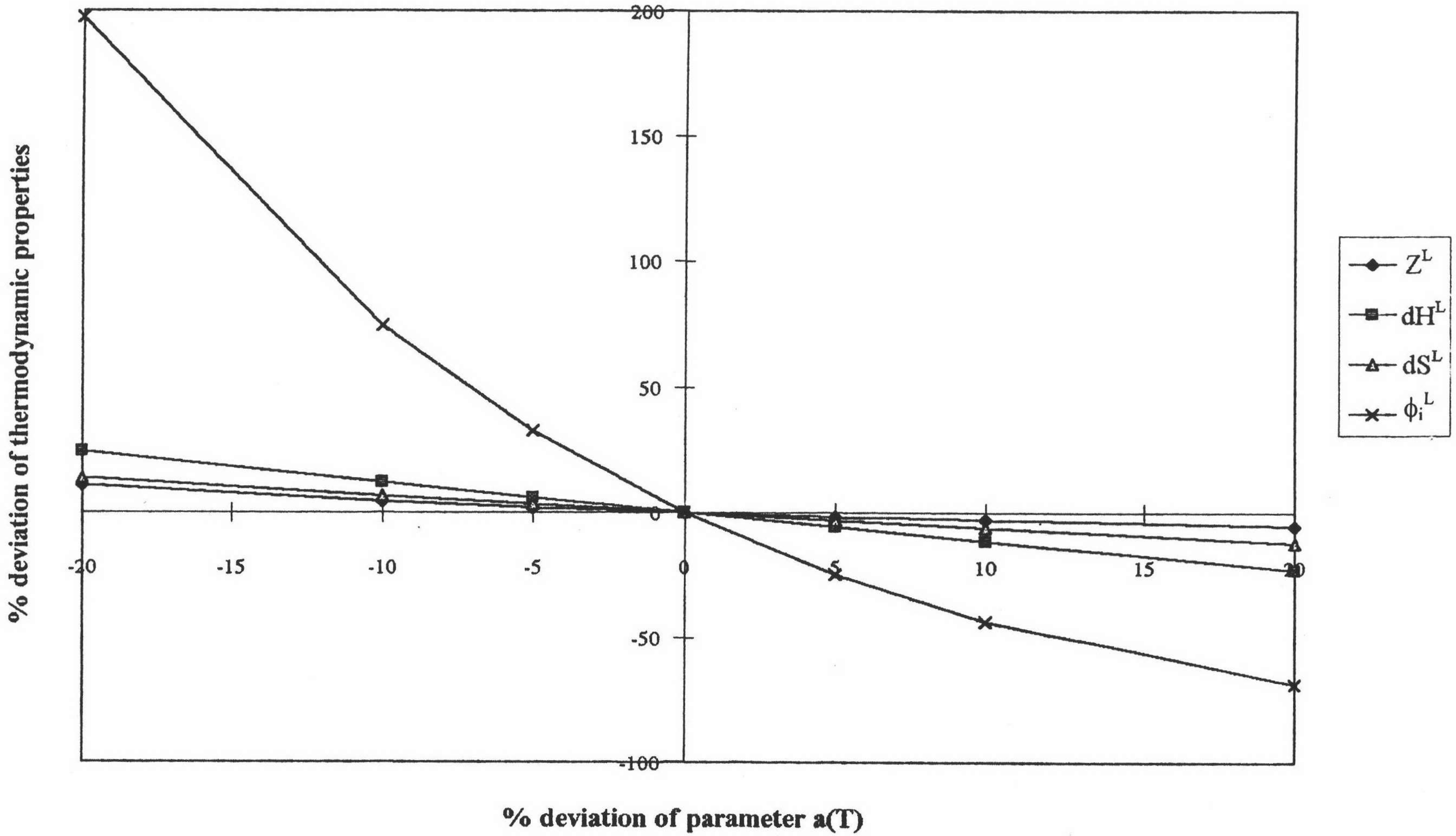

Figure 6.6 PR EOS; n-nonane; at T_b, $0.8P_c$; % deviation of thermodynamic properties as parameter a(T) is varied.

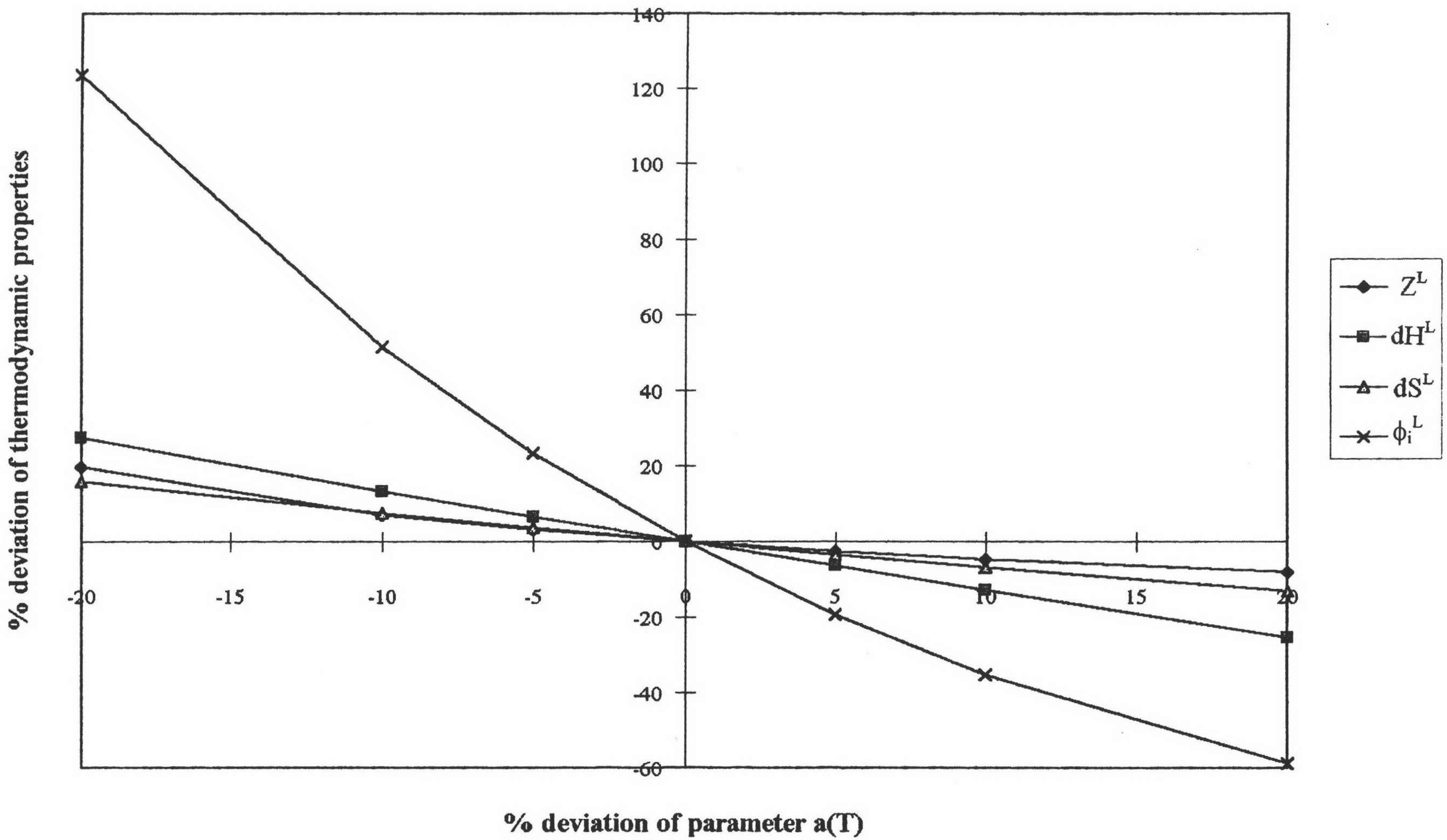

Figure 6.7 PR EOS; n-nonane; at $0.8T_c$, $0.8P_c$; % deviation of thermodynamic properties as parameter a(T) is varied.

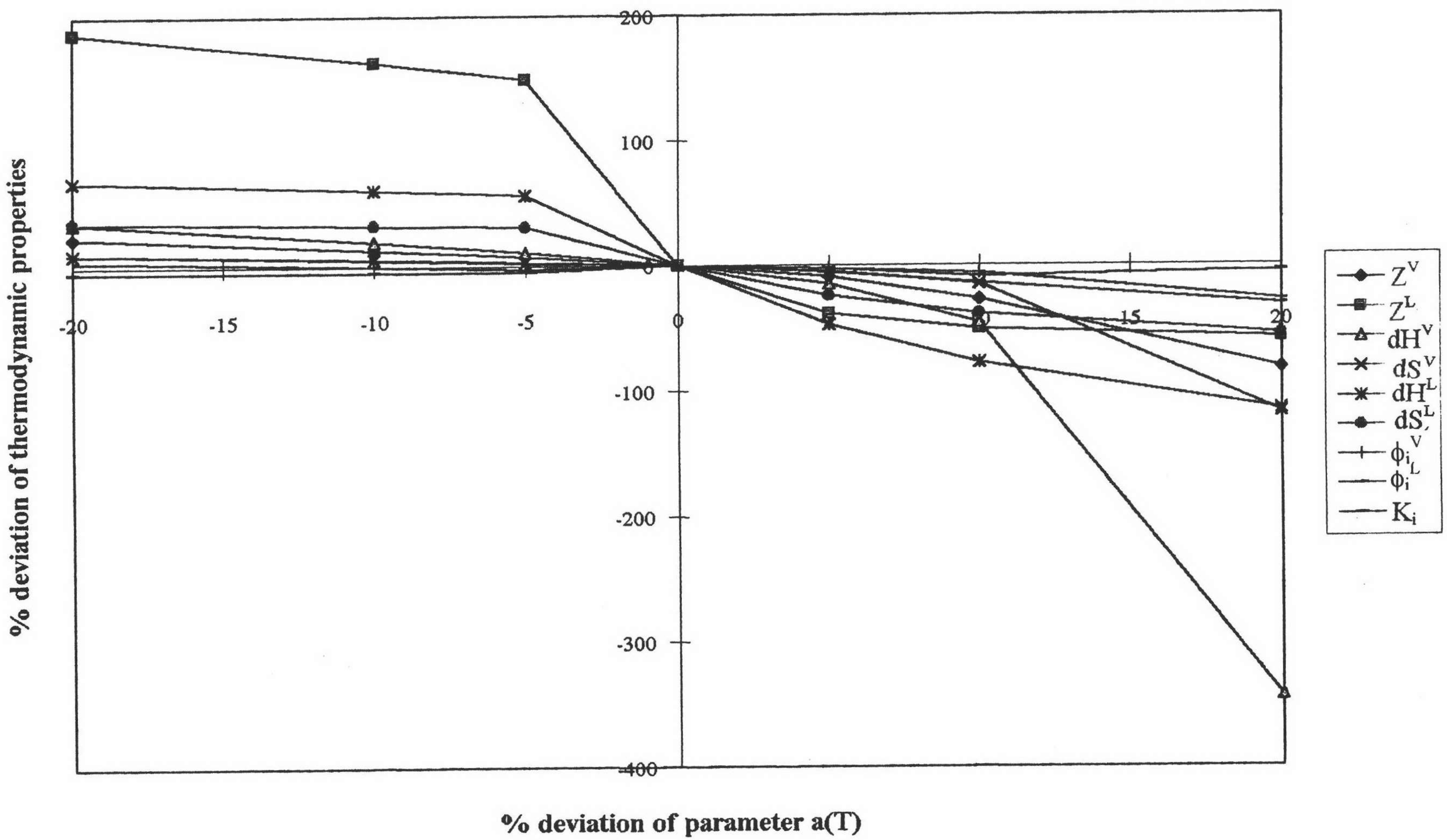

Figure 6.8 PR EOS; n-nonane; at T_c, $0.8P_c$; % deviation of thermodynamic properties as parameter a(T) is varied.

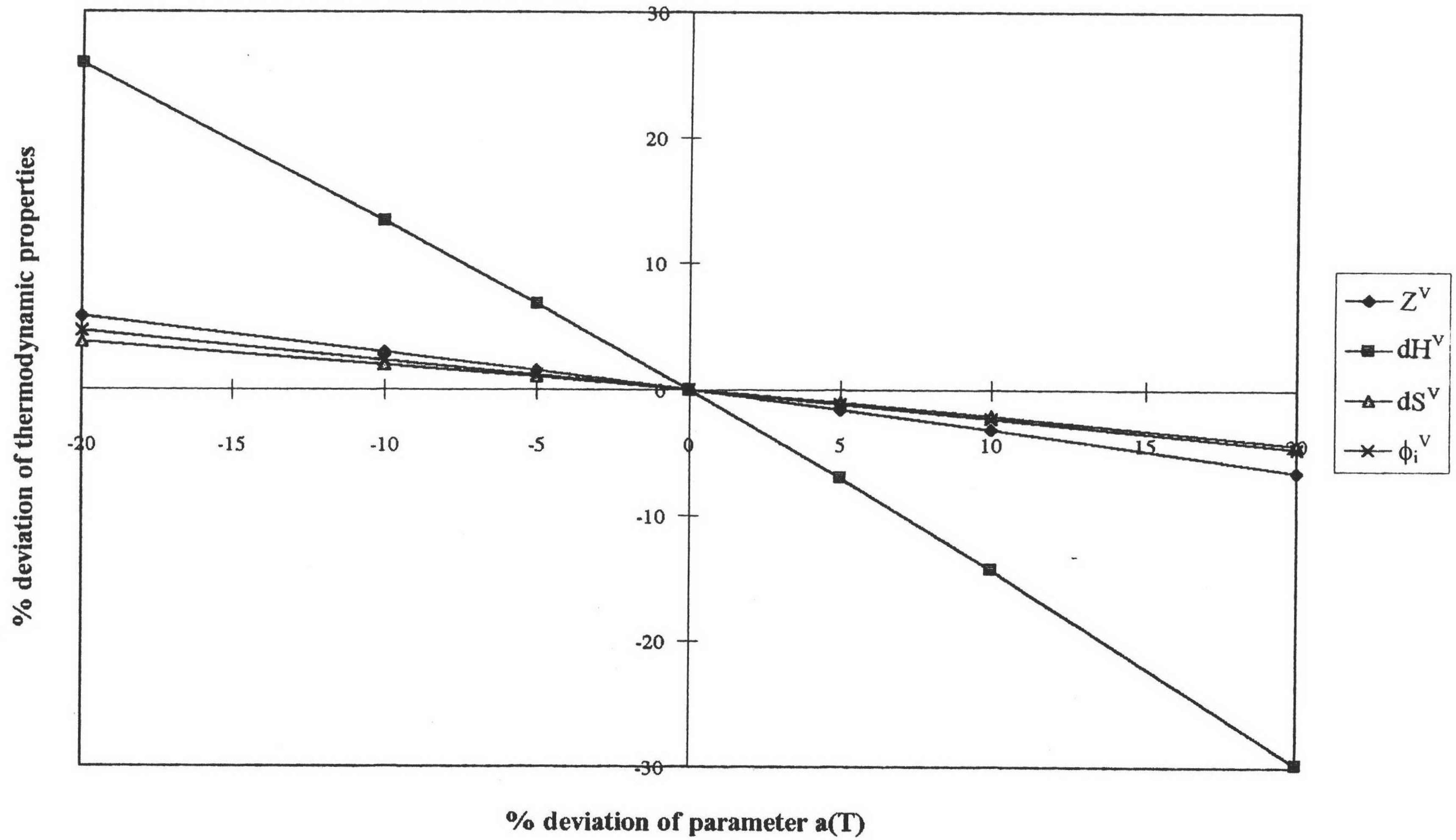

Figure 6.9 PR EOS; n-nonane; at $1.2T_c$, $0.8P_c$; % deviation of thermodynamic properties as parameter a(T) is varied.

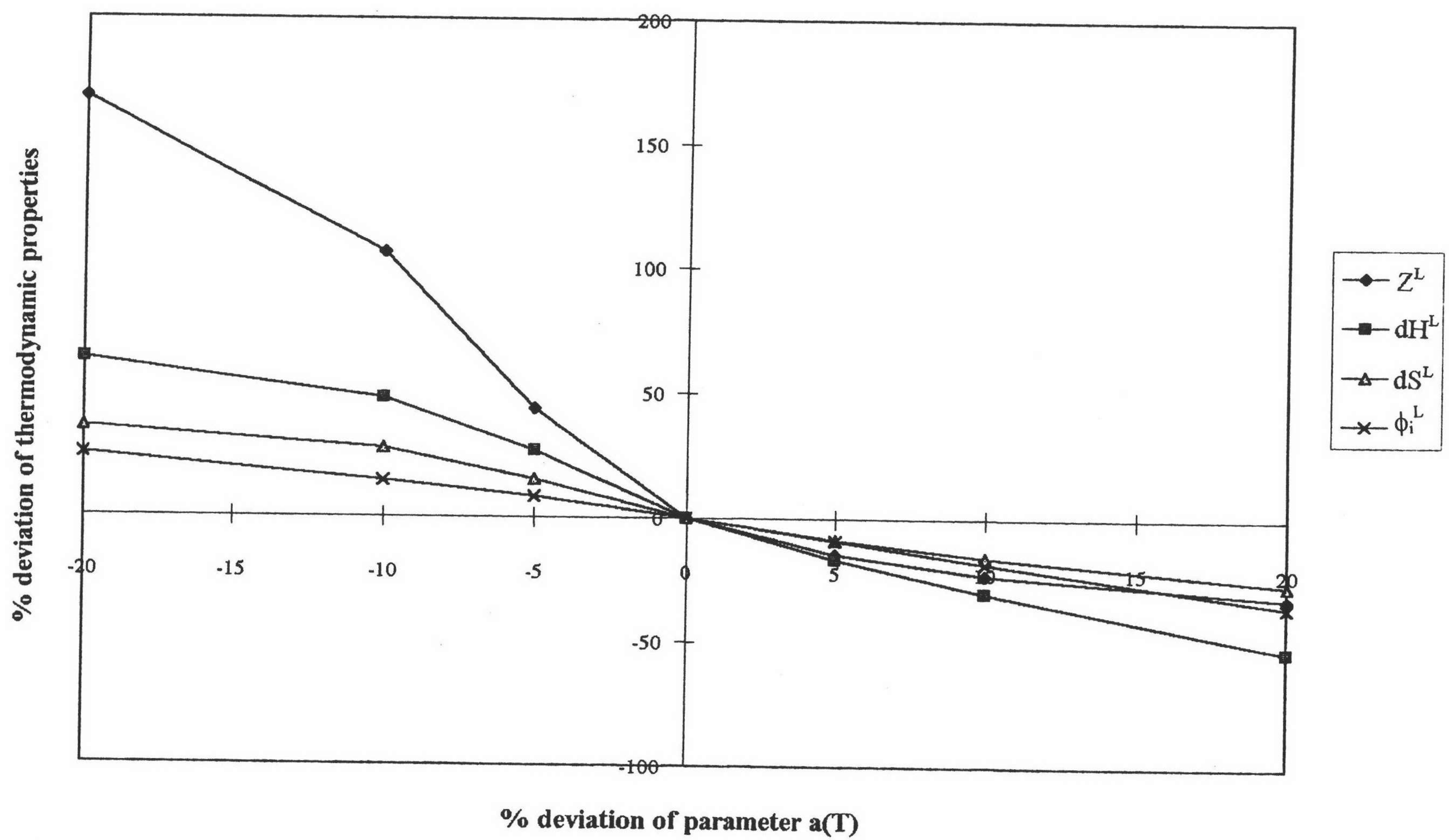

Figure 6.10 PR EOS; n-nonane; at T_c, $1.2P_c$; % deviation of thermodynamic properties as parameter a(T) is varied.

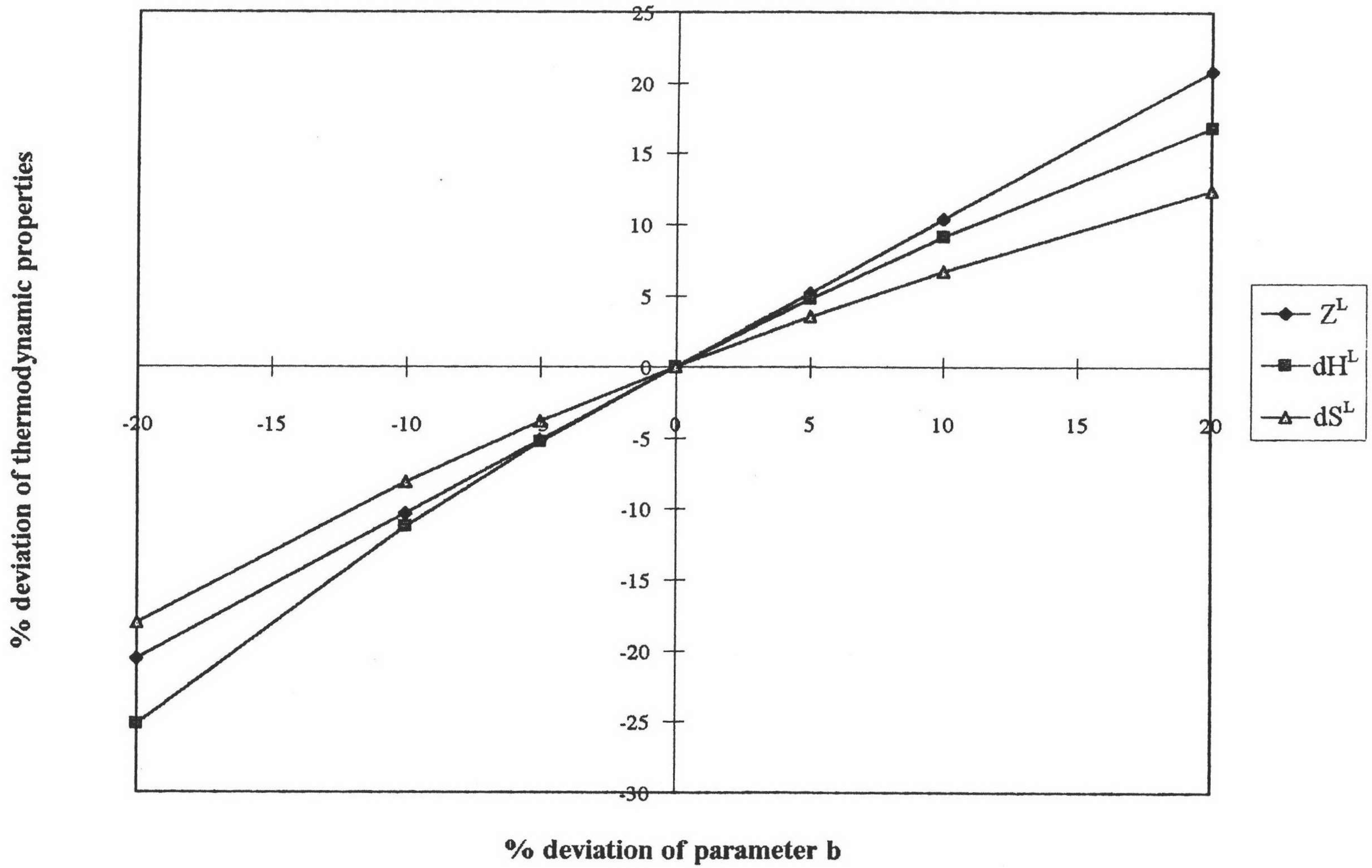

Figure 6.11a PR EOS; n-nonane; at $0.3T_b$, 1 atm; % deviation of thermodynamic properties as parameter b is varied.

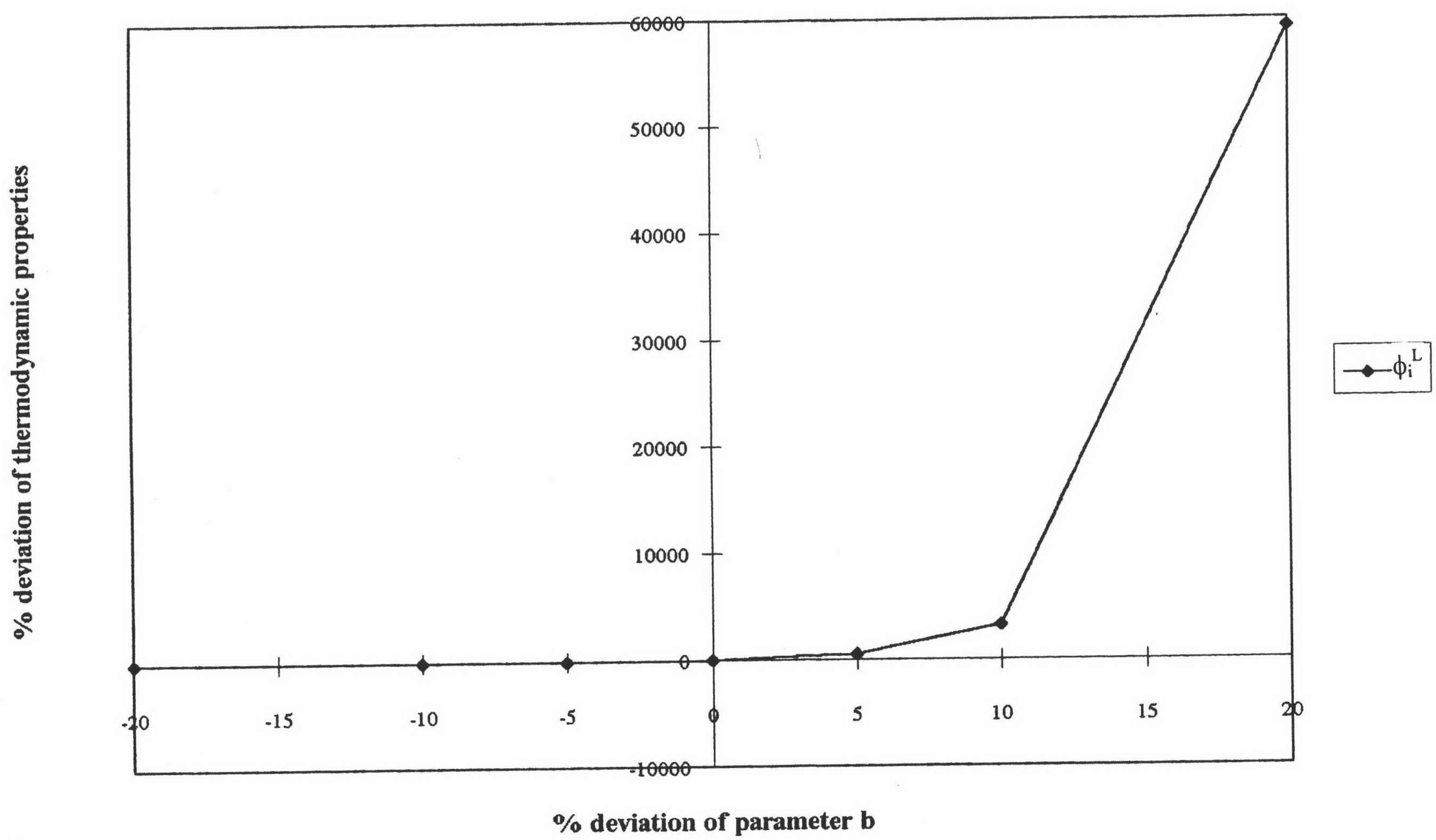

Figure 6.11b PR EOS; n-nonane; at $0.3T_b$, 1 atm; % deviation of fugacity coefficient as parameter b is varied.

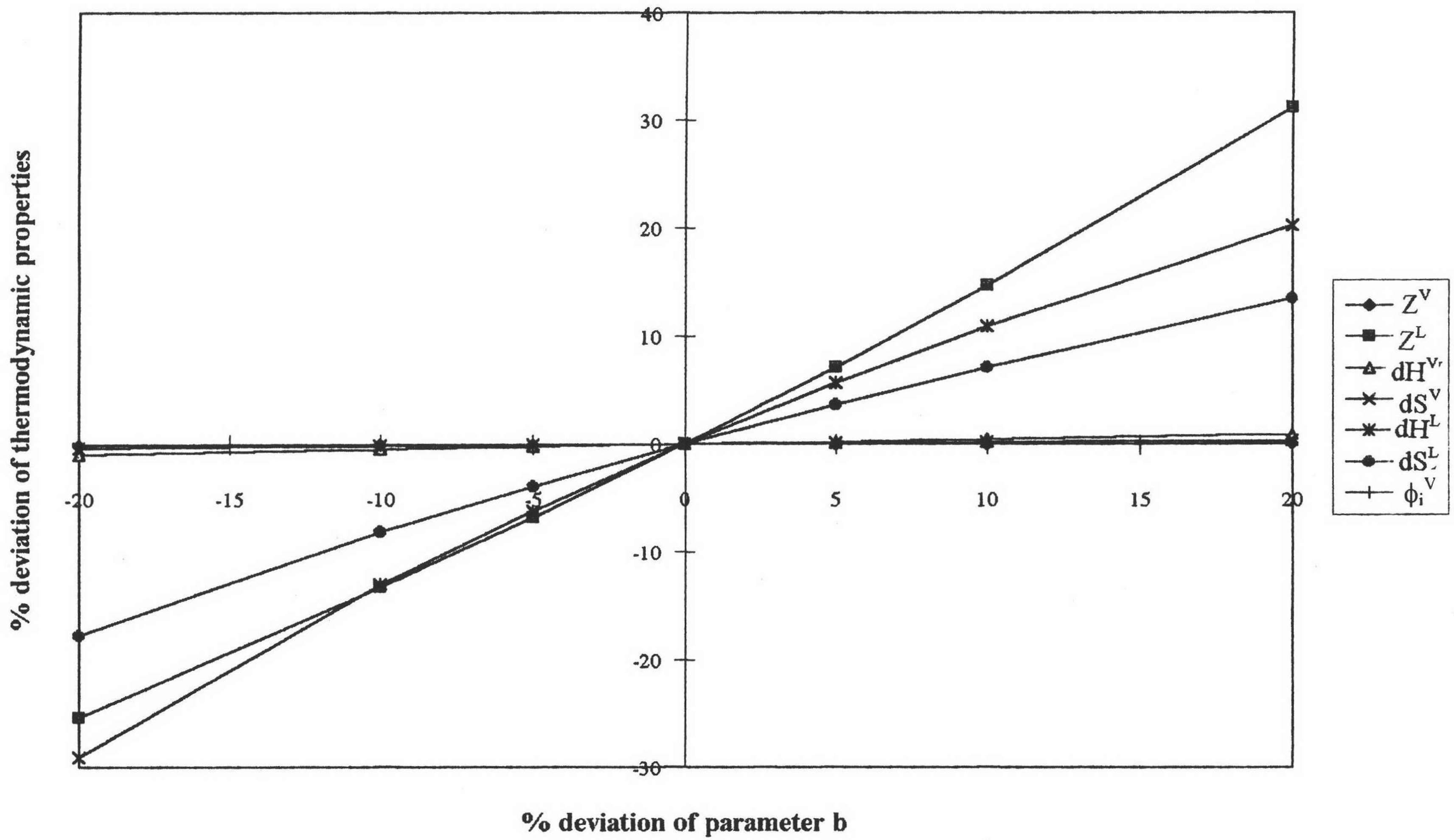

Figure 6.12a PR EOS; n-nonane; at T_b, 1 atm; % deviation of thermodynamic properties as parameter b is varied.

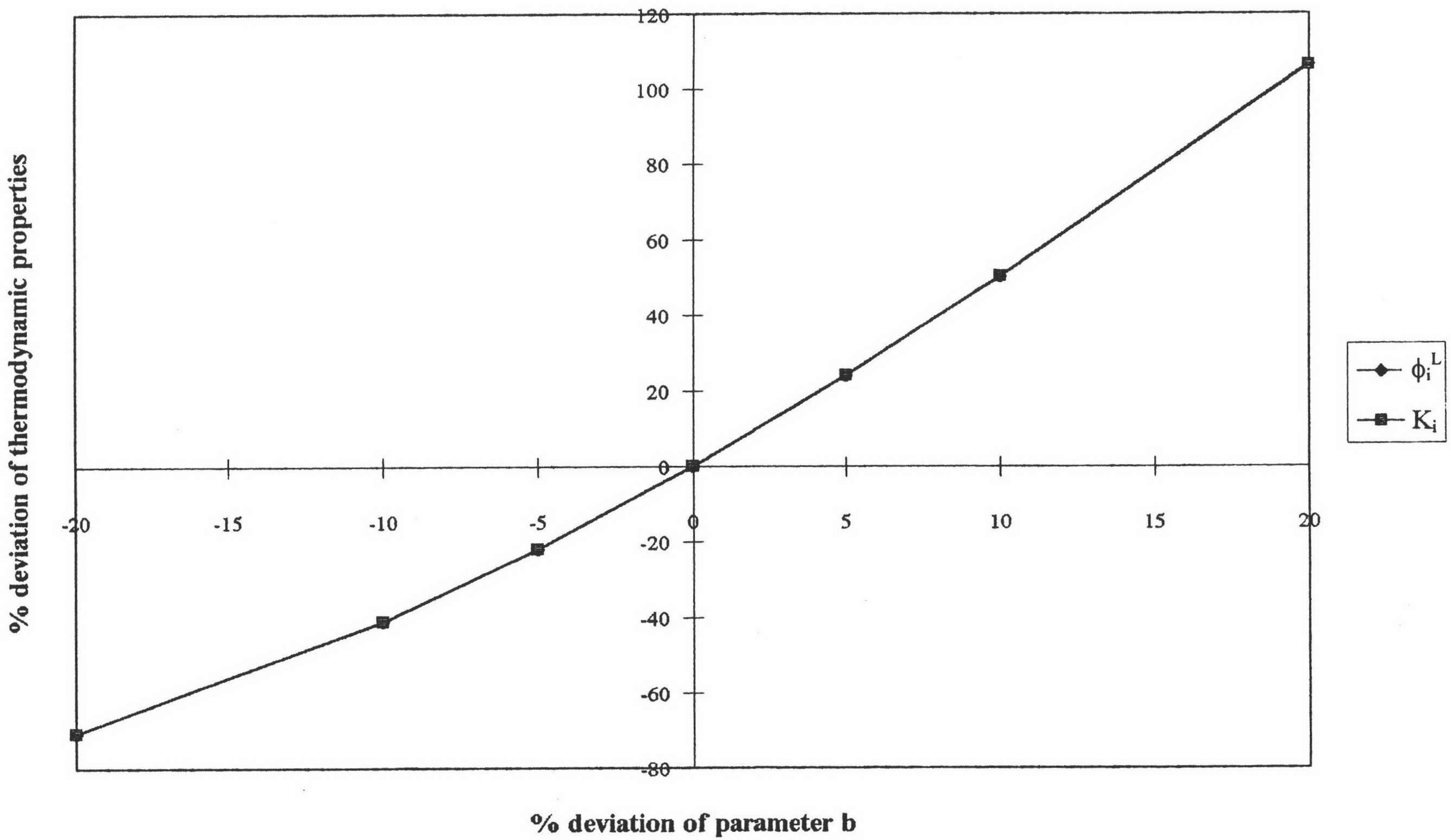

Figure 6.12b PR EOS; n-nonane; at T_b, 1 atm; % deviation of fugacity coefficient and equilibrium ratio as parameter b is varied.

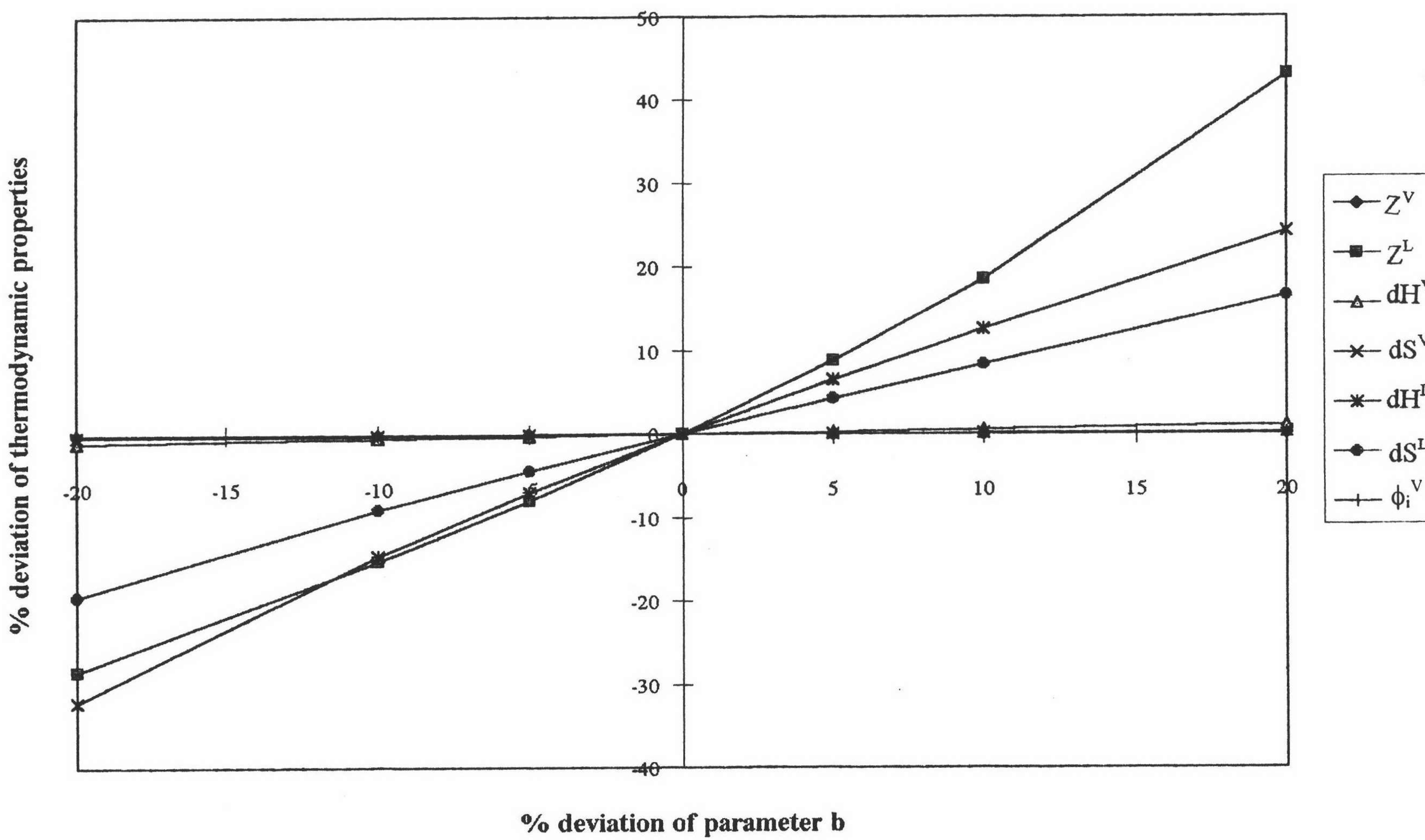

Figure 6.13a PR EOS; n-nonane; at $0.8T_c$, 1 atm; % deviation of thermodynamic properties as parameter b is varied.

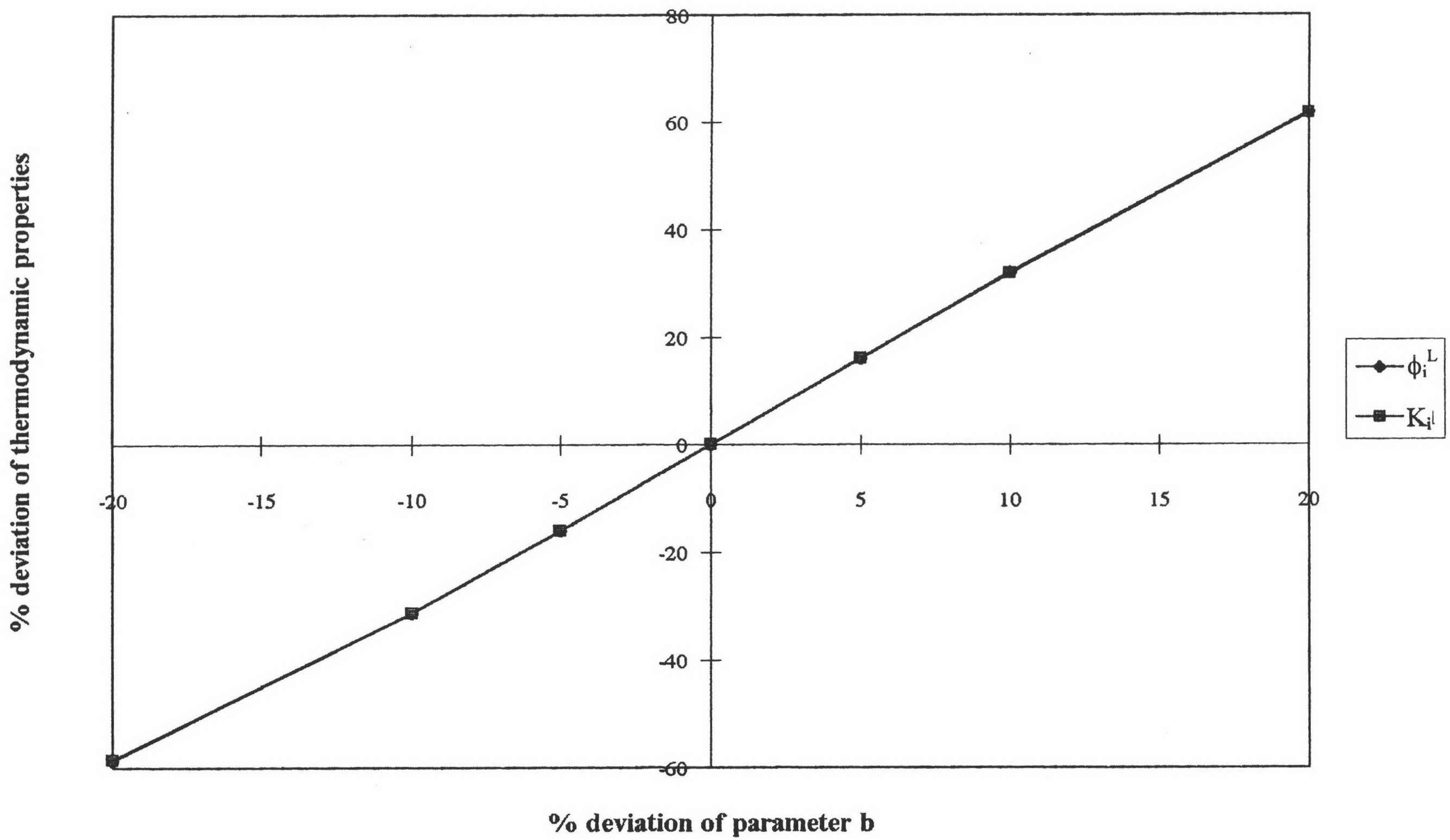

Figure 6.13b PR EOS; n-nonane; at $0.8T_c$, 1 atm; % deviation of fugacity coefficient and equilibrium ratio as parameter b is varied.

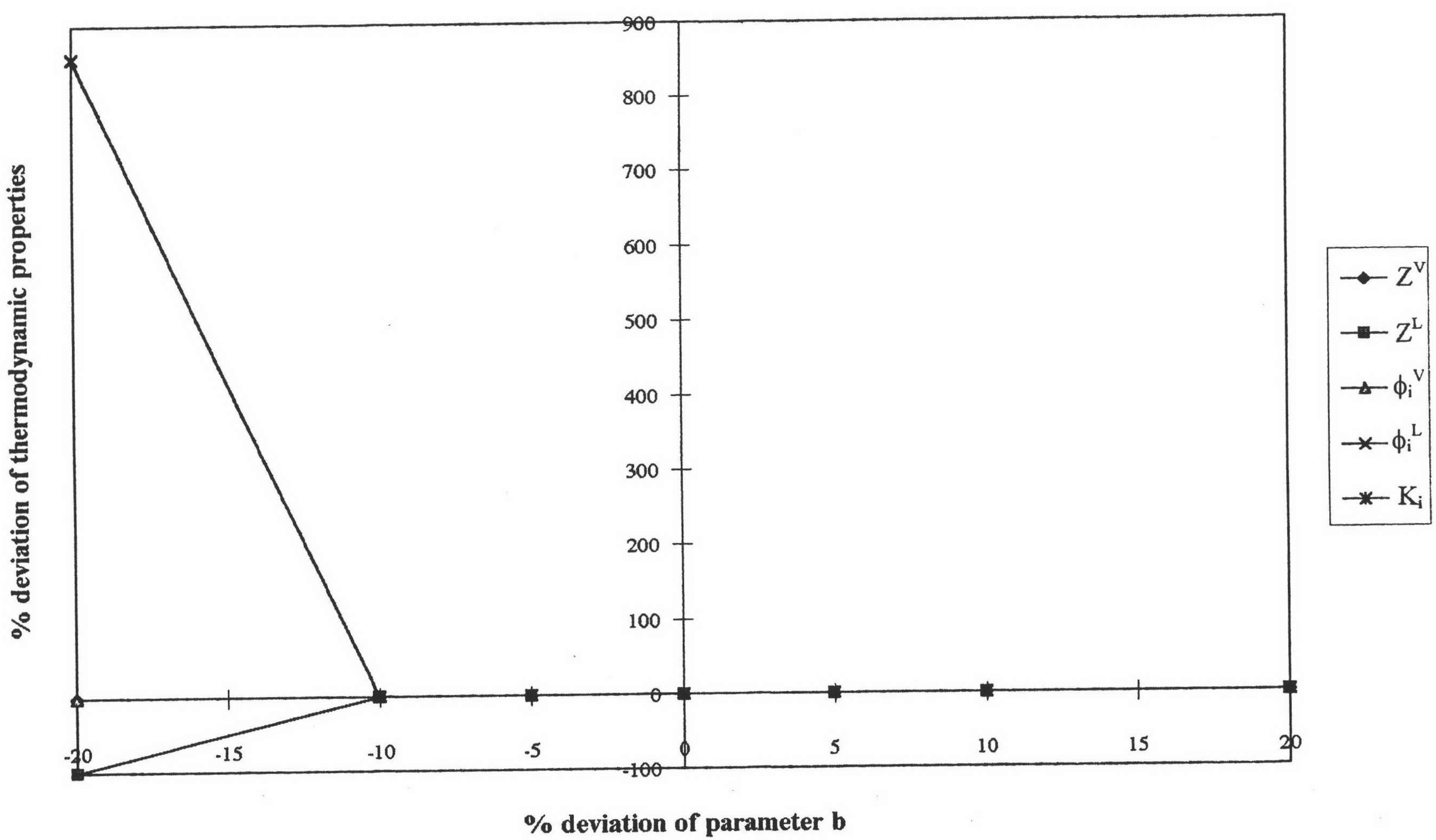

Figure 6.14a PR EOS; n-nonane; at T_c, 1 atm; % deviation of thermodynamic properties as parameter b is varied.

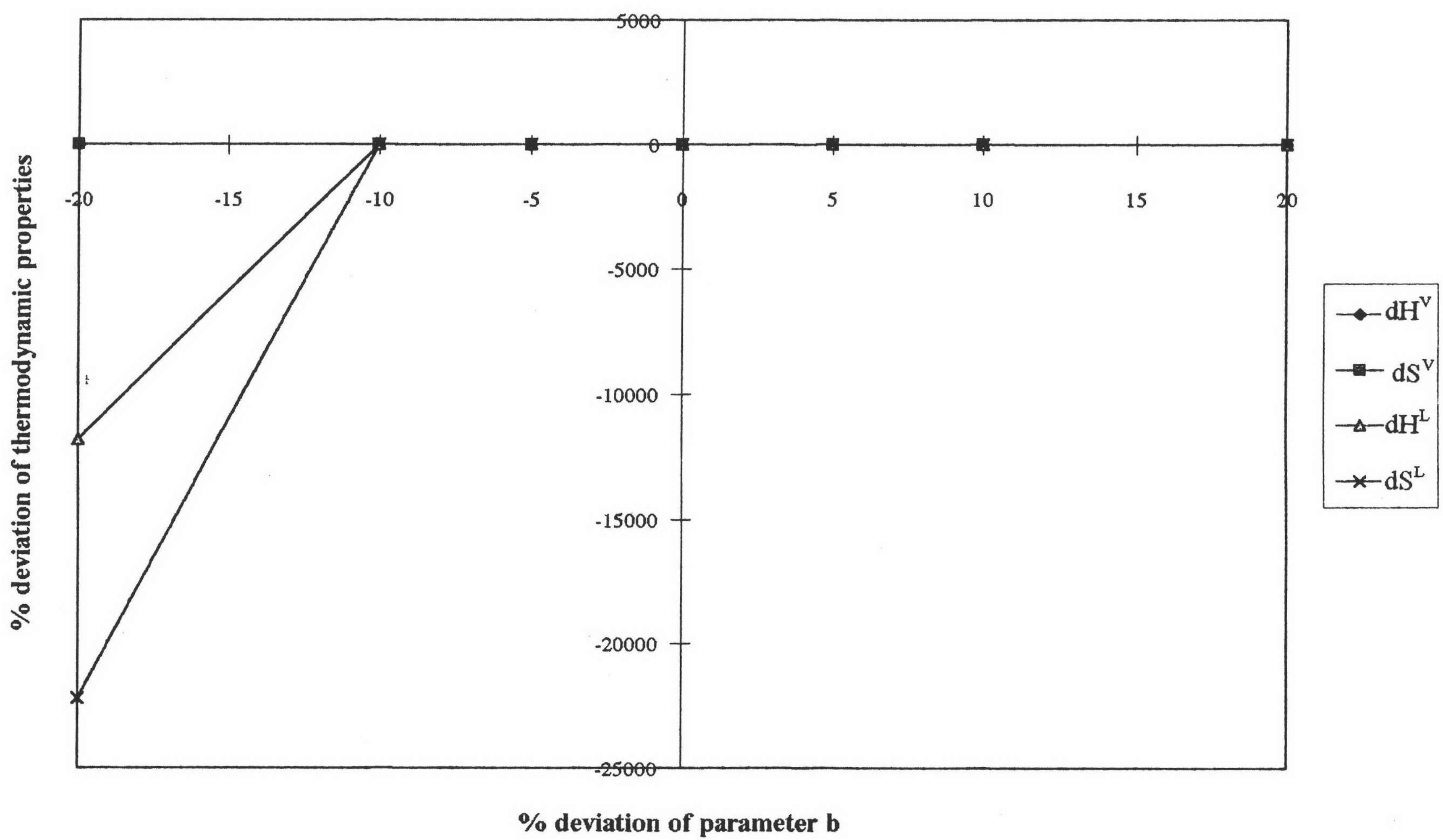

Figure 6.14b PR EOS; n-nonane; at T_c, 1 atm; % deviation of enthalpy and entropy departures as parameter b is varied.

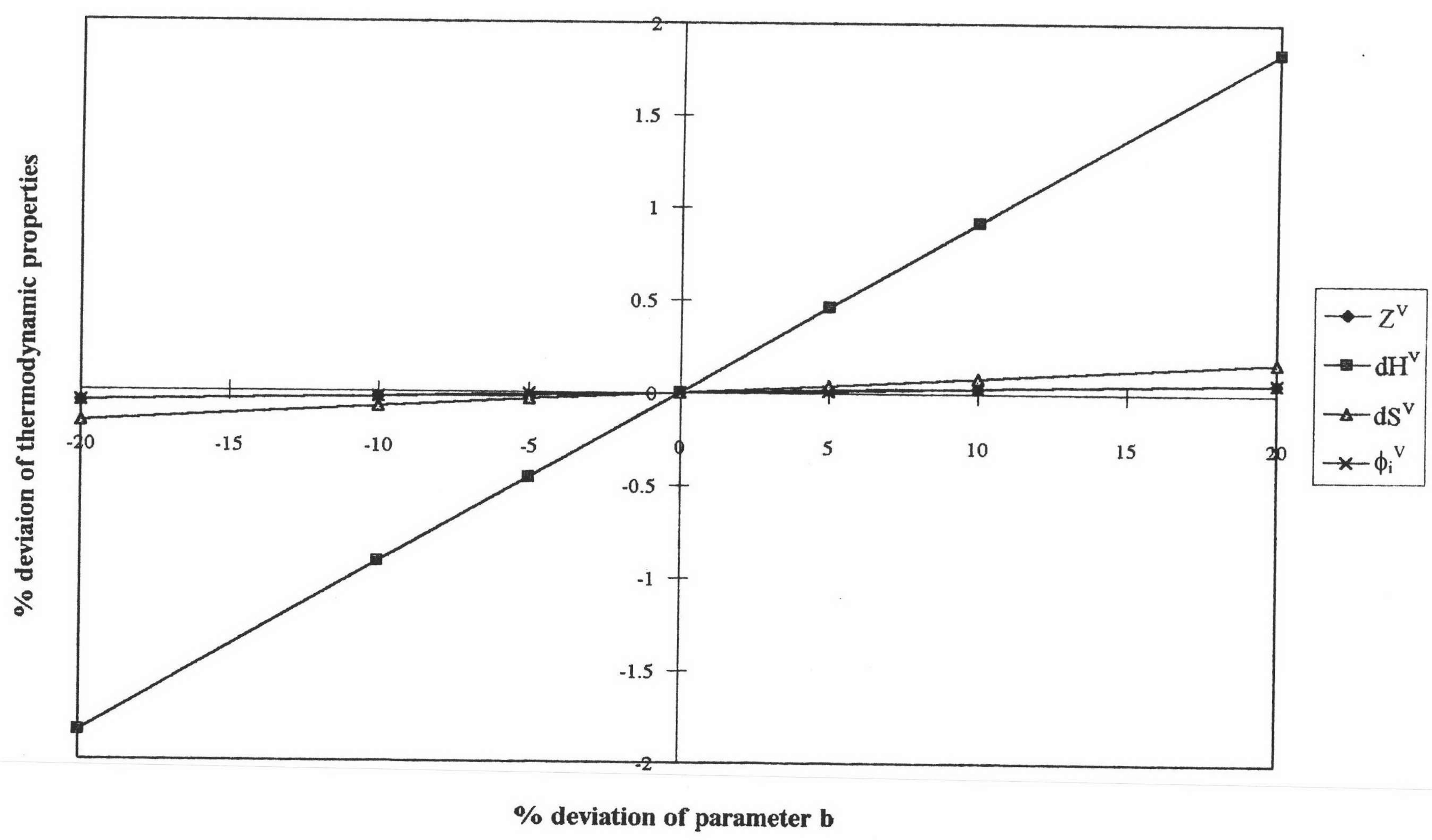

Figure 6.15 PR EOS; n-nonane; at $1.2T_c$, 1 atm; % deviation of thermodynamic properties as parameter b is varied.

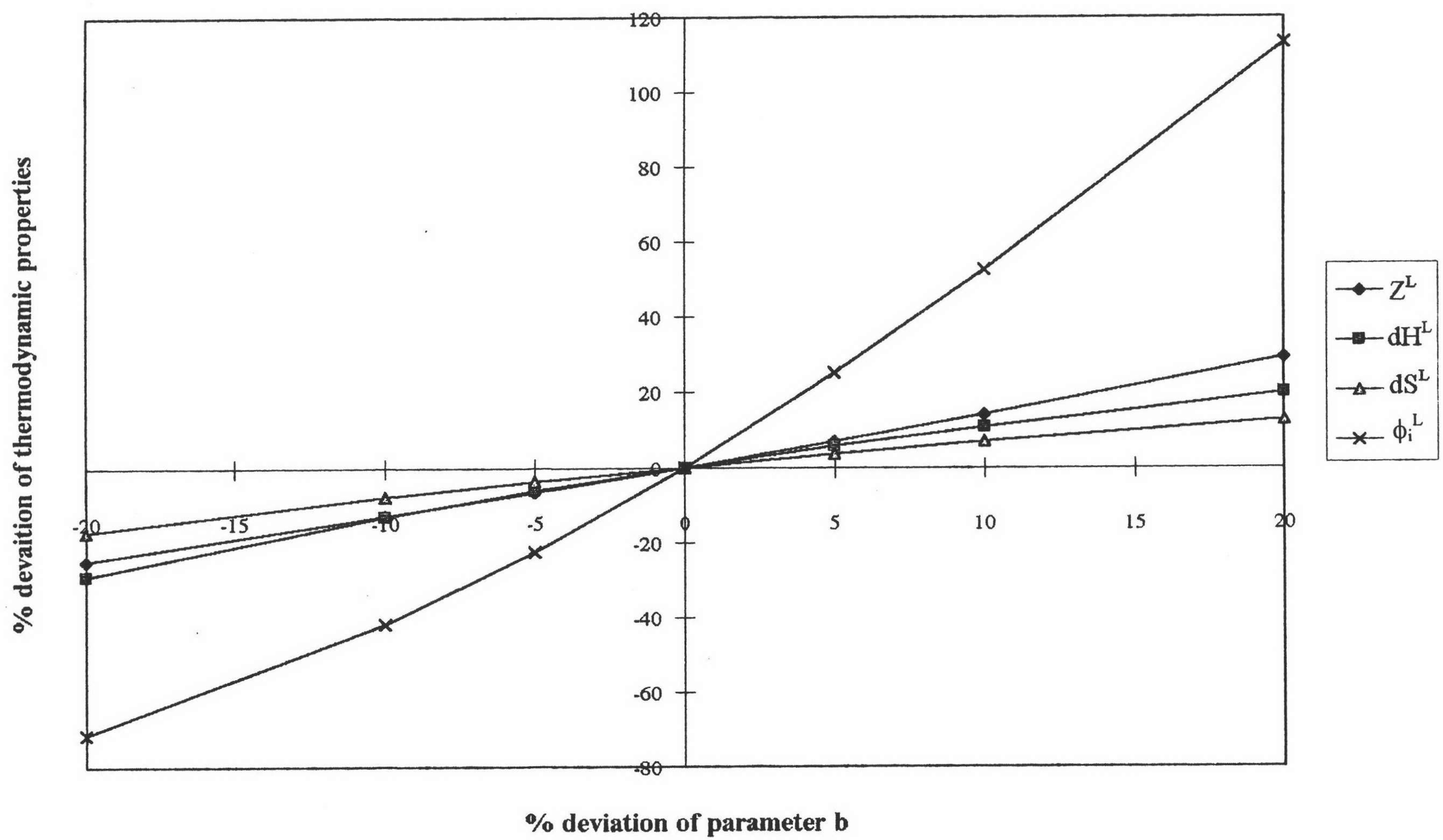

Figure 6.16 PR EOS; n-nonane; at T_b, $0.8P_c$; % deviation of thermodynamic properties as parameter b is varied.

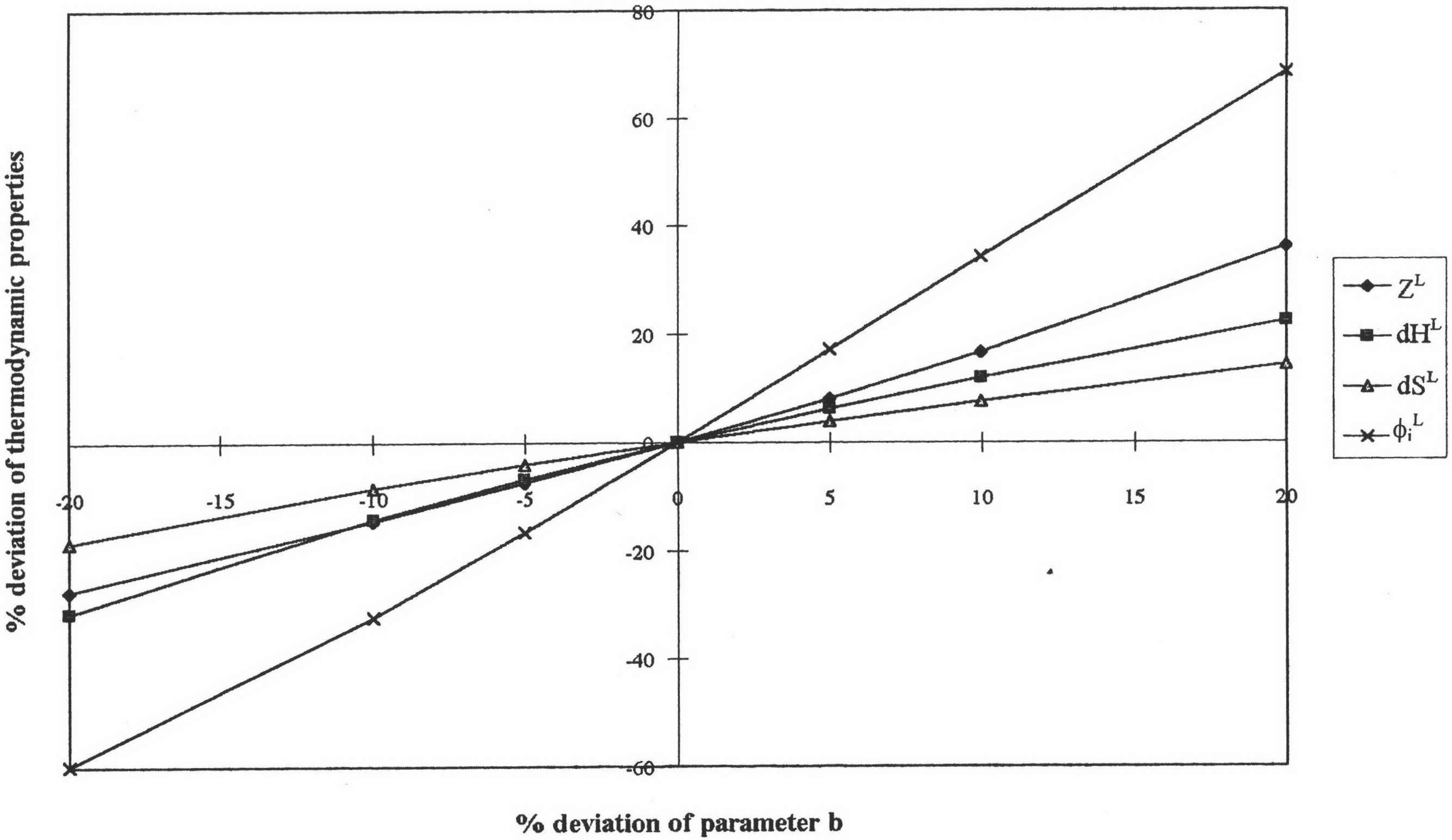

Figure 6.17 PR EOS; n-nonane; at $0.8T_c$, $0.8P_c$; % deviation of thermodynamic properties as parameter b is varied.

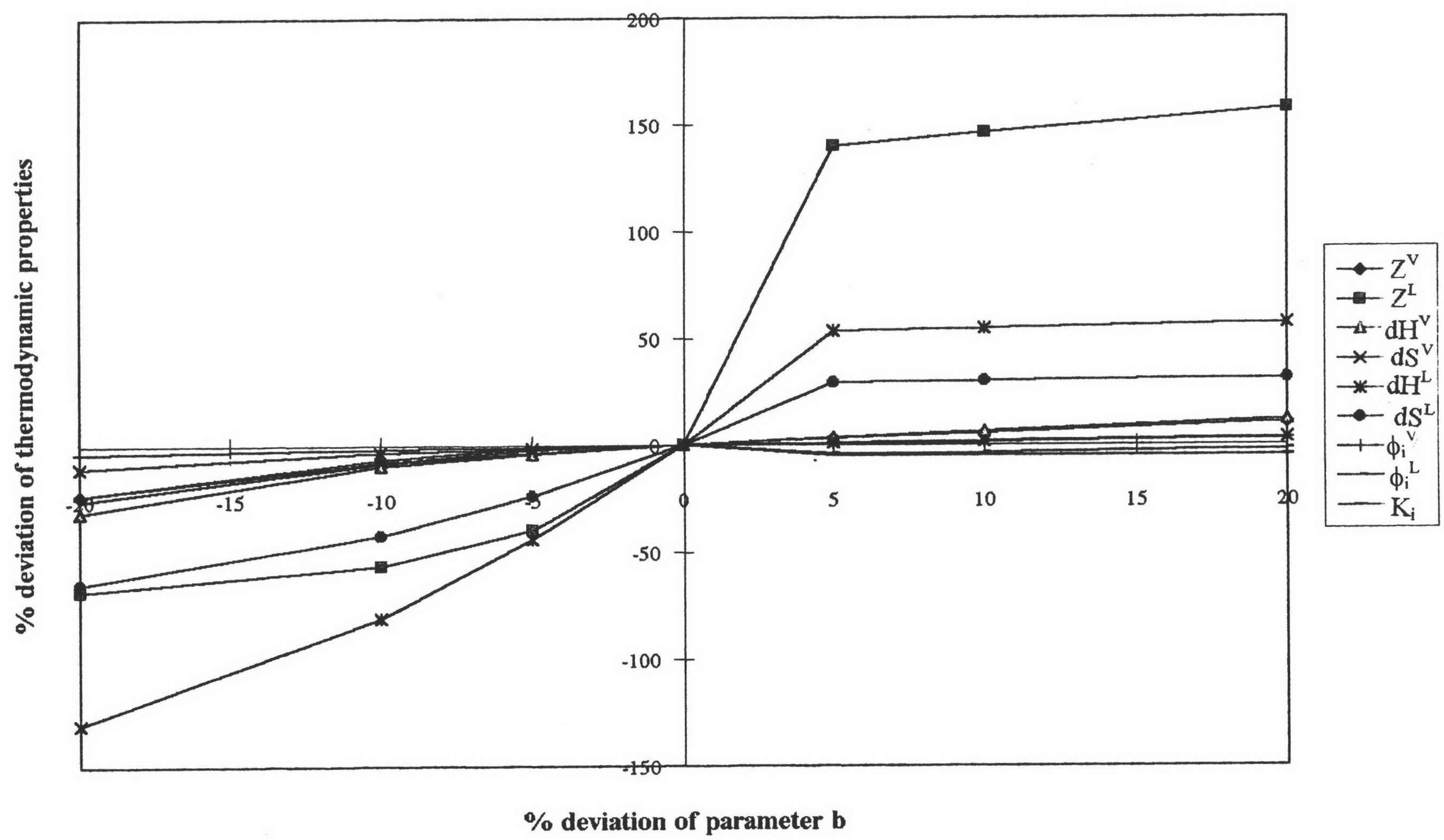

Figure 6.18 PR EOS; n-nonane; at T_c, $0.8P_c$; % deviation of thermodynamic properties as parameter b is varied.

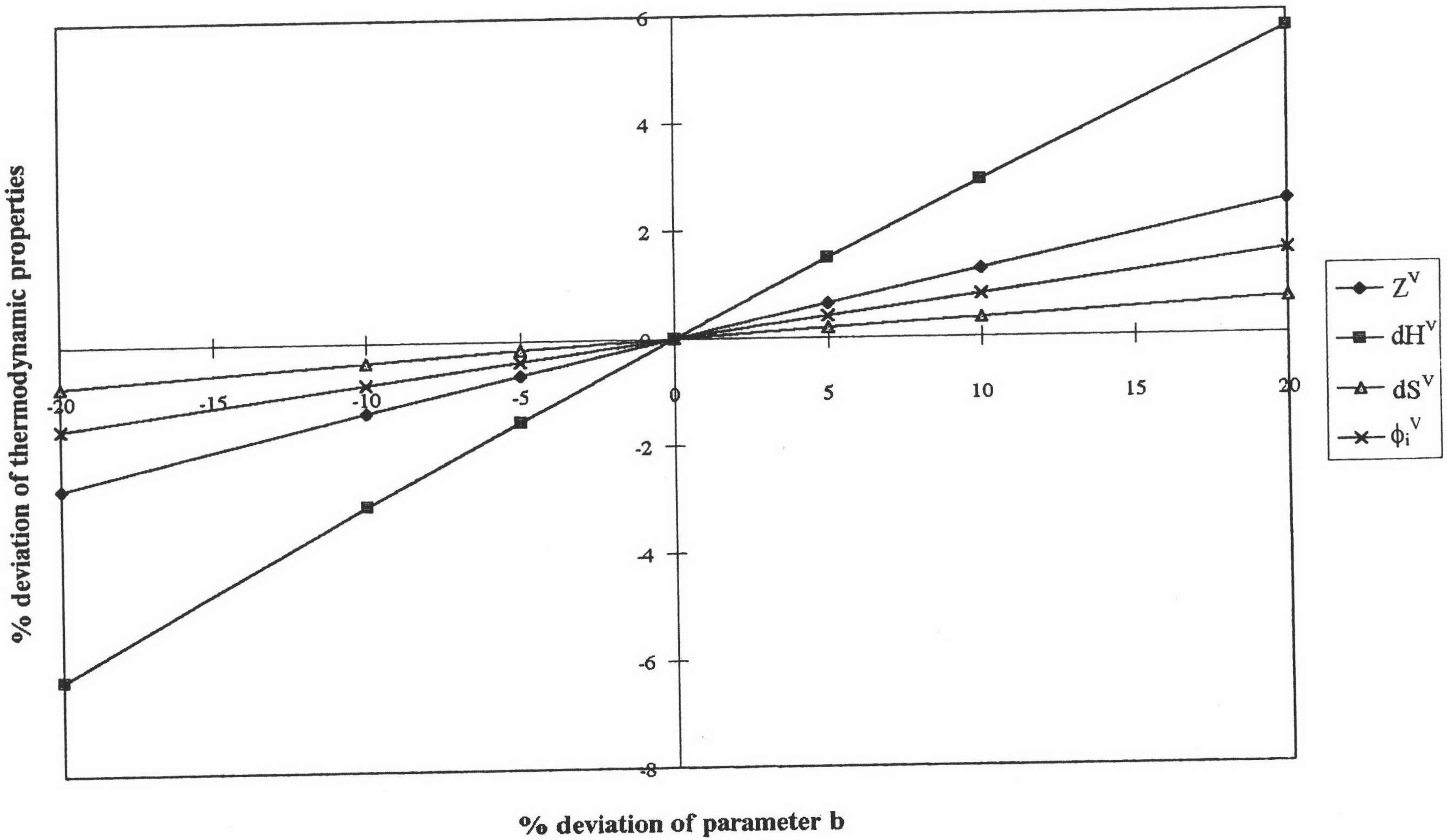

Figure 6.19 PR EOS; n-nonane; at $1.2T_c$, $0.8P_c$; % deviation of thermodynamic properties as parameter b is varied.

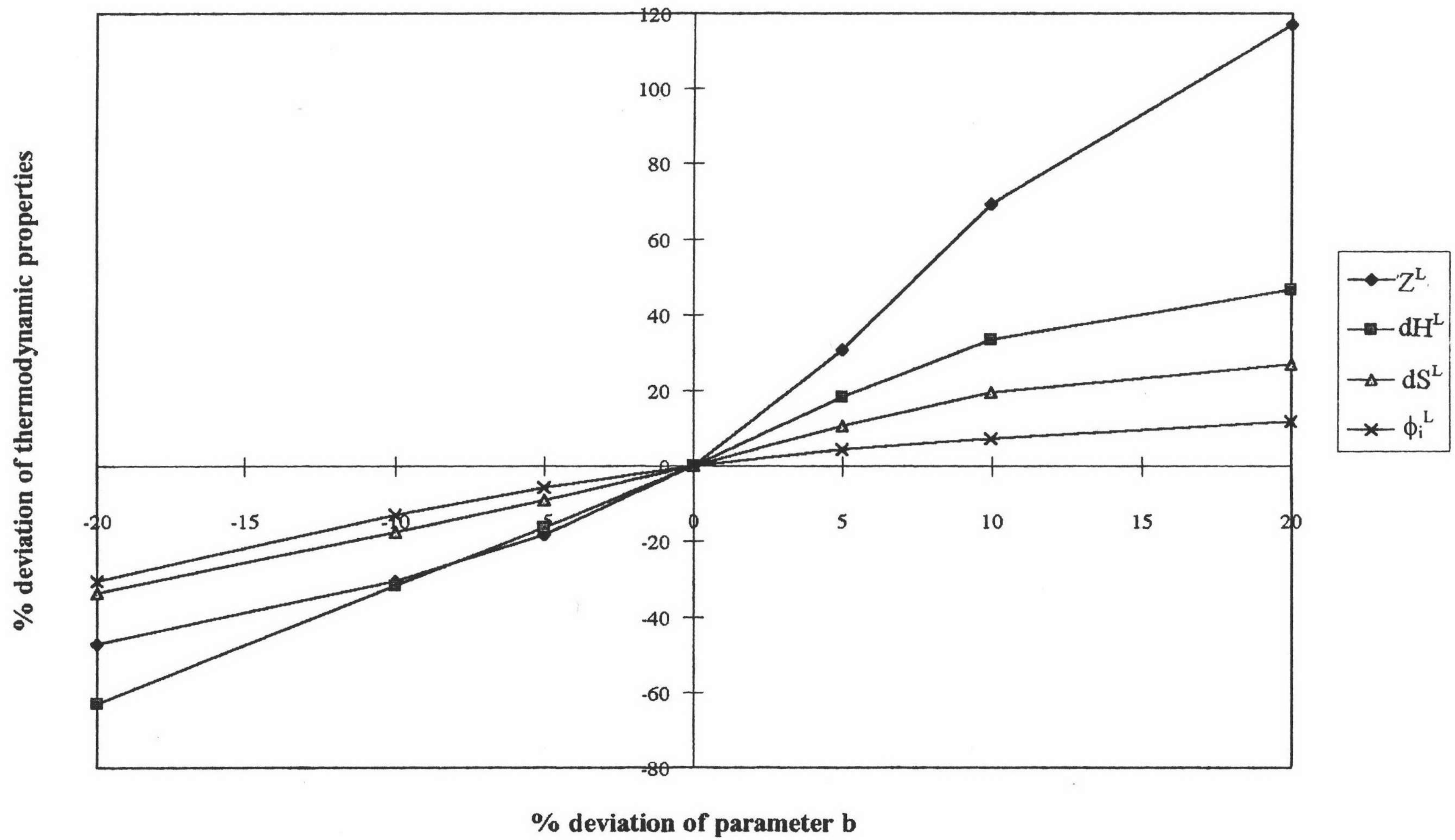

Figure 6.20 PR EOS; n-nonane; at T_c, $1.2P_c$; % deviation of thermodynamic properties as parameter b is varied.

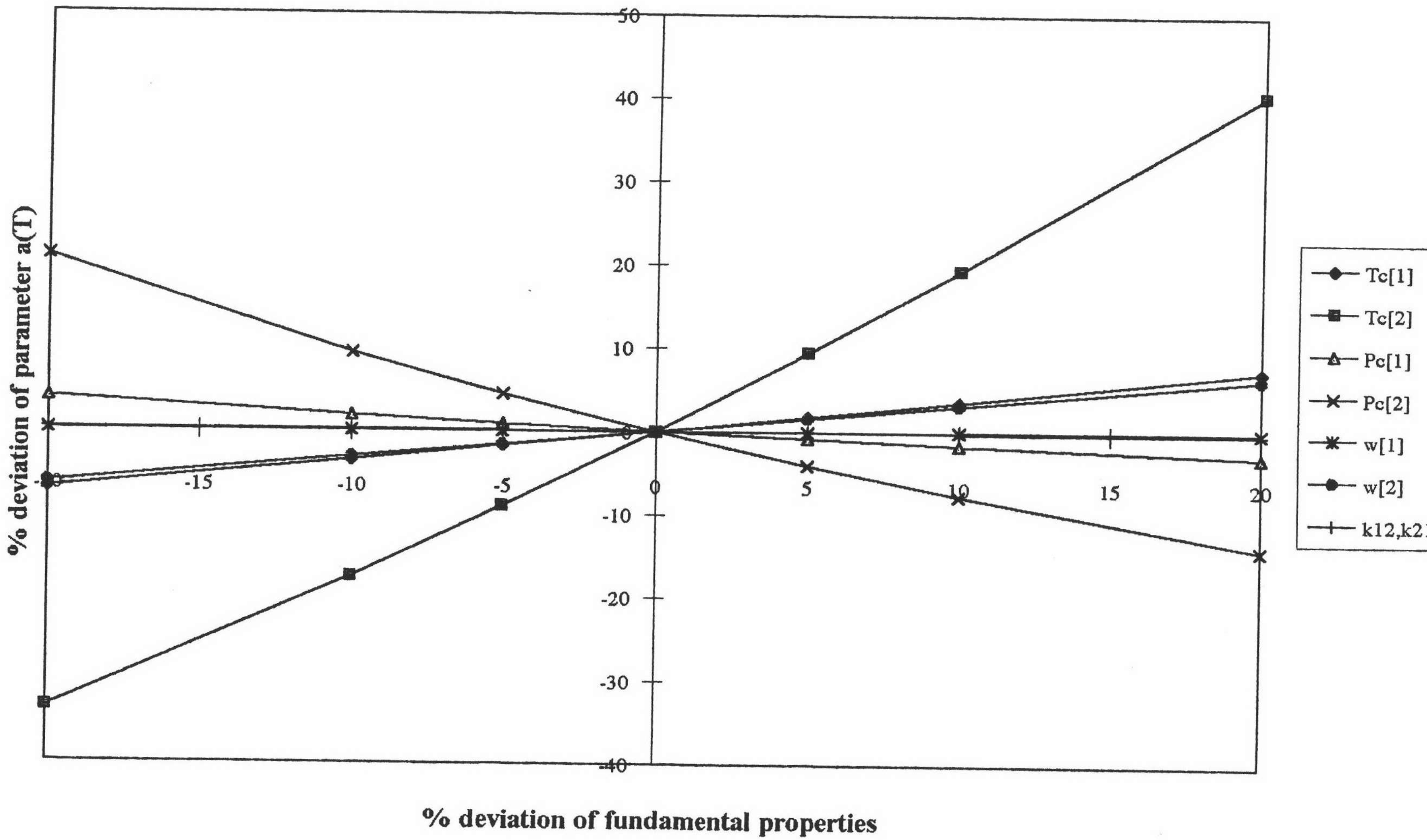

Figure 6.21 PR EOS; 0.5methane/0.5n-heptane; at $0.3T_b$, % deviation of parameter a(T) as fundamental properties are varied.

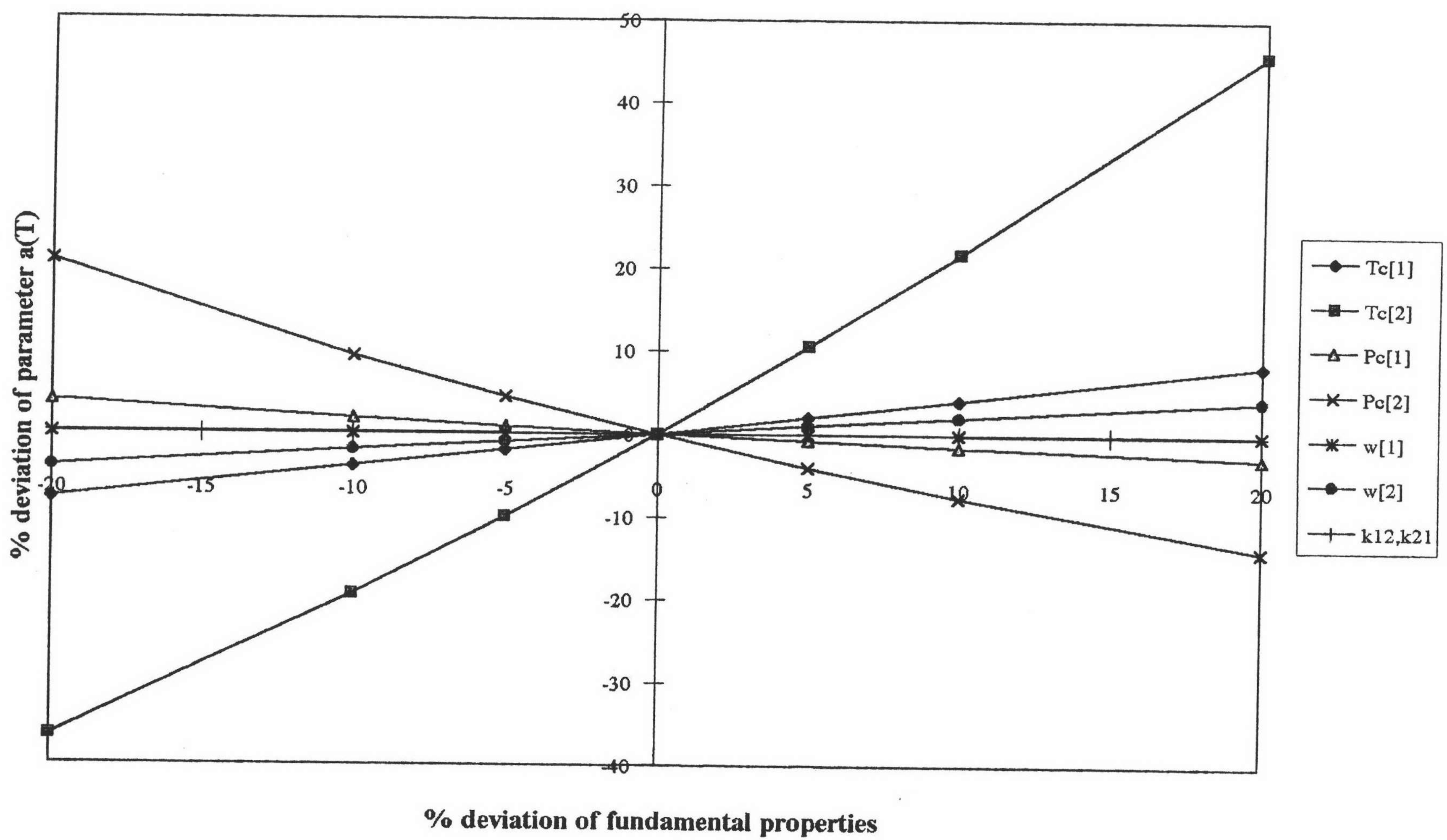

Figure 6.22 PR EOS; 0.5methane/0.5n-heptane; at T_b, % deviation of parameter a(T) as fundamental properties are varied.

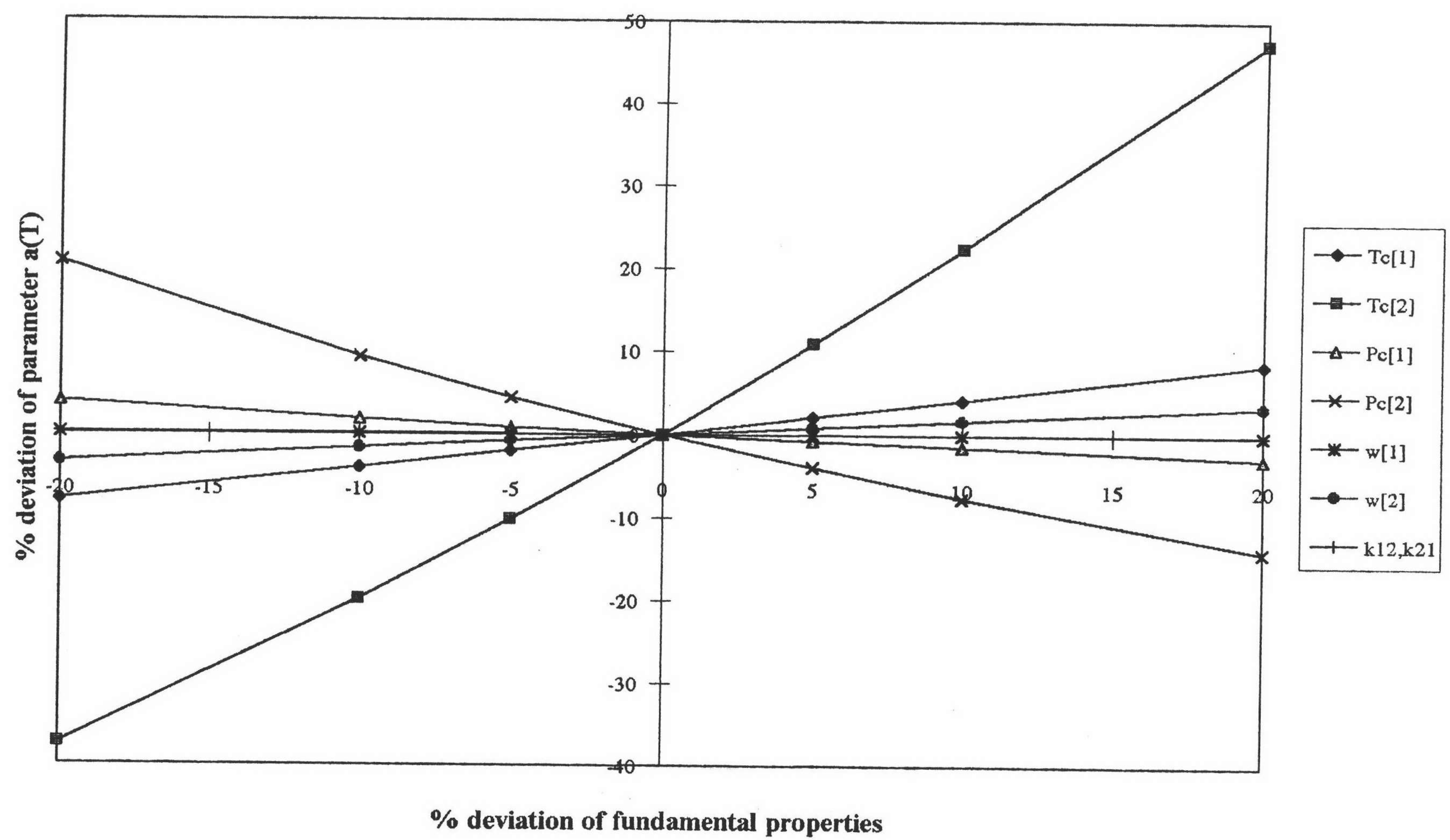

Figure 6.23 PR EOS; 0.5methane/0.5n-heptane; at $0.8T_c$, % deviation of parameter a(T) as fundamental properties are varied.

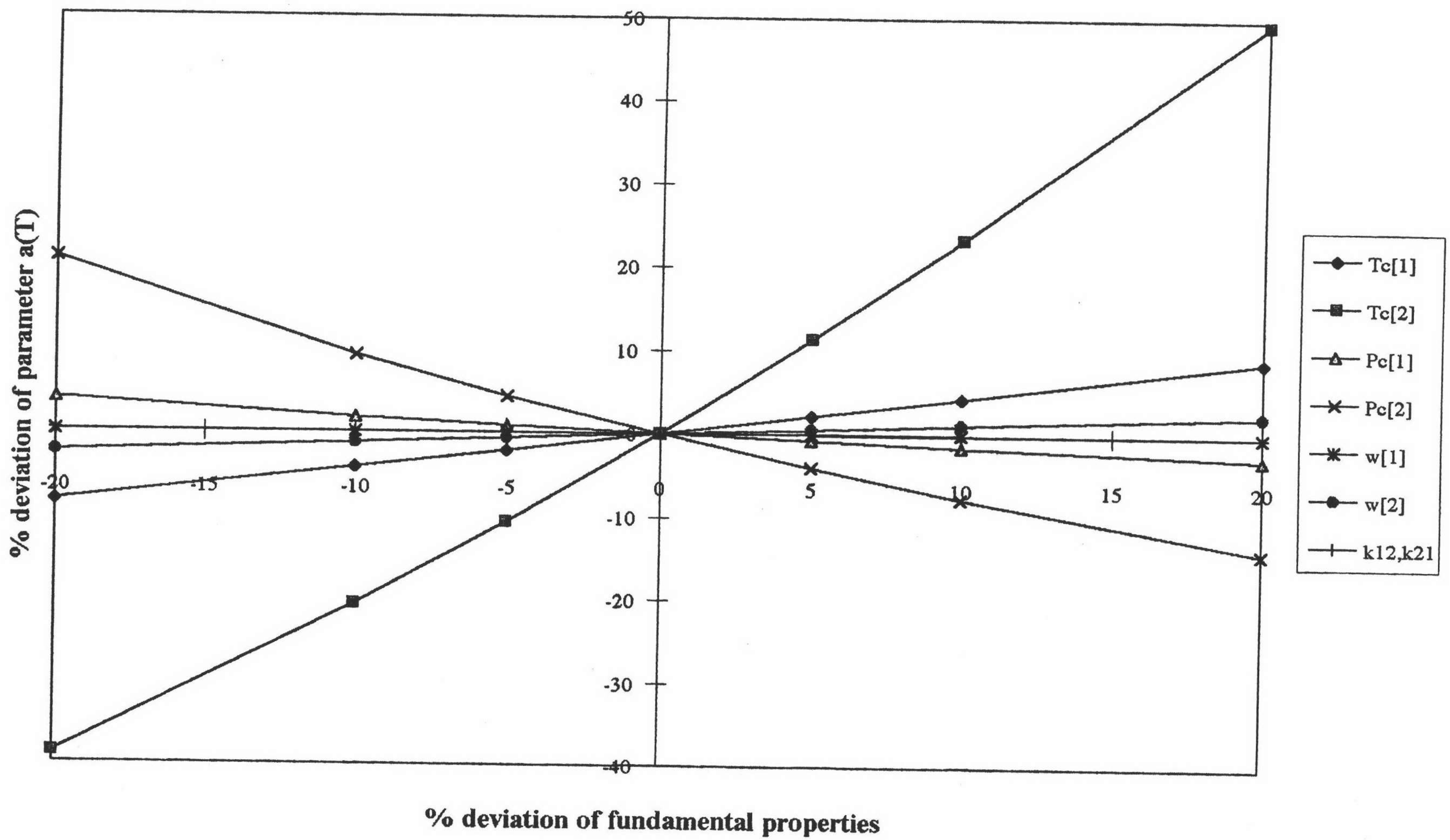

Figure 6.24 PR EOS; 0.5methane/0.5n-heptane; at T_c, % deviation of parameter a(T) as fundamental properties are varied.

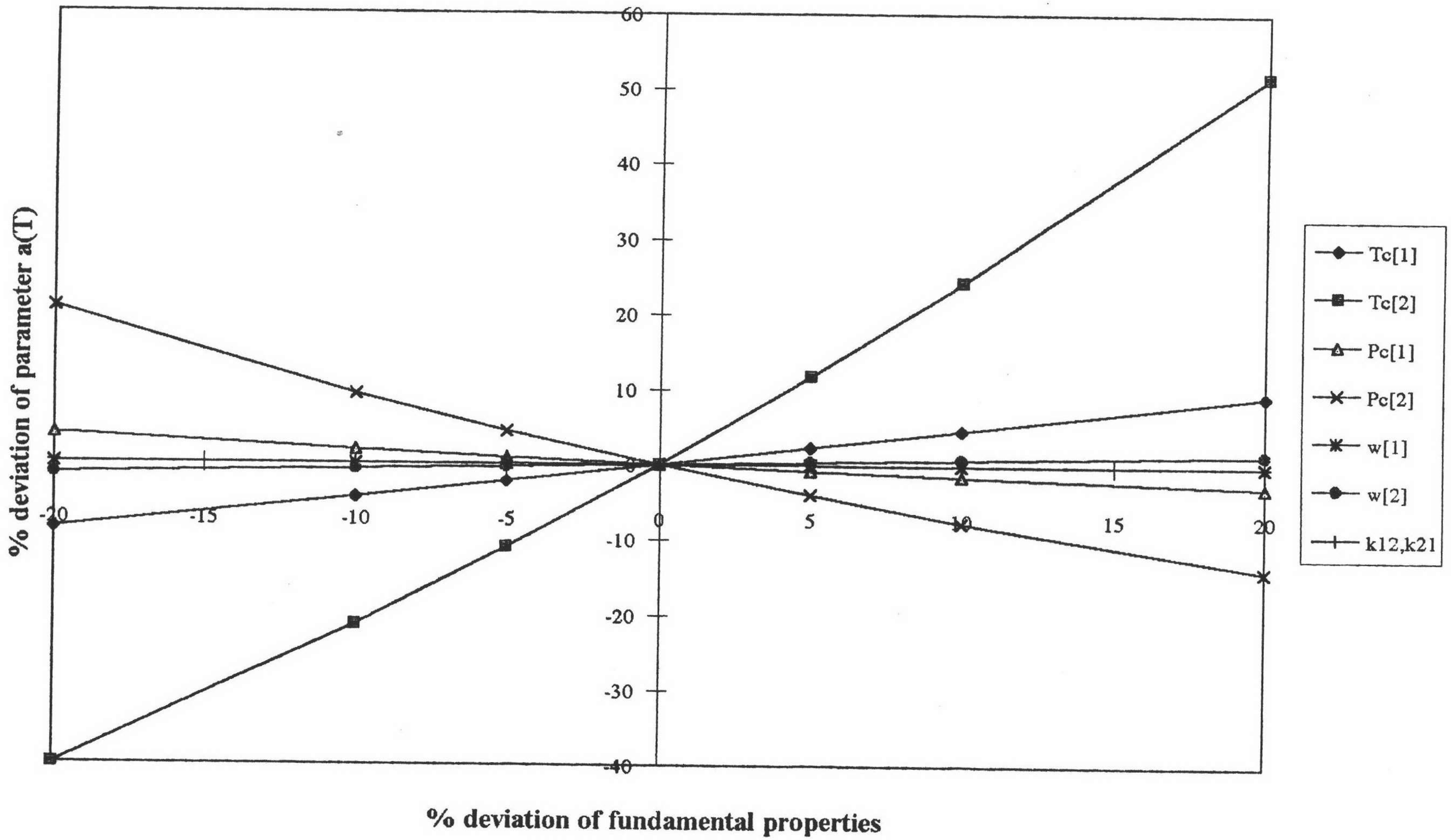

Figure 6.25 PR EOS; 0.5methane/0.5n-heptane; at $1.2T_c$, % deviation of parameter a(T) as fundamental properties are varied.

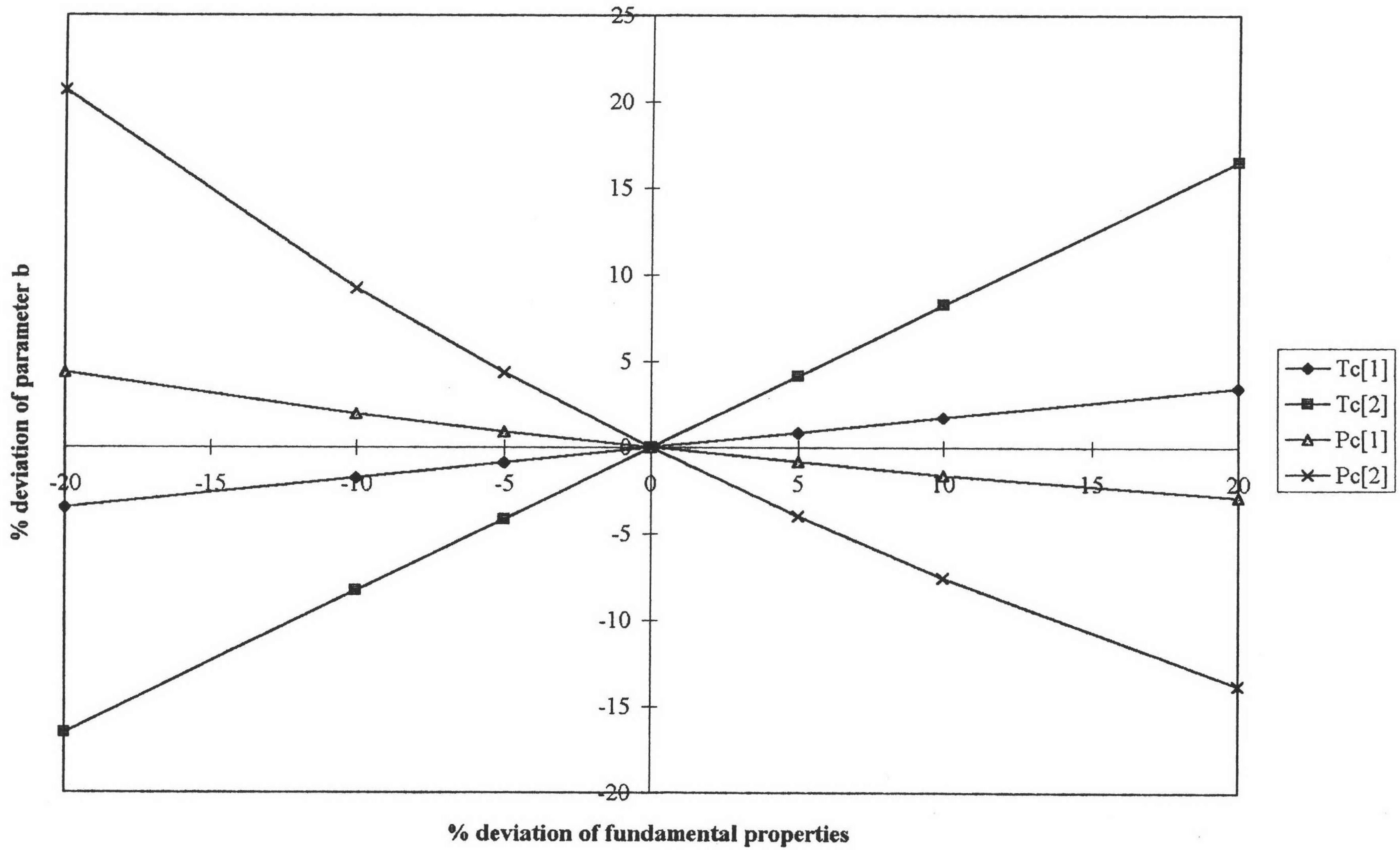

Figure 6.26 PR EOS; 0.5methane/0.5n-heptane; % deviation of parameter b as fundamental properties are varied.